PHOTOCHEMICAL AND THERMAL DEDIAZONIATIONS OF ARYL DIAZONIUM SALTS IN NON-AQUEOUS SOLVENTS

by

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To my parents, Elizabeth, and the Horse.

Acknowledgements

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Abstract

Photodediazoniations, using a high pressure mercury lamp, of p-N,N-dimethylaminobenzenediazonium salts proceed by a heterolytic mechanism via the formation of a triplet p-N,N-dimethylaminophenyl cation. The triplet state cation has been shown to be more stable than the singlet by Gaussian 70 molecular orbital calculations. The product of the photodediazoniation of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate in the solid state was proposed to be a 1:1 p-N,N-dimethylfluoroaniline phosphorus pentafluoride adduct, and formed from an ion-pair precursor in a concerted reaction. The photodediazoniation of p-N,N-dimethylaminobenzenediazonium salts (PF_6^-, BF_4^-, SbF_6^-) in acetonitrile and 2,2,2-trifluoroethanol solutions, yielded products consistent with heterolytic mechanisms already accepted for the thermal dediazoniation of other aryl diazonium salts in these solvents. A heterolytic mechanism via the formation of a carbonylic adduct is proposed for the photolysis in acetone solution, while in 1,1,3,3-tetramethylurea and 1-methyl-2-pyridone solutions the isolation of the novel carbonylic adducts 2-(p-N,N-dimethylaminophenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate and 2-(p-N,N-dimethylaminophenoxy)-1-methylpyridinium hexafluorophosphate respectively was achieved. The photolysis of other diazonium hexafluorophosphates having absorption bands in the range 373 - 411 nm also yielded analogous carbonylic adducts in these solvents, while the scope of these reactions was expanded to include hexafluoroantimonate and hexachlorostannate diazonium salts. Thermal dediazoniation of ortho-methyl substituted benzenediazonium salts in the carbonylic solvents 1,1,3,3-tetramethylurea, 1-methyl-2-pyridone, 1,3-dimethyl-2-imidazolidinone, and cyclohepta-2,4,6-triene-1-one (tropone) were shown to yield isolatable carbonylic adducts in parallel with the photodediazoniations. The ease of hydrolysis of the novel carbonylic adduct (2',6'-dimethylphenoxy)tropylium hexafluorophosphate, indicated that adducts formed on dediazoniation in acetone solution should be highly susceptible to hydrolysis. From Gaussian 76 molecular orbital calculations, the schematic energy profile for the Nα, Nβ rearrangement in the 2,6-dimethylbenzenediazonium ion was shown to be very similar to that for the benzenediazonium ion.

The sky's course runs a-foul and in reverse,
a jaundiced people sink beneath the curse.
Given to untruth plotting never a-right,
You say, and lie, that no sage sees the light.
                    Against your nearsightedness
                    I employ this reproving verse.

The heavens send down the hard, pull in your smirk
Gainst sky's square kick, no man has time to shirk.
Words fit to fact
folk will enact;
Calm discourse
needeth no force.

From a different line of work, my colleagues,
I bring you an idea. You smirk.
It's in the line of duty. Wipe off that smile, and
as our grandfathers used to say:
Ask the fellows who cut the hay.

Attributed to the Earl of Fan
in King Li's time, 877 - 841 B.C.

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1 GENERAL INTRODUCTION

1.1 INDUSTRIAL INTRODUCTION

1.1.1 The commercial use of diazo reproductions

The main use of diazo-emulsions today is for the reproduction or copying of high contrast line or engineering drawings. The reproduction, known as a diazotype, is an accurate copy of the original unlike that obtainable by standard xerography techniques. The diazotype is also cheaper to produce than a xerography photocopy. Several diazotypes may be produced from an original drawing or from other diazotypes, allowing several draftsmen to work simultaneously. Diazo reproduction techniques gradually superseded the old "blueprint" process for the copying of line drawings. The advantages of the diazo process were that the shelf-life of the sensitized papers was far superior to the old ferrocyanide papers and, the process was "positive-acting" i.e. a positive image of the original is produced. Diazo-emulsions do not compete with silver salt emulsions, since they are insufficiently light sensitive for taking "snap-shots". This difference in sensitivity arises from the fact that the silver process involves a chain initiation by light giving an amplification factor of about 1×10^5, while the diazo photodecomposition requires one photon for each molecule to be decomposed. In the reproduction of line drawings however diazo-emulsions are much cheaper than silver emulsions and the processing is relatively quick. Papers are sensitized with only 1-3% w/v concentration of diazonium salts and applied as a thin coating. The major cost of the sensitized paper lies in the paper rather than its coating. The diazo process also has an added advantage for microfilm work due to the fine grain size. The azo dye in the image area can be less than 1/300 of the size of a silver halide particle, and giving therefore a better definition than is achievable with the silver halide process. Diazonium salts are being used in lithography[1] and in the production of printed circuitry[2] demonstrating the extreme versatility of these compounds.

1.1.2 The first diazo reproduction process

The first diazo copying paper, which could be stored in the dark for some time, was prepared by Green, Cross and Bevan[3,4] in 1890. The paper was surfaced with a solution of primuline, a diazotisable dyestuff, and diazotised on the surface by treatment with nitrous acid. After drying, the paper was ready for the copying of the line drawing, which had been drawn previously onto some transparent material. The drawing was placed over the diazotised paper and exposed to light long enough to photodecompose all the diazo compound not covered by the dark lines of the drawing. By brushing with a solution of a coupler, e.g. β-naphthol or α-naphthylamine, the dyeline was developed. Finally the paper was washed leaving a copy which was respectively red or purple on a yellowish background. Although this process was the precursor of those in present use, there was much need for improvements in the diazotype paper. Users now demand at least four properties of a paper:-

1. To give reproductions in black or dark colours, which can be developed quickly and which are fast to light, air and water.
2. A clear white or colourless background.
3. The sensitive diazo-emulsion coating must not be unduly perishable nor have any effect on the paper.
4. The process of operation must be simple and especially should avoid the necessity of drying the print.

1.1.3 The modern diazo processes

Of the vast number of organic processes devised for duplication and described in the patent literature, it is the process based on the light sensitivity of diazonium salts which remains the most popular. Broadly, there are two different modes of producing the final image, the second one now to be described being the most important.

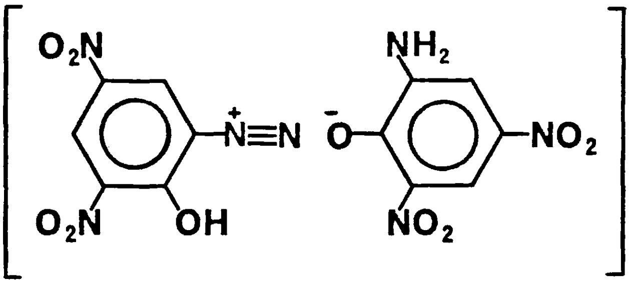
Firstly, those employing the principle of Green, Cross and Bevan[3,4], in which the diazonium salt alone is present in the emulsion and development is accomplished by treating the paper, after exposure, with a coupling component. When an alkaline solution of the phenolic coupler is applied in this way it is known as the "semi-dry" or "semi-wet" process. The most commonly used "semi-wet" coupling component is 1,3,5-trihydroxybenzene, which reacts with the diazonium compound to form mono-, bis-, and tris-azo dyes that are yellow, brown and blue, respectively, and the combination of which gives a black image.

Secondly, those papers in which both the diazonium salt and the coupling component are present in the same layer and coupling is prevented prior to development by one of several ways viz, by the nature of the diazonium compound, by control of the acidity or by protection of the phenol until the time of development. The development is usually carried out by the introduction of a base, such as ammonia vapour, to permit the coupling reaction to take place. When a naphthol such as the sodium salt of 2,3-dihydroxynaphthalene-6-sulphonic acid is employed in combination with acetoacetanilide, then the naphthol gives a blue dye and the anilide a yellow one, the combination of which results in a black image. This second type of process is called the "dry process".

The light to which the diazo-emulsions are exposed must supply sufficient energy to photochemically destroy all the diazonium salt in the nonimage areas, unlike silver emulsions, and is thus completely responsible for the formation of the image. Because of these high energy requirements, powerful light sources rich in ultraviolet-blue radiation must be used for exposing material sensitized with diazonium compounds. The most suitable and most generally used are high pressure mercury vapour lamps. The light output of these lamps is limited to narrow bands, the mercury lines having peaks at 313, 334, 365, 405, 436, 546, and 577 nm (see fig 4.2.1-1). Of these, the 365 and 405 nm lines are the most important for the diazo reproduction processes. The 313 and 334 nm lines are of little use, while those at 546 and 577 nm are of no practical use. The emission at 436 nm is necessary more in papers sensitized with "superfast" diazonium salts such as the substituted p-morpholino diazonium compounds. These "superfast" diazonium salts can also be decomposed by exposure to tungsten or fluorescent lamps, since their absorption spectra are shifted to the violet and blue regions of the spectrum.

1.1.4 Photosensitive diazonium salts utilized in diazo reproduction

The first reported diazonium salt was isolated by Griess[5,6] in 1858. It was a discovery made by chance, since he attempted to convert picramic acid to the corresponding phenol using nitrous acid. He carried out the reaction at low temperature and isolated a crystalline solid which he concluded was a totally new type of compound[7,8]. The compound isolated by Griess was later shown to be the diazonium picramate I.



I

Thermal instability has always been known to be a fundamental property of diazonium salts and Griess found that I decomposed "with violent explosion" when heated on a water bath.

After Green, Cross and Bevan's[3,4] first diazo reproduction process, attempts were made in the 1890's to stabilise diazonium salts and prolong their industrial effectiveness. In 1892 the isolation of benzenediazonium chloride as a double salt with platinic chloride $PhN_2^+Cl^-\frac{1}{2}PtCl_4$, by Michaelis and Ruhl[9], started investigations on a whole range of metallic double salts, including those of cadmium chloride and stannic chloride. It was not long before zinc chloride was evaluated as the most widely applicable salt for stabilisation purposes[10,11]. The diazonium chloride zinc chloride double salts generally have sufficient solubility in water to allow their use in 1-5% concentrations. They are also sufficiently insoluble to permit their efficient isolation from diazotisation solutions, the recovered yields being improved by adding salt.

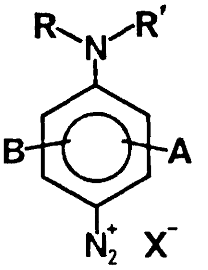
Of the numerous other available methods of stabilisation, the one which deserves mention is the preparation of diazonium tetrafluoroborates[12,13,14]. When a solution of tetrafluoroboric acid is added to an aqueous solution of the diazonium salt, the crystalline diazonium tetrafluoroborate is obtained in good yield (1) Diazonium hexafluorophosphates

$$PhN_2^+Cl^- + HBF_4 \longrightarrow PhN_2^+BF_4^- + HCl \qquad (1)$$

may be produced in a similar way from hexafluorophosphoric acid. The stability of diazonium tetrafluoroborates and hexafluorophosphates, in general, is similar to that of the zinc chloride double salts but they are usually a lot less water soluble than the latter. The solubility of tetrafluoroborate and hexafluorophosphate diazonium salts in organic solvents renders them particularly useful for resin film rather than paper coating applications.

Simple diazonium salts such as that derived from aniline itself, are relatively thermally unstable and are only slowly destroyed by light. They tend to have only low coupling activity. A search for derivatives having more of the appropriate properties started in the early 1920's.

In 1927 Van der Grinten patented a range of disubstituted p-phenylenediamine derivatives.

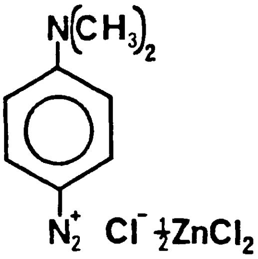


A,B = Substituent groups

R,R' = Alkyl groups

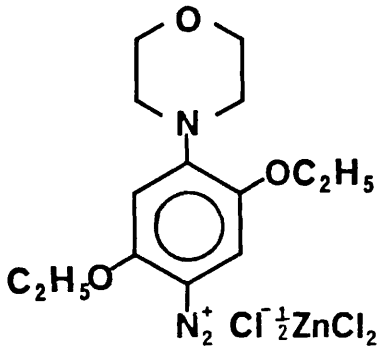
$X^- = Cl^- \frac{1}{2}ZnCl_2$ etc.

Even now, these compounds still have the widest application and of the commercially prepared diazonium compounds the largest number consist of compounds of this general formula. The simplest member is p-N,N-dimethylaminobenzenediazonium chloride[15] (IIa) zinc chloride double salt, which has a medium sensitivity

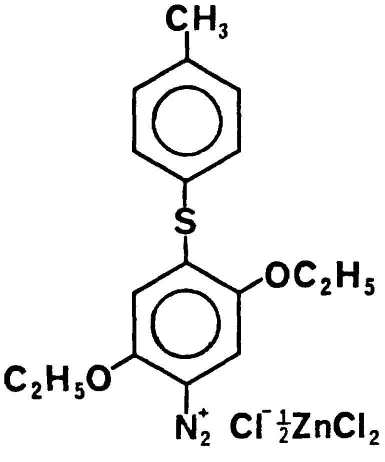


IIa

to light and a moderate coupling activity. These properties render IIa suitable for the "dry process". In contrast the "superfast" compound 2,5-diethoxy-4-morpholinobenzenediazonium chloride[16] zinc chloride double salt (III) has a high light sensitivity, but with a sufficiently low coupling activity to be used in the "dry process".



III

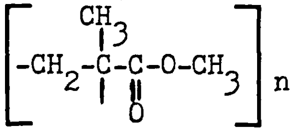


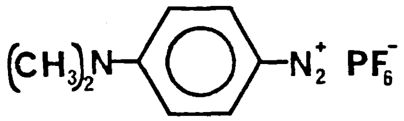
IV

The replacement of the morpholino group by the p-tolylthio group in the 4-position of III to give IV[17], produces a molecule with comparable light sensitivity but a many-fold increase in coupling activity. The product IV is only suitable for the "semi-wet" process where there is no chance of coupling prior to development. In this way diazonium salts can be designed to meet the requirements of both light sensitivity and coupling activity.

1.1.5 The yellowing of the background in diazotypes

It has been found that the background of some diazotypes (photodecomposed areas) becomes darker after a period of time. This problem, known as "yellowing", prevents these diazotypes from becoming a permanent copy of the original. Industrial research[18] has shown that this "yellowing" is associated with phenols produced from the photolysis of the diazonium salt. Although some attempts were made to develop diazonium salts with low "yellowing" characteristics, a more fundamental understanding of the mechanisms of phenol formation in diazo-emulsions was required.

The formation of phenols is not only encountered in photolysed paper coatings, where the coating is applied from an aqueous solution of the diazonium salt, but also occurs with films coated from organic solutions. Industrially, the "dry process" organic coating of films is performed with the diazonium salt, coupler, and other components dissolved in methylethylketone (MEK) together with a resin eg: polymethylmethacrylate  $\left[-CH_2-\underset{|}{\overset{CH_3}{\overset{|}{C}}}-\underset{\underset{O}{\|}}{C}-O-CH_3\right]_n$ which are coated onto a polymer film. Although a considerable amount of the MEK remains within the resin solid solution, water is known to be present only in low concentrations. In view of the low concentrations of water present in these organic films, the work presented in this thesis investigates the dediazoniation reactions of aryl diazonium salts in non-aqueous solvents. The diazonium salt p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb), which posesses considerable solubility in organic solvents and shows a high degree of "yellowing", was chosen for our initial investigations.



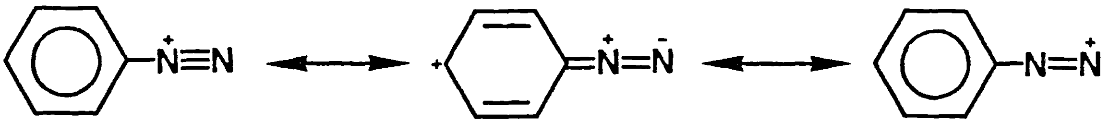
IIb

1.2 THE STRUCTURE OF ARYL DIAZONIUM SALTS

1.2.1 Crystallographic data

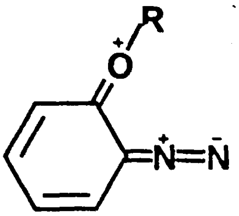
Three sets of crystallographic data are reproduced here. They are the data for benzene diazonium chloride[19], o-methoxybenzenediazonium chloride ferric chloride double salt[20], and p-N,N-dimethylaminobenzenediazonium chloride zinc chloride double salt[21,22] (IIa), which are given in table 1.2.1-1. The reliability of such X-ray crystallographic data is usually indicated by the R factor, the residual error index, and by σ, the standard deviation. The lower the value of R, the lower is the discrepancy between observed and calculated structure factors.

On examination of the data for benzenediazonium chloride[19] and o-methoxybenzenediazonium chloride ferric chloride double salt[20] we see that the N-N bond distances are close to that of molecular nitrogen (1.097 Å)[23], which would indicate that the extreme form V predominates over VI and VII in the ground state. From this data we therefore conclude



V VI VII

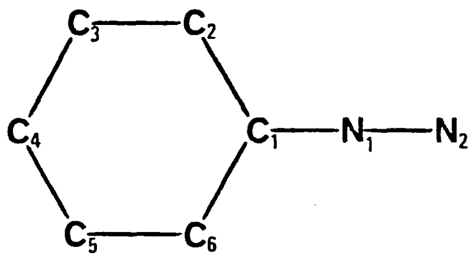
that the N-N bond is essentially a triple bond in these two diazonium salts. The crystallographic data for the o-methoxybenzenediazonium salt[20] does not provide any evidence of π-bonding between the oxygen and the ring (C-2), and Nα and the ring (C-1) as is shown in structure VIII, since the N-N bond (1.11 Å)



VIII

Table 1.2.1-1 Crystallographic data for a) benzenediazonium chloride[19], b) o-methoxybenzenediazonium chloride ferric chloride double salt[20], and c) p-N,N-dimethylaminobenzenediazonium chloride zinc chloride double salt[21,22](IIa).

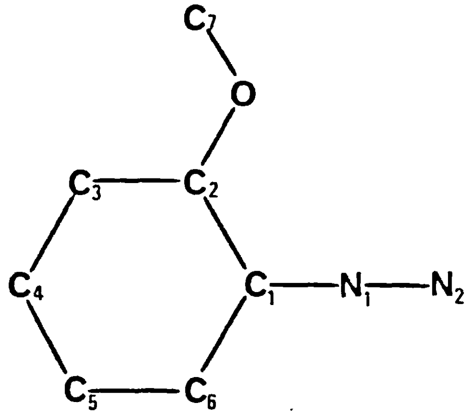
a)



	Å		
(N-1)-(N-2)	1.097	(C-1)-(N-1)-(N-2)	180°
(N-1)-(C-1)	1.385	(C-1)-(C-2)-(C-3)	117.6°
(C-1)-(C-2)	1.374	(C-2)-(C-3)-(C-4)	119.8°
(C-2)-(C-3)	1.383	(C-3)-(C-4)-(C-5)	121.7°
(C-3)-(C-4)	1.376	(C-6)-(C-1)-(C-2)	124.8°

R = 0.06 σ = 0.006-0.010 Å and 0.6-0.7°

b)



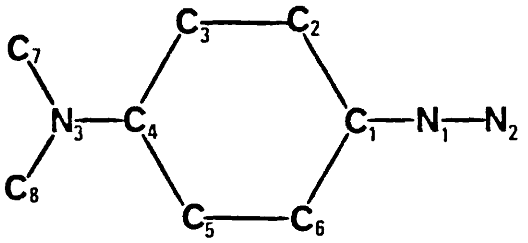
	Å		
(N-1)-(N-2)	1.11	(C-1)-(N-1)-(N-2)	179°
(C-1)-(N-1)	1.48	(C-2)-(C-1)-(N-1)	118°
(C-1)-(C-2)	1.38	(C-1)-(C-2)-(C-3)	119°
(C-2)-(C-3)	1.40	(C-2)-(C-3)-(C-4)	114°
(C-3)-(C-4)	1.41	(C-3)-(C-4)-(C-5)	126°
(C-4)-(C-5)	1.41	(C-4)-(C-5)-(C-6)	124°
(C-5)-(C-6)	1.49	(C-5)-(C-6)-(C-1)	103°
(C-6)-(C-1)	1.48	(C-6)-(C-1)-(C-2)	134°
(C-2)-O	1.36	(C-1)-(C-2)-O	117°
O-(C-7)	1.45	(C-2)-O-(C-7)	120°

R = 0.13 σ = 0.01-0.02 Å

continued...

Table 1.2.1-1 continued

c)

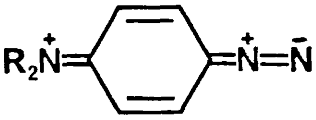


R = 0.141

	Å		
(N-1)-(N-2)	1.182	(C-1)-(N-1)-(N-2)	169.9°
(C-1)-(N-1)	1.433	(C-2)-(C-1)-(N-1)	110.9°
(C-1)-(C-2)	1.524	(C-1)-(C-2)-(C-3)	108.9°
(C-2)-(C-3)	1.374	(C-2)-(C-3)-(C-4)	128.3°
(C-3)-(C-4)	1.495	(C-3)-(C-4)-(C-5)	116.7°
(C-4)-(C-5)	1.476	(C-4)-(C-5)-(C-6)	118.3°
(C-5)-(C-6)	1.480	(C-5)-(C-6)-(C-1)	117.3°
(C-6)-(C-1)	1.360	(C-6)-(C-1)-(C-2)	129.8°
(C-4)-(N-3)	1.355	(N-3)-(C-4)-(C-3)	122.8°
(N-3)-(C-7)	1.532	(C-4)-(N-3)-(C-7)	119.5°
(N-3)-(C-8)	1.509	(C-7)-(N-3)-(C-8)	120.0°

is virtually the same as that in benzenediazonium chloride(1.097 Å), and the(C-1)-Nα bond(1.48 Å) is even longer than that in benzenediazonium chloride (1.385 Å). A (C-2)-O bond distance of 1.36 Å, being comparable to that in 1,4-dimethoxybenzene[24] and p,p'-dimethoxybenzophenone[25], also indicates that the methoxy group is not conjugated with the rest of the molecule.

The crystallographic data presented for IIa[21,22] does indicate the presence of some conjugation in the ground state as shown in structure IX. This conjugation is supported by



IX

a N-N distance(1.182 Å) longer than benzenediazonium chloride, and a (C-4)-(N-3) distance (1.355 Å) shorter than those in 2,5-dichloroaniline[26] and p-toluidine[27]. The (C-4)-(N-3) distance being similar to that in p-nitroaniline[28] and p-N,N-dimethyl nitroaniline[29], for which conjugation between the nitro and amino groups is accepted. The reliability of the crystallographic data for IIa is however doubtful since the (C-1)-(C-2) and (C-6)-(C-1) distances are vastly different (1.524 and 1.360 Å, respectively) whereas they should be equal. The standard deviations in atomic coordinates were not reported by the authors[21,22].

1.2.2 IR spectroscopic data

In 1956 Whetsel[30], while investigating the IR spectra of azo dyes, observed that a monosubstituted aryldiazonium salt had a sharp absorption band at 2250 cm^{-1}. Since the absorption band of the nitrile group (2255 cm^{-1} for benzonitrile[31]) was close to this value, it seemed reasonable to regard the N-N bond of the diazonium salt as a triple bond. The Raman spectrum of molecular nitrogen[32] has a band at

2330 cm^{-1}. Whetsel[30] therefore decided to investigate the position of this IR absorption band in other diazonium salts, since there was a lack of such data at the time.

Most of the diazonium salts investigated had absorption bands in the range 2294-2237 cm^{-1}. The absorption band for the benzenediazonium ion[33] has been reported to be close to 2290 cm^{-1}. These diazonium salts were regarded as having essentially a N-N triple bond. An exception[33] to this was found for the p-amino, and p-dialkylamino-benzenediazonium ions, whose spectra were said to display considerable N-N double bond character. These diazonium salts have their N-N absorption bands at much lower wavenumbers, and a finite contribution from the quinonoid structure IX was considered likely. Nuttall[33] came to the same conclusions as Whetsel[30] when he repeated some of the work. Representative N-N stretching frequencies obtained by Nuttall are reproduced here in table 1.2.2-1.

Table 1.2.2-1 IR N-N stretching frequencies (cm^{-1}) of some aryl diazonium salts [a] [33]

	BF_4^-	PF_6^-
benzenediazonium	2297	2290
o-methylbenzenediazonium	2290	2289
p-methylbenzenediazonium	2299	2287
p-nitrobenzenediazonium	2321	2310
p-methoxybenzenediazonium	2265	
p-N,N-dimethylaminobenzenediazonium	2268w 2181s	2252w 2178s
p-N,N-diethylaminobenzenediazonium	2260w 2173s	2250w 2170s
p-aminobenzenediazonium	2170	

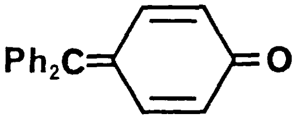
w = weak s = strong

a All spectra recorded as nujol mulls.

From table 1.2.2-1 we can see that there is essentially a triple bond for the o-methyl, p-methyl, p-nitro, p-methoxy, and benzenediazonium ions. The p-N,N-dimethylamino, p-N,N-diethylamino, and p-aminobenzenediazonium ions have their N-N absorption bands in the range 2181-2170 cm^{-1}, showing considerable double bond character.

1.2.3 UV spectroscopic data

Many workers have been interested in the electronic structure of aryl diazonium salts. The simplest diazonium compounds absorb UV radiation in the range 220-330 nm. These compounds have been regarded as having benzenoid structures since benzenoid compounds are known to absorb light in this region[34]. Particular interest has been shown in the p-amino and p-alkylamino substituted aryl diazonium salts which, unlike the vast majority of diazonium salts, are coloured and generally have high thermal stability. Anderson[34,35], observing similarities in the UV spectra of these compounds to that of diphenylquinomethane (X), regarded the p-amino and p-alkylamino compounds as having the analogous



X

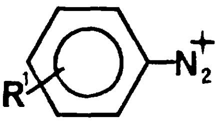
quinonoid structure IX. A list of absorption maxima for various aryl diazonium salts has been compiled from the literature[36,37] (table 1.2.3-1).

Table 1.2.3-1 UV Absorption maxima of various aryl diazonium ions

a R^1[36]	λmax(nm)
H	264
p-Cl	283
m-Cl	266
o-Cl	269
p-CH_3	279
m-CH_3	279
o-CH_3	269
p-OCH_3	315
m-OCH_3	275
o-OCH_3	355
p-NO_2	
m-NO_2	232
o-NO_2	280

b R^2	R^3[37]	λmax(nm)	ε
H	H	353	37,400
CH_3	CH_3	375	38,900
C_2H_5	C_2H_5	380	40,300
CH_3	H	366	38,600
C_2H_5	H	368	41,100
Ph	H	377	30,200
Ph	Ph	388	24,100

a)



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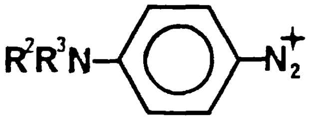


As can be seen from table 1.2.3-1 there is considerable variation in the position of the UV absorption maxima in passing from p-amino (353 nm) to the p-diphenylamino derivative (388 nm), and therefore a variation in structure is likely. If all of these compounds had a quinonoid structure then little variation in their UV spectra would be expected. The p-amino, p-alkylamino, and p-phenylamino substituted aryl diazonium salts are therefore now thought to have structures with varying degrees of quinonoid character, in keeping with both the IR data[30,33] and some theoretical calculations[38].

1.3 CLASSIFICATION OF REACTIONS OF ARYL DIAZONIUM SALTS

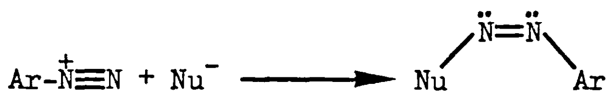
1.3.1 Reaction nomenclature

The systematic nomenclature of substitution reactions proposed by Bunnett[39] and adopted by Zollinger[40] will be used in this text. Regardless of mechanism, all reactions in which both nitrogen atoms of an azo or diazo compound are replaced by another group are designated dediazoniations. This term may be preceded by the name of the entering group. Therefore hydrolysis is designated as hydroxydediazoniation, and replacement of the diazo group by fluorine as fluorodediazoniation. In addition a reaction may proceed thermally or photochemically. Hydroxydediazoniations may therefore be further divided into photolytic hydroxydediazoniation and thermolytic hydroxydediazoniation reactions.

1.3.2 Types of reaction

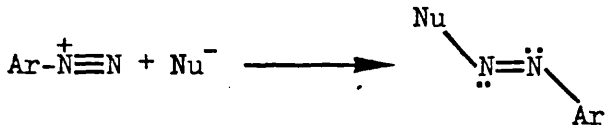
1.3.2.1 Reactions with nucleophiles at the β-nitrogen

Nucleophiles reacting with the β-nitrogen of aryl diazonium ions may be anions (^-OH, ^-OR, ^-OAr, ^-CN, $^-N_3$), ammonia, amines and, in diazo coupling reactions, π -electron systems usually containing electron-donating substituents. The product of the reaction is in many cases a syn-azo compound (XI) in spite of the fact that the anti isomer (XII) is thermodynamically more stable.



(2)

XI



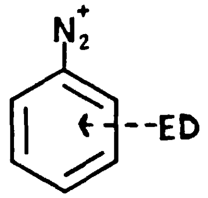
(3)

XII

Zollinger[41], observing that syn compounds are formed in reactions with -OH, -OMe, and -CN, regarded the transition state as "reactant-like" or early on the reaction coordinate. In an early transition state repulsive interaction between the nucleophile and the aryl group is small owing to their large separation. The repulsion between the lone pair at N_β and the aryl group becomes paramount and therefore a syn product is preferred. This is consistent with the general expectation that coordination of a cation with a small anion, having a localized or almost localized charge, is likely to proceed through a more reactant-like transition state. However reaction of a cation with an anion such as phenoxide whose charge is highly delocalized would be expected to have a more product-like transition state and therefore favour the formation of the anti isomer. In investigations[42] which are discussed from another point of view, Ritchie and Wright[43] found ρ+ve values between 2.3 and 2.6 for Hammett plots for the rates of coordination of substituted benzenediazonium ions with hydroxide, cyanide, azide and arylsulphinic acid anions, and ρ+ve values between 3.5 and 5.2 for the respective equilibrium constants. The ρ+ve values for the diazo coupling reactions with 2-naphthol-6-sulphonic acid dianion and 2-naphthylamine-6-sulphonic acid dianion[44] are, 3.85 and 4.26 respectively. These ρ+ve values are significantly higher than those of reactions with other nucleophiles, but comparable to the ρ+ve values of the equilibria mentioned. This indicates that the transition states of diazo coupling reactions are more product-like than for diazonium ion coordination with anions like ^-OH, ^-CN, and $^-N_3$. This comparison therefore supports the previous explanation for syn vs anti-azo product formation of Zollinger[41].

1.3.2.2 Formation of complexes with electron donors

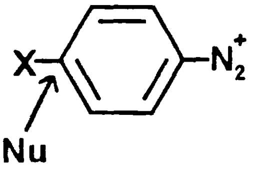
Complex formation[45] is greatly facilitated by the electron-attracting effect of the diazonium group[46].

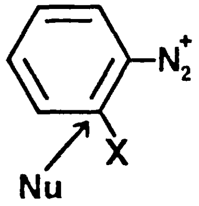


Zollinger investigated the visible and NMR spectra of 0.1 mol dm^{-3} aqueous hydrochloric acid solutions of o- and p-nitrobenzene diazonium ions in the presence of 2-naphthol-6,8-disulphonic acid anions, and concluded that a complex is rapidly formed. The spectroscopic data indicated that the structure of the complex was a charge-transfer π-complex between the diazonium ion and the electron donor (ED), 2-naphthol-6,8-disulphonic acid anion. Charge-transfer complexes were also observed between diazonium ions and naphthalene, naphthalene-1-sulphonic acid, 1-naphthyl methanesulphonic acid, and 2-naphthol-1-sulphonic acid. It was concluded that these complexes are probably intermediates in the electrophilic aromatic substitution diazo coupling reaction. The importance of charge-transfer complexes in dediazoniations with dimethylsulphoxide as solvent will be discussed later (ch 1.6.2.2).

1.3.2.3 Substitution of nucleofugal leaving groups

Substitution of a nucleofugal leaving group (X) in the ortho or para position of the aryl nucleus can occur.

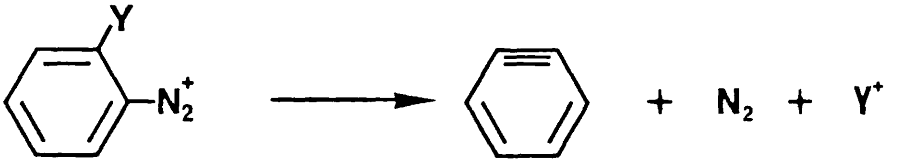




A well known[47] example is the substitution of nitro by hydroxyl groups in solutions of the 2,4-dinitrobenzene diazonium ion. The reaction probably follows an S_NAr mechanism[48,49] of nucleophilic aromatic substitution.

1.3.2.4 Formation of arynes

Arynes could be formed by the loss of molecular nitrogen and an electrofugal ortho substituted leaving group (Y) such as a proton[50-52] or carboxylate[53,54].

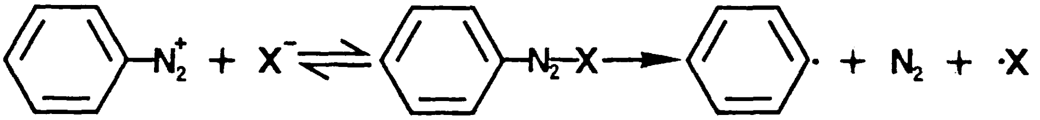


(4)

This type of E_2 elimination of a proton and molecular nitrogen to form aryne intermediates, initiated by a base eg. acetate ion, was however ruled out experimentally by Swain[72] and Zollinger[40,55,56] as not being of general importance in aryl diazonium ion solvolysis reactions (see ch 1.5.2.1).

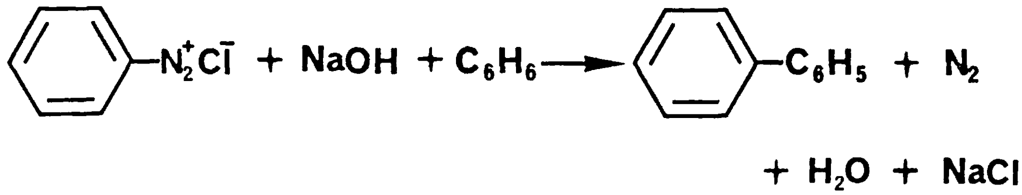
1.3.2.5 Homolytic cleavage of the (C-1)-Nα bond

Examples of homolytic cleavage of the (C-1)-Nα bond include both photochemical and thermal protodediazoniations in organic solvents which will be discussed in some detail later (ch 1.7 and ch 1.6 respectively). Other examples include the Gomberg-Bachmann[57] and Sandmeyer[58] reactions which both follow mechanism 5 in homolytic cleavage of the (C-1)-Nα bond.



(5)

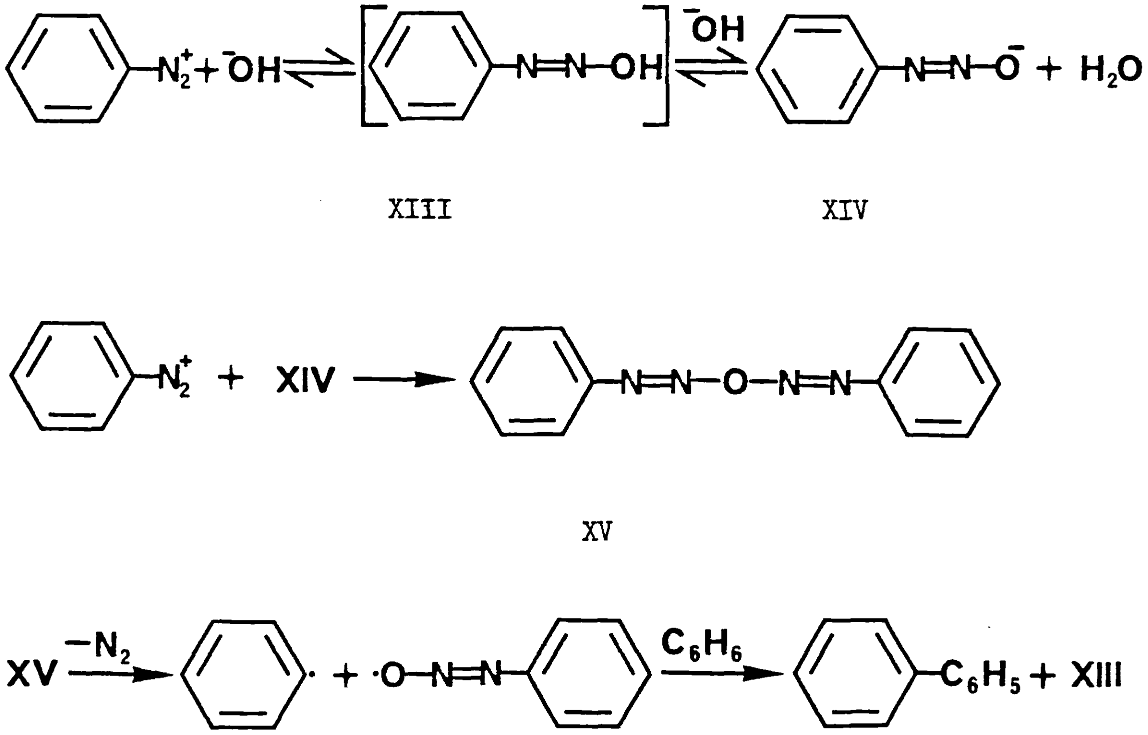
Rüchardt[59] proposed that the Gomberg-Bachmann[57] reaction (6)



(6)

proceded by the scheme 1.3.2.5-1 in which XIV corresponds

Scheme 1.3.2.5-1



to X$^-$ in mechanism 5. The catalytic function of cuprous salts in Sandmeyer[58] reactions can be explained in a similar way[47b,60], (Scheme 1.3.2.5-2), in which

Scheme 1.3.2.5-2

$$\mathrm{CuCl} + \mathrm{Cl}^- \rightleftharpoons \mathrm{CuCl_2}^-$$

$$\mathrm{ArN_2}^+ + \mathrm{CuCl_2}^- \longrightarrow (\mathrm{ArN{\equiv}NClCuCl})$$

XVI

$$XVI \longrightarrow Ar\cdot + N_2 + CuCl_2$$

$$Ar\cdot + CuCl_2 \longrightarrow ArCl + CuCl$$

$CuCl_2^-$ corresponds to X^- in mechanism 5.

1.3.2.6 Heterolytic cleavage of the (C-1)-Nα bond

Heterolytic cleavage of the (C-1)-Nα bond can occur photochemically and thermally in aqueous acid and organic solvents, and often occurs along with homolytic cleavage. The heterolytic cleavage of aryl diazonium salts to form aryl cations is the major topic of discussion of this chapter.

1.4 BALZ-SCHIEMANN AND RELATED FLUORODEDIAZONIATIONS

1.4.1 Synthetic uses

Balz and Schiemann[61] observed that dry aryl diazonium tetrafluoroborates can be made to decompose thermally to yield an aryl fluoride, with liberation of nitrogen and boron trifluoride (7).

$$\mathrm{ArN_2^+BF_4^-} \xrightarrow{\Delta} \mathrm{ArF} + \mathrm{N_2} + \mathrm{BF_3} \tag{7}$$

They also predicted that this procedure, now known as the "Schiemann reaction", was applicable to any diazotizable amino group. Schiemann and his school, in a summarizing paper[62], substantiated the claim and established the "Schiemann fluorination" as a practicable method for the introduction of fluorine into aromatic and hetero-aromatic structures. The low yields attending the preparation of certain diazonium salts did however prompt research into the use of other complex anions. The stable diazonium salts of other complex fluorine acids have also been investigated[63-66].

$$\left(\mathrm{ArN_2}\right)_2^{2+}\ \mathrm{SiF_6^{2-}} \xrightarrow{\Delta} 2\mathrm{ArF} + 2\mathrm{N_2} + \mathrm{SiF_4} \tag{8}$$

$$\mathrm{ArN_2^+PF_6^-} \xrightarrow{\Delta} \mathrm{ArF} + \mathrm{N_2} + \mathrm{PF_5} \tag{9}$$

$$\mathrm{ArN_2^+SbF_6^-} \xrightarrow{\Delta} \mathrm{ArF} + \mathrm{N_2} + \mathrm{SbF_5} \tag{10}$$

The preparation of hexafluorosilicates by Roe[63] was comparable to that of tetrafluoroborates. However their transformation into aryl fluorides was found to be generally less efficient than that of tetrafluoroborates. Lange and Müller[65] were the first to show that hexafluorophosphates could be used in aryl fluorinations, but it was not until 1963 that a more systematic investigation of their potential use was made[67]. The lower solubility of diazonium hexafluorophosphates means that they can be precipitated almost quantitatively from aqueous solution, while the liberation of phosphorus pentafluoride, a weaker Lewis acid than boron trifluoride, means fewer side reactions could be expected.

The synthetic use of the photodecomposition of aryl diazonium salts in the solid state has been limited to one investigation by Petterson[68]. Petterson, using a 350 nm UV light source, photolysed samples of crystalline aryl diazonium tetrafluoroborates and hexafluorophosphates, that had been coated as a thin film. In some cases yields of aryl fluorides were higher than those obtained by the thermal reaction, and were particularly good in the case of diazonium salts with electron donating substituents (eg. p-$N(C_2H_5)_2$, p-$N(CH_3)_2$, p-OCH_3, p-NHPh).

1.4.2 Mechanistic investigations

Schiemann[61,69] proposed that the thermal stability of aryl diazonium tetrafluoroborates was due to the electrostatic bonding of an unstable diazonium cation to the complex tetrafluoroborate anion, and that the decomposition of the anion to boron trifluoride required approximately the same amount of energy as is produced by the decomposition of the diazonium ion to the aryl cation. A value of 290 kJ mol^{-1} was calculated by De Boer and Van Liempt[70] for the anion dissociation on the basis of the following equation.

$$BF_{3(g)} + F^-_{(g)} \longrightarrow BF_4^-{}_{(g)}$$

Recently as part of his mechanistic studies[71-75] of reactions of aryl diazonium tetrafluoroborates in solution, Swain sought to determine whether the tetrafluoroborate anion reacts directly as such in the Schiemann reaction or whether it first dissociates. Swain had already excluded[72] direct reactions of aryl diazonium ions (mechanisms 11 and 12)

$$ArN_2^+ + BF_4^- \longrightarrow ArF + N_2 + BF_3 \qquad (11)$$

$$ArN_2^+ + F^- \longrightarrow ArF + N_2 \qquad (12)$$

and shown that ArN_2^+ first dissociates to a singlet aryl cation (Ar^+) in the rate determining step, leaving only the following possibilities (13 and 14) for the step forming the aryl fluoride.

$$Ar^+ + BF_4^- \longrightarrow ArF + BF_3 \qquad (13)$$

$$\left.\begin{array}{l} BF_4^- \rightleftharpoons BF_3 + F^- \\ Ar^+ + F^- \longrightarrow ArF \end{array}\right\} \qquad (14)$$

Since mechanism 14 would require a reciprocal dependence of the rate of formation of the aryl fluoride from Ar^+ on the concentration of boron trifluoride, Swain[75] studied the thermal decomposition of p-t-butylbenzene diazonium tetrafluoroborate in methylene chloride solution, with added boron trifluoride, at 25°. He concluded that tetrafluoroborate ion is the source of fluorine in the aryl fluoride (mechanism 13) and not the fluoride ion (mechanism 14), since the product distribution was not affected by the addition of excess boron trifluoride.

1.5 HETEROLYTIC THERMAL DEDIAZONIATIONS IN SOLVOLYSIS

1.5.1 Early mechanistic developments

On the basis of early work by Crossley and co-workers[76], from 1940, the thermal hydrolysis of aryl diazonium salts in aqueous acid was assumed to proceed by an SN1 mechanism. Crossley[76] studied benzenediazonium chloride and various mono substituted derivatives and concluded that rate measurements, over 96% of the reaction, indicated decomposition was first order with respect to the aryl diazonium chloride. This was observed over the entire concentration range studied with molar ratios of water to diazonium salt between 1280:1 and 2.36:1. The nature of the decomposition products as well as the reaction velocity depended on the initial diazonium concentration. With the highest benzenediazonium chloride concentration the yield of phenol was only 24%, with accompanying amounts of chlorobenzene, benzene, and biphenyl. The rate measurements of 24 monosubstituted benzenediazonium chloride derivatives indicated that, with the exception of the o-methoxy derivative, the reactions were first order. The compounds studied included ortho, meta, and para, methyl, methoxy, phenyl, hydroxy, fluoro, carboxyl, and nitro benzenediazonium chlorides. The stability of these benzenediazonium chlorides was increased by the presence of the substituents with the exception of m-hydroxy, o and m-methyl, o and m-methoxy, and m-phenyl groups.

A two step mechanism was proposed to explain the observations. The first step was the rate limiting irreversible loss of nitrogen from the diazonium ion to form the aryl cation[77] and nitrogen (15). This was followed by the fast reaction

$$ArN_2^+ \xrightarrow{slow} Ar^+ + N_2 \qquad (15)$$

of the aryl cation with either water (16) or with other nucleophiles eg. the chloride ion (17).

$$Ar^{+} + H_2O \xrightarrow{fast} Ar\text{-}\overset{+}{O}H_2 \underset{}{\overset{fast}{\rightleftharpoons}} ArOH + H^{+} \qquad (16)$$

$$Ar^{+} + Cl^{-} \xrightarrow{fast} ArCl \qquad (17)$$

In 1952 Lewis and Hinds[78] raised doubt over the existence of a solely first order process, since in the presence of fairly concentrated hydrochloric acid, Blumberger[79] and Crossley[76] had noted small increases in the rate of decomposition. Lewis[78] argued, from the data of Pray[80], that the effect of the presence of neutral salts on the decomposition rate appears to be small, but nevertheless did depress it when in high salt concentrations. Lewis therefore studied the decomposition of p-nitrobenzenediazonium tetrafluoroborate in aqueous hydrobromic acid solutions and subjected it to an increasing concentration of sodium bromide. His kinetic data fitted a model that included a second order term consistent with a SN2 bimolecular displacement of nitrogen by the bromide ion as a minor pathway (18).

$$ArN_2^{+} + Br^{-} \longrightarrow ArBr + N_2 \qquad (18)$$

In 1964 Lewis[81,82] furthered the investigation of reactions whose kinetics were influenced by the concentration of nucleophiles in the system. He investigated the quantitative relationship between the extent of isotopic rearrangement[81] (19) and

$$Ar^{15}\overset{+}{N}\equiv N \rightleftharpoons Ar\overset{+}{N}\equiv{}^{15}N \qquad (19)$$

acceleration of the rate of decomposition by added thiocyanate ion[82] in the aqueous acid hydrolysis of p-methylbenzenediazonium and benzenediazonium ions. The diazonium salts were prepared as the diazonium-α-^{15}N ion ($Ar^{15}\overset{+}{N}\equiv N$), and the product forming reactions were assumed to be 20, 21, and 22.

$$ArN_2^+ + H_2O \longrightarrow ArOH + H^+ + N_2 \qquad (20)$$

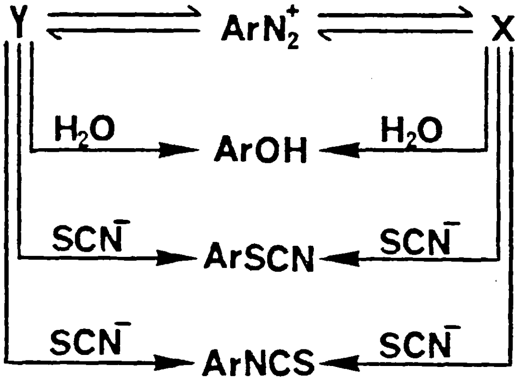
$$ArN_2^+ + SCN^- \longrightarrow N_2 + ArSCN \xrightarrow{H_2O} ArSCONH_2 \qquad (21)$$

$$ArN_2^+ + SCN^- \longrightarrow ArNCS + N_2 \qquad (22)$$

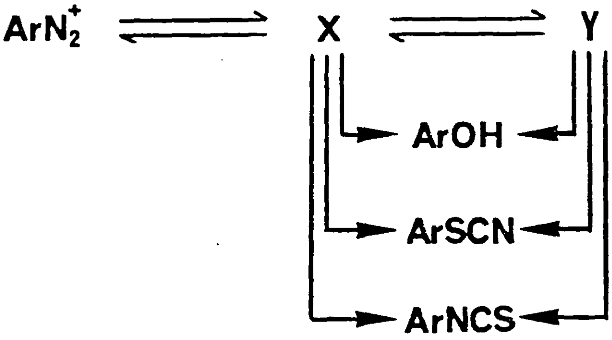
A plot of the apparent first-order rate constants for the yield of phenols, as a function of thiocyanate concentration showed; a sharp initial increase in rate with thiocyanate concentration, and a sharp decrease in the yield of phenols at low thiocyanate concentration. Since a simpler "no intermediate" or "one intermediate" kinetic model failed to mathematically fit this complex behaviour, Lewis[82] speculated that a two intermediate mechanism may occur.

Two schemes were therefore proposed fitting a two intermediate mechanism which were kinetically indistinguishable.

Scheme 1.5.1-1



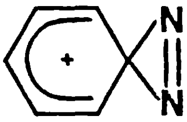
Scheme 1.5.1-2



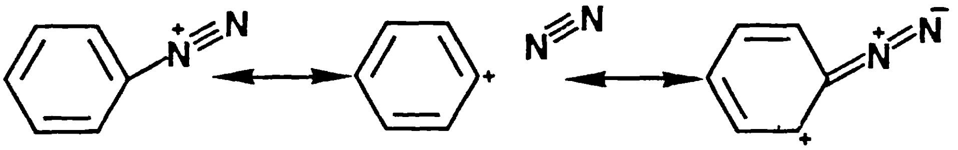
The first intermediate Y was assigned the symmetrical spirocyclic diazirine cation structure (XVII), since within experimental error the rate of return from Y to the diazonium ion was twice the rate of isotopic rearrangement. Intermediate Y was quite selective since

$k^{Y}_{SCN}/k^{Y}_{H_2O}$ = 470 but X, which showed relatively low selectivity,

$k^{X}_{SCN}/k^{X}_{H_2O}$ = 2.8, was suggested to be an excited state of the diazonium ion (XVIII), probably a vibrational state having nearly all the necessary activation energy, reacting by an oriented collision at the nitrogen-bearing carbon atom, but deactivating by most collisions.



XVII

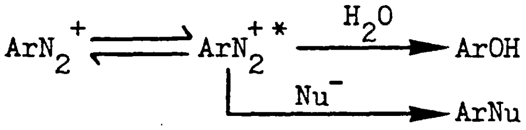


XVIIIa XVIIIb XVIIIc

The mechanism proposed did not discount the possibility that the aryl cation could be an intermediate, as pointed out by Lewis[82], since XVIIIb could be seen as such. Yet a mechanism through XVIII need not necessarily form it.

Lewis[83] in 1969 investigated the effects of several salts on the rates of decomposition of the benzenediazonium ion in aqueous solution. The effects were small but at any concentration the rate increased in the order bisulphate < chloride < bromide < thiocyanate, which agrees with the order for the nucleophilic reactivities[84] of these anions. This result suggested nucleophilic participation in the rate-limiting step. The rates with added bisulphates were slower than in the absence of added salts. This rate reduction was attributed to the lowering of the reactivity of water owing to its involvement in solvating the cation of the added salt. The small rate enhancements due to added sodium chloride and bromide was attributed to the retardation by the sodium ions as above, being overcome by acceleration due to the chloride or bromide ions. These rate accelerations were suggested to be sufficient to account for all the chlorobenzene or bromobenzene formed, without the need to consider competitive reactions proceeding after the rate-limiting step of the reaction. Since it was possible to account for the detailed shape of the rate vs salt concentration plots by the normal salt effect, the reaction route through the spirocyclic diazirine cation intermediate (XVII) did not need to be suggested. Lewis stated that the long accepted mechanism through the aryl cation[77] needed modification to explain the observed rearrangements[81,84], in spite of its success in accounting for substituent and solvent effects. Although the two intermediate mechanisms involving XVII had been rejected, a simpler mechanism[85] scheme 1.5.1-3 had also previously been rejected[81] because it predicted too much rearrangement.

Scheme 1.5.1-3

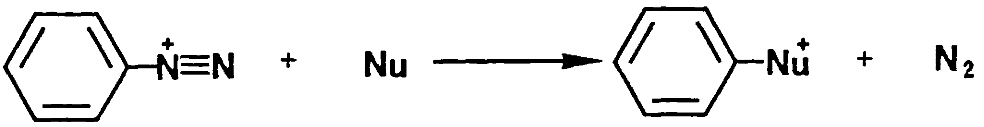


1.5.2 Aryl cations as intermediates

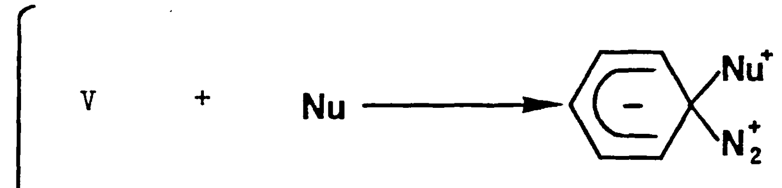
1.5.2.1 Introduction and product analysis

The question of whether aryl cations were intermediates in heterolytic dediazoniations remained to be answered[41] in 1973. The solution to the problem was provided by Swain and co-workers from investigations of substituent effects[71,72,86] on the kinetics of aqueous dediazoniations, and[71,73,74] from the primary kinetic isotope effects in ^{15}N-aryl diazonium ion dediazoniations and secondary kinetic isotope effects using deuterium labelled aryl diazonium salts.

Swain[71] considered eight possible mechanisms for the rate-limiting step of the reaction.

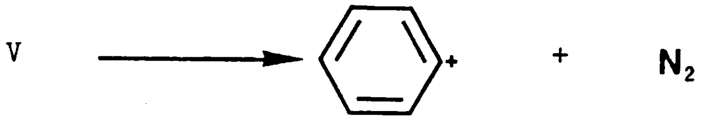


V XIX (23)



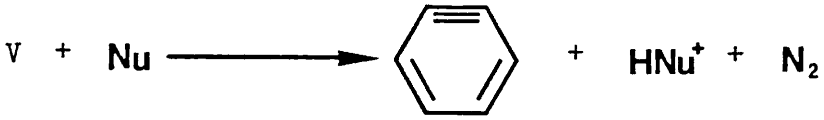
XX (24)

$$\mathrm{XX} \longrightarrow \mathrm{XIX} + N_2 \qquad (25)$$



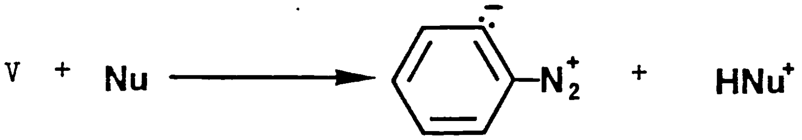
XXI

(26)



XXII

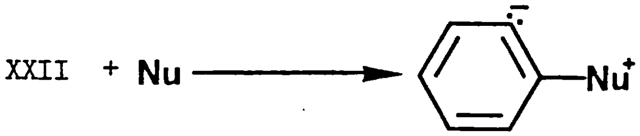
(27)



XXIII

(28)

$$\text{XXIII} \longrightarrow \text{XXII} + N_2 \qquad (29)$$



XXIV

(30)

Nu $=$ H_2O , Br^-, Cl^-, or F^-.

The benzyne mechanisms 27-30 were all excluded for the decomposition of diazonium ions in aqueous solutions, without strong bases, by the absence of isomerized products since o-methylbenzenediazonium chloride yielded no m-cresol and m-methylbenzenediazonium chloride yielded no o-cresol. The absence of a benzyne mechanism was demonstrated for benzenediazonium tetrafluoroborate by the negligible formation of ring deuterated phenol in DCl-D_2O solvent. The products indicated an ionic rather than a free radical mechanism. Formation of phenyl radicals[87,88] or of a triplet phenyl cation[89-91] was ruled out by the low yields ($< 5\%$) of benzene obtained from benzenediazonium tetrafluoroborate in acetone or acetic acid as solvents, and the failure of any intermediate to undergo addition of bromine. The remaining possibilities, 23-26, have species in which there is complete electron pairing.

1.5.2.2 Selectivity towards nucleophiles and solution thermodynamics

The selectivity towards nucleophiles of the species (V or XXI) responsible for product formation although low was measurable. This selectivity ($k_{Cl^-}/k_{H_2O} = 3$)[92,85] was even lower than that of the t-butyl cation ($K_{Cl^-}/K_{H_2O} \doteq 4$)[93]. Swain considered that due to a high degree of resonance the benzenediazonium ion (V), proposed in mechanisms 23 and 25, is more stable than the trityl ion ($k_{Cl^-}/k_{H_2O} = 3100$)[94] and ought to show even greater selectivity.

All mechanisms except 26 were able to be excluded upon the observation that there was $< 2\%$ reduction in the first order rate constant (k_1) from hydrolysis in 14 to 21 mol dm^{-3} H_2SO_4 in spite of HSO_4^- being a much poorer nucleophile than water, and a change of over 1000 fold in water activity. This implied that the extent of covalent bonding between carbon and Nu in the transition state is extremely small or zero.

Evidence against covalent bonding of water to carbon in the transition state of the hydrolysis reaction was also deduced from the large positive entropy of activation, 43.9 ± 4.2 J mol^{-1} deg^{-1}, for 0.1 mol dm^{-3} benzenediazonium chloride at 25^{o} [76]. This value is within 8 J mol^{-1} deg^{-1} of that for the hydrolysis t-butyl chloride where covalent bonding of water to carbon is not expected, but ~ 92 J mol^{-1} deg^{-1} higher than that for the hydrolysis of benzyl chloride, methyl bromide, or methyl p-toluenesulphonate, where water is known to bond in the transition state.

1.5.2.3 H_2O-D_2O solvent isotope effect (k_{H_2O}/k_{D_2O})

In calculations of secondary isotope effects for O-H-O systems, Swain[95] treated O-H bonds in the reactants and products as being $H\text{-}O^-$, $H\text{-}O\overset{+}{-}$ or H-O- in type. A transition state bond may be of intermediate character. Taking n, for any O-H bond, as the fraction in energy representing the extent of conversion to products (n = 0 for a reactant-like and n = 1 for a product-like transition state). The complete isotope effect is than given by the product of such contributions for all the O-H bonds. From measurements of deuterium distribution between water and hydroxonium ion[96-98], an estimate of the limiting isotope effect for the complete conversion of a $D\text{-}O\overset{+}{-}$ to an $H\text{-}O\overset{+}{-}$ bond at 25^{o} is 1.5. For example this conversion happens six times ($k = (1.5)^6 = 11$) in 31.

$$2D_3O^+ + 3H_2O \xrightleftharpoons{k} 3H_3O^+ + 2D_2O \qquad (31)$$

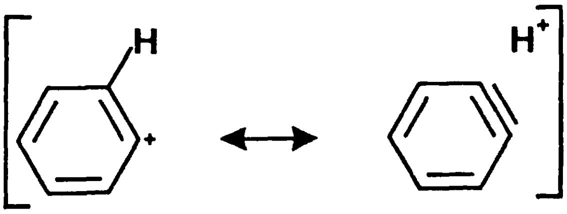
Using factors of 1.5, the predicted values[95] are $(1.5)^3 = 3.4$ and $(1.5)^2 = 2.2$ for complete conversion to hydroxonium or phenyloxonium ion respectively, at the transition state for mechanisms 26, 29 or 30. Slightly less than 3.4 or 2.2 would be expected for formation of unstable benzyne or anionic intermediates in mechanisms 25, 27, or 28; while $(2.2)^{\frac{1}{2}} = 1.5$ is expected for a transition state mid-way between reactants and products. It would be still less for earlier transition states. A value of unity would be expected for mechanism 26 where water plays no part in the formation of the transition state. Swain's[72] best experimental value for K_{H_2O}/K_{D_2O} was 0.98 ± 0.01, for 0.1 mol dm^{-3} benzenediazonium chloride at 35°. On the basis of the H_2O-D_2O solvent isotope effect all mechanisms were excluded except 26. The evidence of some selectivity between nucleophiles[85,92], although small, showed that the nucleophile was involved in the activated complex for the product determining step, rather than in the rate limiting step. The evidence therefore specifically excluded a one step mechanism 23 [83,99,100] and the addition-elimination mechanism (24 + 25)[78] but still permitted the operation of the elimination-addition mechanism 26 proceeding through the phenyl cation intermediate XXI due to W.A. Waters[77].

1.5.2.4 Nitrogen and aromatic hydrogen isotope effects

Swain[74] measured separately the α and β-nitrogen kinetic isotope effects in the solvolysis of benzenediazonium tetrafluoroborate in aqueous 1% H_2SO_4 at 25°. Brown and Drury[101], in a competition experiment measured the ratio $^{14}\mathrm{N}{\equiv}^{14}\mathrm{N}/^{15}\mathrm{N}{\equiv}^{14}\mathrm{N}$ evolved using the natural abundance ^{15}N in the benzenediazonium ion, and had inferred that the α-N isotope effect was 1.045 by assuming a simple two-atom (^{12}C-^{15}N) model with no β-N isotope effect. They also found this value to be relatively insensitive to substituents (2-CH_3, 3-CH_3, 4-CH_3, 3-Cl) and temperature (7-68°). Swain was unwilling to assume that the β-N isotope effect was one. Since the N≡N bond is so strong, it seemed to be reasonable to treat the leaving group as a rigid unit of 28 or 29 mass units[102] and thereby assume that the α and β-N isotope effects were the same. The specific labelling of α and β-^{15}N in the benzenediazonium ion was therefore undertaken by Swain[74] to find whether the truth lay between the two extremes. Since rearrangement during dediazoniation (see ch 1.5.1) would affect the separate α and β-N isotope effects, Swain first re-investigated it and a value of 1.6% rearrangement confirmed the results of Lewis[81,82] for benzenediazonium tetrafluoroborate.

Taking the minor amount of rearrangement into account, an α-N isotope effect of 1.0384 ± 0.0010 and β-N isotope effect of 1.0106 ± 0.0003 were determined. Swain interpreted the very large α-N isotope effect (1.038) as indicative of greatly reduced C-N bond vibrational energy at the transition state, corresponding to almost complete formation of a phenyl cation. The smaller β-N isotope effect (1.011) implied that the N≡N leaving group could not be considered as a rigid 28 or 29 mass unit, and that during passage along the reaction coordinate the N-N bond order increases slightly above that of the reactant benzenediazonium ion. The spirodiazirine structure intermediate XVII and XVIIIa proposed by Lewis[82], predicted insufficient weakening of the C-N bond at the transition state to explain the large α-N isotope effect. The intermediates XVII and XVIIIa were therefore rejected by Swain as being involved in the rate determining step.

The constancy of ring hydrogen isotope effects (k_H/k_D) of benzenediazonium tetrafluoroborate measured by Swain[73] in H_2SO_4, CH_3CO_2H and CH_2Cl_2 at 25°, indicated that the same mechanism was occuring in these solvents. The secondary kinetic hydrogen isotope effect was 1.22 ± 0.01 for each ortho position, and for each meta and para position 1.08 ± 0.01 and 1.02 ± 0.01 respectively. Swain argued that delocalization of the positive charge into the ring of the proposed singlet cation XXI, or its immediately preceding transition state, is not possible since the vacant orbital lies in the plane of the ring. This leaves hyperconjugation as the only means of stabilization.



Since hyperconjugation should strongly stabilize an otherwise localized carbonium ion, the observed large secondary hydrogen isotope effect in the ortho position (1.22) is expected for the singlet cation XXI. Lewis and Boozer had previously demonstrated that β-hydrogen isotope effects of 1.1-1.3 are observed in SN1 solvolyses[103], and that the value is highly dependent on conformation. A value of 1.10 per β-D was observed in t-butylchloride solvolysis[104,105] where hyperconjugation is hindered by free rotation. The solvolysis of XXI, where the dihedral angle remains at 0° throughout carbonium ion formation, should therefore have a near maximum secondary isotope effect of 1.2-1.3. Swain's observed ring hydrogen isotope effects therefore offered strong support for the phenyl cationic nature of the solvolytic transition state and against any triplet type structure with the charge resident in the π cloud.

1.5.2.5 Dual substituent constant analysis

Swain[72] showed from the kinetic data of Crossley[76] that log (k/k_H) values for a range of meta and para mono substituted aryl diazonium chlorides in 0.1 mol dm^{-3} HCl solvolysis at 25°, obeyed the linear free energy relationship using $\mathcal{F}$ and $\mathcal{R}$ ("field" and "resonance") substituent constants that he had defined and tabulated previously[86].

The dual substituent equations are

$$\log (k/k_H)_m = f\mathrm{m}\mathcal{F} + r\mathrm{m}\mathcal{R} + i\mathrm{m}$$

$$\log (k/k_H)_p = f\mathrm{p}\mathcal{F} + r\mathrm{p}\mathcal{R} + i\mathrm{p}$$

$f\mathrm{m} = -2.74$, $f\mathrm{p} = -2.60$, $r\mathrm{m} = -3.18$, $r\mathrm{p} = 5.08$, $i\mathrm{m} = 0.27$, $i\mathrm{p} = -0.25$

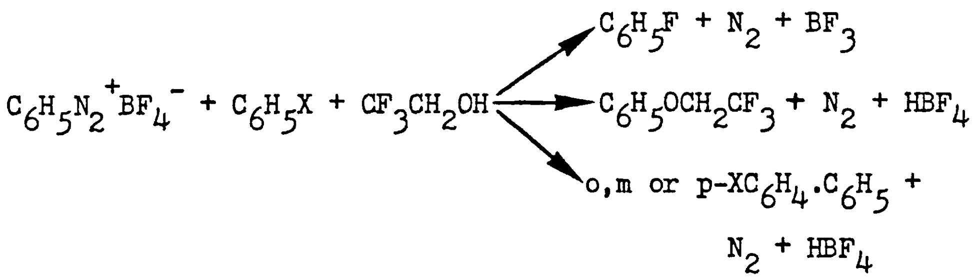
Correlation coefficients of 0.984 and 0.992 show the excellent fit of the data for meta and para substituents. The field constants $\mathcal{F}$ represent all influences except those transmitted by resonance or π bonds, and thus electron supplying (-ve $\mathcal{F}$) substituents should facilitate the departure of N_2 with its previously bonding electron pair by stabilizing the transition state with respect to the reactant diazonium ion. The transition state should therefore be close to the electron deficient phenyl cation structure XXI. The electron supplying substituents in the para position increase the double-bond character of the C-N bond, and stabilize strongly the reactant with respect of the transition state.

1.5.3 Dediazoniations in fluorinated alcohols

1.5.3.1 Heterolytic aryldediazoniations

Since 1968, three research groups[40,90,106-108] have found independently that under certain conditions aryldediazoniations do not follow the homolytic Gomberg-Bachmann pathway, some unexpected biphenyl derivatives being formed. This was able to be explained by a mechanism involving electrophilic aromatic substitution. Zollinger[40], in 1973, on finding 2,2,2-trifluoroethanol (TFE) to be a relatively good solvent for aryl diazonium salts and the exclusive formation of the heterolytic decomposition products viz aryl ethers and aryl fluorides in it, investigated the mechanism of heterolytic arylations using aryl diazonium ions in TFE solutions. The thermal decomposition of benzenediazonium tetrafluoroborate in the presence of mono-substituted benzenes (C_6H_5X) in TFE yielded three types of products (scheme 1.5.3.1-1):fluorobenzene, phenyl 2,2,2-trifluoroethylether , and o-, m-, or p-substituted biphenyl derivatives.

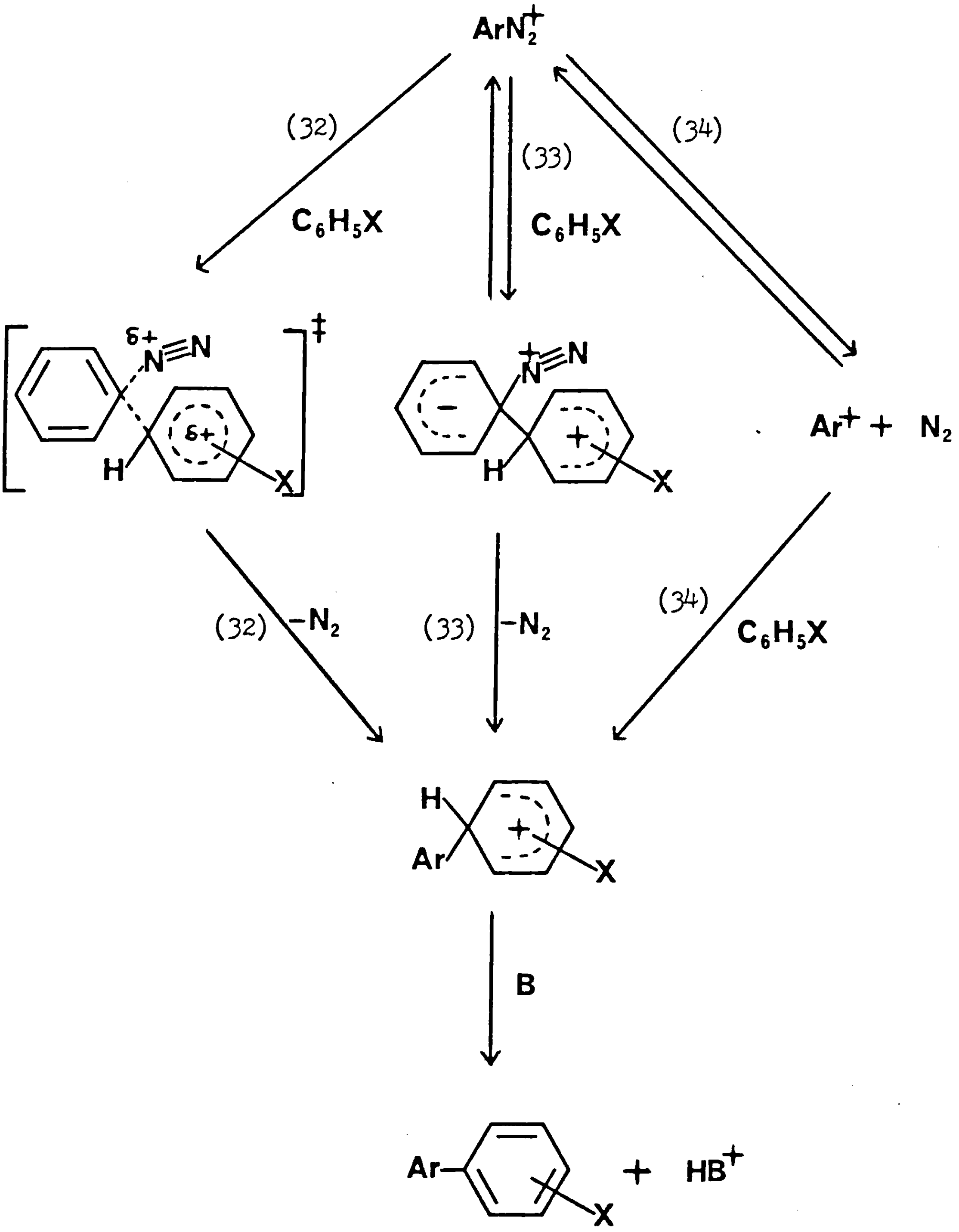
Scheme 1.5.3.1-1



The yield of biphenyl derivatives was found to increase with the nucleophilicity of the aromatic substrate as follows: $X = NO_2 < CF_3 < H < CH_3$ which, although the three reactions of scheme 1.5.3.1-1 are in competition is nevertheless the sequence expected for electrophilic arylation. The electrophilic character of the arylation was also apparent from the ratio of the isomeric biphenyl products. The product studies also indicated that a highly unselective electrophile was involved.

In some kinetics studies Zollinger[40], showed that the rate of disappearance of diazonium salt was first-order in diazonium salt and first-order in aromatic substrate up to a mol fraction of ~0.154. The ratio of fluorobenzene to phenyltrifluoroethyl ether was independent of the nature of the aromatic substrate. These kinetic results were thought to be consistent with three dediazoniation mechanisms (scheme 1.5.3.1-2), an SN2-type mechanism (32), an SNAr or addition-elimination mechanism (33) and the SN1 mechanism (34). It was concluded that mechanism 34 was only compatible with the experimental data if the aryl cation behaves as a steady state intermediate and that in this case, aryl cations would have to react much faster with molecular nitrogen than with the aromatic substrate. Zollinger regarded the SN1 mechanism (34) as being extremely unlikely if the first step leads to a free nitrogen molecule. It was however suggested that an SN1-like mechanism in which the first step of the reaction leads to an encounter complex between an aryl cation and an "activated" nitrogen molecule could not be ruled out. The SNAr mechanism (33) was excluded with certainty since the reaction did not show the typical substituent effects associated with SNAr substitutions. Mechanism (32), corresponding almost exactly to the SN2-mechanism at Sp^3 carbon atoms, although not previously revealed in aromatic substitutions, was not in conflict with the experimental evidence or any

Scheme 1.5.3.1-2



fundamental theory. Zollinger clearly favoured a bimolecular rate-limiting step, as he concluded in a review[41] article at the time, since there was no unambiguous evidence for a purely SN1 mechanism, but there existed a growing body of evidence[78,81,82] for the occurrence of a bimolecular rate-limiting step. The existence of aryl cations in solution was, at that time (1973), questionable.

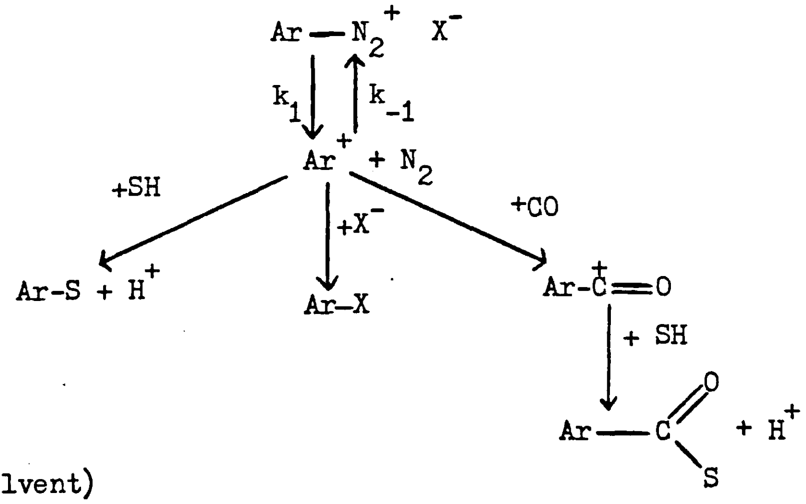
1.5.3.2 Isotopic N_α,N_β rearrangement and exchange with external nitrogen in dediazoniation

After Swain and co-workers[71-74] had established the existence of aryl cations in dediazoniation solutions, questions still remained unanswered concerning many aspects of the decomposition. The occasional influence of nucleophile concentration on the reaction rate could not be interpreted, and in particular a thorough investigation of the reversibility of aryl cation formation was required. Zollinger[109], in rejecting an SN2-like mechanism, pursued these questions and the possibility of formation of an encounter complex[40,110] between an aryl cation and an "activated" nitrogen molecule which he had previously raised[40].

In 1974, he presented the first evidence for a reaction of nitrogen molecules with a purely organic reagent in solution[110]. In studying the thermal dediazoniation of $^{15}N_\beta$-labelled benzenediazonium tetrafluoroborate in TFE a significant amount (8%) of isotopic rearrangement occurred and, under a nitrogen (^{14}N-^{14}N) pressure of 300 atm 2.46 ± 0.40% of this "external" nitrogen was incorporated into the residual diazonium salt at 70% dediazoniation. With carbon monoxide replacing nitrogen and at a pressure of 320 atm a 5.2% yield of 2',2',2'-trifluoroethylbenzoate was obtained as a decomposition product. Lewis[81] had previously shown that in water no decomposition products derived from carbon monoxide were formed. A change to the less nucleophilic TFE from water showed more than a fourfold increase in ratio of the rate of rearrangement[109] to the rate of solvolysis (k_r/k_s); the rearrangement rate (k_r) increased by a factor of eight and the dediazoniation reaction (k_s) increased by a factor of 1.5. The ratio k_r/k_s was found not to be significantly different with p-OCH_3 and p-CH_3 substituted diazonium ions, and to be relatively independent of both temperature and pressure changes.

Zollinger[109] argued that although an SN1 mechanism with competing additions of the various nucleophiles to the free aryl cation, (scheme 1.5.3.1-3), following the rate-limiting step, coincides with all the qualitative results, it did not explain all the data on the basis of the aryl cation being the only steady-state intermediate. This oversimplification of scheme 1.5.3.1-3 was demonstrated by the fact that if the reverse step (k_{-1}) was the same for the N_α, N_β rearrangement and the exchange with external nitrogen, a decrease in the ratio of k_r/k_s for the reaction under high pressure nitrogen would have been expected. The form of the kinetic equation derived from scheme 1.5.3.1-3 was also not in agreement with the rate data obtained for the reaction under increasing pressure.

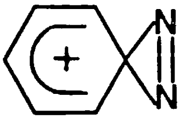
Scheme 1.5.3.1-3



(SH, solvent)

The need was paramount to obtain kinetic data from which to distinguish a simple one intermediate mechanism from a more sophisticated one involving at least two intermediates. The requirements for systems showing a higher proportion of rearrangement and exchange with molecular nitrogen were soon achieved. In 1978 Zollinger[111] showed that by changing the solvent to 1,1,1,3,3,3-hexafluoro-2-propanol(HFIP), the rate of isotopic rearrangement (10.47%) and exchange with external nitrogen (6.26%)at 70% reaction were both increased for the dediazoniation of benzenediazonium tetrafluoroborate. Even greater proportions were obtained using 2,4,6-trimethylbenzenediazonium tetrafluoroborate which gave 20.89% rearrangement and 6.33% exchange at 300 atm of nitrogen in TFE solvent. The corresponding results for 2,4,6-trimethylbenzenediazonium tetrafluoroborate in HFIP solvent gave by far the highest amount ever observed of isotopic rearrangement (36.97%) and exchange with external nitrogen (16.50%) at 70% dediazoniation. These reactions had been studied for some para substituted benzenediazonium salts already, and it had been found that the substituent had very little effect on the extent of N_α-N_β rearrangement in water[112] and in TFE[109]. On the other hand variations of ortho substituents were shown to have a significant influence. This was explained in terms of steric interference by the ortho groups to the approach of solvent molecules. The much smaller nitrogen molecule is able to reach the reaction site of the intermediate more easily, and in consequence, both more rearrangement and exchange was observed relative to the other solvolysis products.

Zollinger[113] therefore presented a detailed investigation of the dediazoniation of 2,4,6-trimethylbenzenediazonium tetrafluoroborate in 2,2,2-trifluoroethanol. The dediazoniation rate, the isotopic N_α-N_β rearrangement, and the exchange reaction of the diazonium group with external nitrogen were monitored under a constant pressure of 300 atm mixed nitrogen/argon gas, as a function of the partial pressure of nitrogen. The volume of activation for the dediazoniation of 2,4,6-trimethyl benzenediazonium tetrafluoroborate in TFE ($\Delta V^{\neq}$ = + 11.06 $cm^3 mol^{-1}$) was close to that found for the benzenediazonium salt in TFE ($\Delta V^{\neq}$ = + 11.4 $cm^3 mol^{-1}$) and was consistent with a transition state having the carbon-nitrogen bond considerably stretched, but not consistent with a spirodiazirine cation (XVII).



XVII

The effect of varying the partial pressure of nitrogen but keeping the total applied pressure constant was examined. The amount of ^{15}N label remaining in the diazonium ion after 70% dediazoniation decreased linearly with increasing concentration of nitrogen in TFE. This agreed with the assumption that the exchanged product was formed in a reaction of an intermediate with molecular nitrogen. The observed behaviour provided support for the proposed mechanisms in which the N_α-N_β rearrangement and exchange reactions proceed through different intermediates. This was also evident from the fact that the amount of rearranged product in every case was several times greater than the amount of exchanged product, although the concentration of free $^{15}N\equiv^{14}N$ molecular nitrogen in solution was orders of magnitude smaller than that of the dissolved $^{14}N\equiv^{14}N$ nitrogen added to the solution.

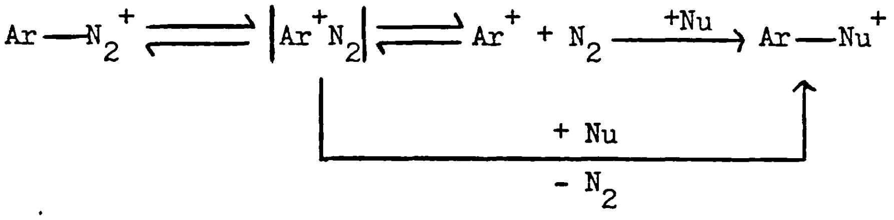
The most conclusive evidence for the proposed dediazoniation (scheme 1.5.3.1-5) was provided by the effect of changing the nitrogen concentration in TFE on the overall dediazoniation rate, k_s[113]. The curve-fitting of the overall dediazoniation rate against dissolved nitrogen concentration plot on the basis of both a "one-intermediate" and a "two-intermediate" model (viz. schemes 1.5.3.1-4 and 1.5.3.1-5 respectively), and subsequent statistical treatment[114], provided additional evidence for the "two-intermediate" mechanism.

Scheme 1.5.3.1-4

$$Ar{-}N_2^+ \rightleftharpoons Ar^+ + N_2 \xrightarrow{+Nu} Ar{-}Nu^+$$

$$k_s = \frac{a}{b[N_2] + C}$$

Scheme 1.5.3.1-5

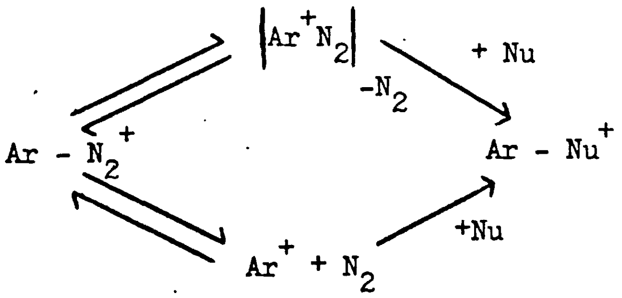


$$k_s = \frac{a'[N_2] + b'}{c'[N_2] + d'}$$

The first intermediate in scheme 1.5.3.1-5 $|Ar^+N_2|$ was described as a molecule-ion pair analogous to ion pairs postulated by Winstein[115], while the second was described as a "free"aryl cation which may be solvated.

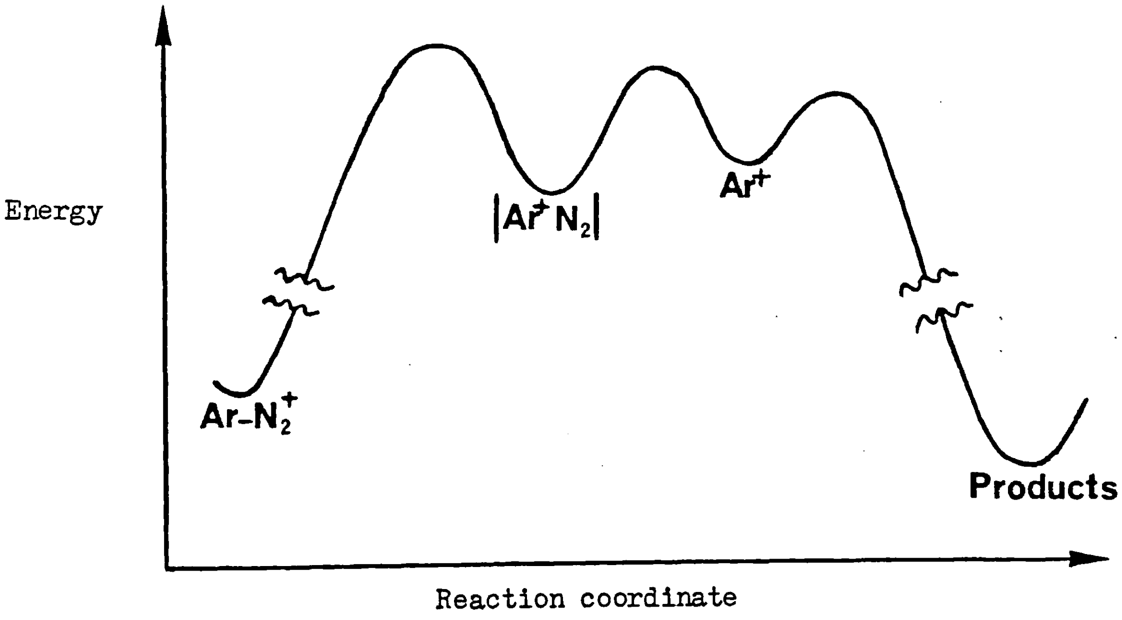
An additional"two-intermediate"mechanism (scheme 1.5.3.1-6), which could mathematically also fit the rate data, was rejected when the

Scheme 1.5.3.1-6



nature of the intermediates involved was considered. A molecular-ion pair $|Ar^{+}N_2|$ was expected logically to lie on the path from the diazonium ion to the free aryl cation. In conclusion Zollinger said that the energy of the second intermediate was only slightly higher than that of the first intermediate, $|Ar^{+}\ N_2|$, in TFE and HFIP since it was demonstrated that a significant part of the reaction occurred through the second intermediate for the exchange with nitrogen and reaction with carbon monoxide[113]. In water, however, the first intermediate reacts easily with the more nucleophilic solvent giving less N_{α}-N_{β} rearrangement. The external nitrogen or carbon monoxide reactions with the second intermediate were not observed in water but this may be due to the low solubility of these gases in water. The activation energy for the direct solvent capture by the first intermediate was said to be smaller in water than the activation energy for the interconversion of the first into the second intermediate. A crude qualitative synopsis of the progress of the main organic species during the course of the reaction had previously been supplied as an energy vs. reaction coordinate plot[110] and is shown in fig 1.5.3.1-1.

Fig 1.5.3.1-1



1.6 THERMAL DEDIAZONIATIONS IN OTHER ORGANIC SOLVENTS

1.6.1 Dediazoniations in acidic methanol

The thermal dediazoniation of aryl diazonium salts in acidic methanol has been found to yield both protodediazoniation and methoxydediazoniation products by several research groups[87,88,116-121]. The effects of dissolved oxygen, nitrogen and other additives have been found to significantly alter the product distribution of these dediazoniations. Bunnett and Yijima[122] in 1977 carefully restudied some earlier work[117] on the thermolysis of p-bromo- and p-methoxybenzenediazonium tetrafluoroborate in acidic methanol, determining reaction rates and products in the same experiment. The overall rate constants were dissected into radical (k_r) and ionic components (k_i), on the basis of the yields of products arising from protodediazoniation and methoxydediazoniation respectively. Changing the atmosphere from nitrogen to oxygen depressed k_r by two orders of magnitude but had no significant effect on k_i. These results were interpreted in terms of competing independent radical and ionic mechanisms[122,123], the former severely retarded by oxygen, the latter unaffected. The methoxydediazoniation behaved, therefore, as expected of an ionic mechanism. Its reaction was proposed to occur via aryl cation intermediates (35) as with hydroxydediazoniations[71-74]. The formation of

$$Ar - N_2^+ \longrightarrow Ar^+ + N_2 \xrightarrow{CH_3OH} ArOCH_3 + H^+ \qquad (35)$$

protodediazoniation products through hydride abstraction by aryl cations from methanol[87] (36) was thought to be unlikely under oxygen, since the proportion of protodediazoniation products was further reduced, sometimes to the point of undetectability, upon addition of supplementary radical scavengers[122]. The huge depression in the rate

$$Ar^+ + CH_3OH \longrightarrow ArH + CH_2OH^+ \qquad (36)$$

of protodediazoniation as the atmosphere was changed from nitrogen to oxygen was attributed to scavenging by oxygen of radical intermediates involved in a radical chain mechanism. There was no necessity to invoke the hypothesis, previously proposed by Bunnett[117], that both radical and ionic pathways involve a common intermediate.

The propagation sequence postulated by De Tar and co-workers[87,116] was compatible with the experimental data, and comprises steps 37, 38, and 39.

$$Ar\cdot + CH_3OH \longrightarrow ArH + \cdot CH_2OH \qquad (37)$$

$$\cdot CH_2OH + Ar\text{-}N_2^+ \longrightarrow ArN{=}N\cdot + CH_2OH^+ \qquad (38)$$

$$ArN{=}N\cdot \longrightarrow Ar\cdot + N_2 \qquad (39)$$

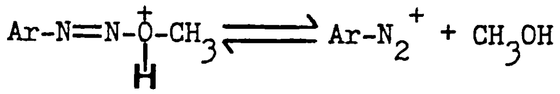
This propagation cycle became slightly modified on consideration of the evidence that arylazo radicals have an independent existence[124]. Other features of the mechanism were substantiated by ESR studies of Beckwith and Norman[125], in which the spectra of reactive intermediates or spin-trapped derivatives thereof were observed.

Protodediazoniation in acidic CH_3OD afforded virtually deuterium free mono-substituted benzenes in accord with Melander's[126] earlier work with a tritium label, and is consistent with aryl radicals abstracting hydrogen from the α carbon of methanol much faster than from the hydroxy group[127,128].

The initiation by homolysis of arylazomethylether to arylazo and methoxyl radicals (40) was rejected since arylazomethylethers were only detected in alkaline methanol solutions[129].

$$Ar\text{-}N{=}N\text{-}OCH_3 \longrightarrow ArN{=}N\cdot + CH_3O\cdot \qquad (40)$$

This implied that in the absence of base the azoether conjugate acids are prone to dissociate to diazonium ion and methanol (41).



$$\mathrm{Ar{-}N{=}N{-}\overset{+}{\underset{H}{O}}{-}CH_3 \rightleftharpoons Ar{-}N_2^+ + CH_3OH} \qquad (41)$$

A subsequent correlation of k_r with hydrogen ion concentration was undertaken by Bunnett[122], and found not to obey the expectations of such a mechanism. Although the nature of the radical initiation is unclear, Bunnett favoured initiation by electron transfer directly from methanol to the diazonium ion (42).

$$\mathrm{Ar{-}N_2^+ + CH_3OH \longrightarrow ArN{=}N\cdot + CH_3OH^{+\cdot}} \qquad (42)$$

A further investigation by Bunnett[123] was conducted in which the substituent effects of various monosubstituted aryldiazonium salts on rates were examined. Except for p-nitrobenzenediazonium tetrafluoroborate, methoxydediazoniation strongly predominated under oxygen and the substituent effects on the ionic mechanism were investigated under these conditions. Although a good correlation of these rates with rates of hydroxydediazoniation in water[117] was found, no correlation with Hammett σ values was obtained*. The ionic reaction was faster with certain substituents (eg. m-CH_3 and m-OCH_3) having positive or small negative σ values, and slow with others (eg. p-NO_2 and p-OCH_3) that have positive or negative σ values of larger magnitudes. No conclusions could be drawn for substituent effects from the rate data

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*It should be noted that Swain did not obtain a correlation of rates with Hammett σ values in his hydroxydediazoniation studies but did find excellent correlations using dual substituent $\mathcal{F}$ and $\mathcal{R}$ (field and resonance) effects. (see ch 1.5.2.5). Since relevant kinetic data was not given by Bunnett in this paper[123], a re-examination using dual substituents was not possible.

of the radical chain mechanism, and a simple relationship here would not be expected.

The protodediazoniation of p-bromobenzenediazonium tetrafluoroborate was stimulated by the addition of good radical sources, such as phenylazotriphenylmethane (PAT) for which the initiation of the radical mechanism would be expected as follows (43).

$$\underset{\textbf{PAT}}{\text{Ph-N=N-CPh}_3} \longrightarrow \text{Ph-N=N}\cdot + \text{Ph}_3\text{C}\cdot \longrightarrow \text{Ph}\cdot + \text{N}_2 \qquad (43)$$

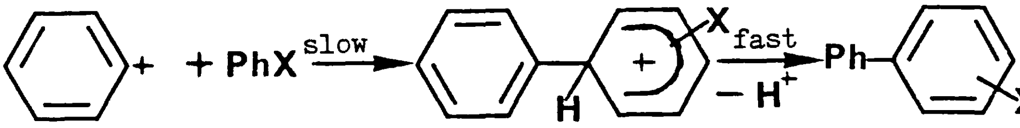
Radical scavengers on the other hand, such as 2-methyl-2-nitrosopropane (t-BuNO), suppressed the protodediazoniation of p-bromobenzenediazonium tetrafluoroborate.

1.6.2 Dediazoniations in dimethylsulphoxide

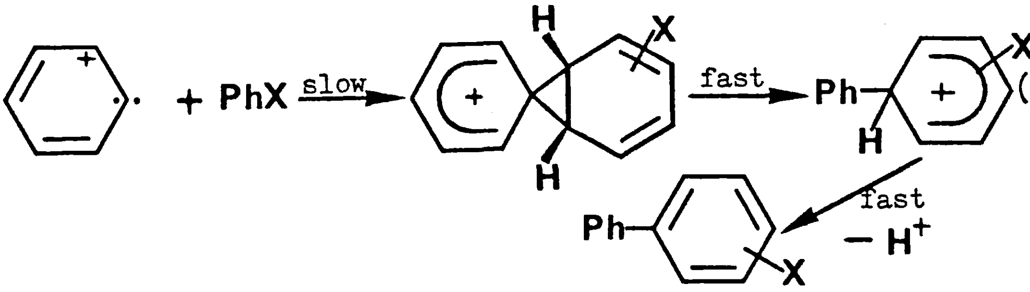
1.6.2.1 Aryldediazoniations

The arylation of aromatic substrates in dimethylsulphoxide which accompany dediazoniation, has been investigated since 1970[108]. Kobayashi and co-workers[108] were prompted to investigate arylations in homogeneous solutions consisting of aromatic solvents and dimethylsulphoxide, following Abramovitch and Saha's studies in heterogeneous media[90] and later studies in homogeneous media[130].

Kobayashi[108] investigated the phenylation of substituted benzenes with benzenediazonium tetrafluoroborate in homogeneous dimethylsulphoxide solutions, and measured the amount of substituted biphenyls obtained. The o-, m-, and p-biphenyl product distribution and partial rate factors were obtained. The rate constants of the dediazoniations were measured and the decompositions followed first order kinetics. The yields of biphenyls; 7% with nitrobenzene, 12.4% with chlorobenzene, and 20.8% with methoxybenzene as substrate follow the order expected for electrophilic substitution reactions. The biphenyl isomer distribution showed regioselectivity towards the reactive species derived from the diazonium ion; benzenes substituted with methoxy, methyl, ethyl, and chloro groups giving mainly o- and p-products, while those substituted with methoxycarbonyl and nitro groups gave mainly m-products. This confirmed that the reactions are electrophilic in nature. The variations in the partial rate factors compared with that in nitration[131] and sulphonylation[132] of aromatic compounds show that substrate selectivity is very small here. The distribution of isomeric substituted biphenyls was however vastly different from that obtained by the use of the phenyl radical, generated from phenylazotriphenylmethane[133] in a separate study. Phenylation by benzenediazonium tetrafluoroborate under an oxygen atmosphere did not significantly change the yields of biphenyls, as would be expected if a free radical mechanism operated. The low selectivity of the electrophile was explained in terms of arylation by the phenyl cation. A biradical phenyl cation was favoured by Kobayashi and others[89,90] but was later disputed by Swain[71]. Kobayashi adopted Abramovitch and Gadallah's[90] suggestion that the rate-determining step in these reactions was not the formation of a σ complex (mechanism 44), but the addition of the biradical phenyl cation to an aromatic double bond to form various spirocyclopropane phenonium ions, followed by ring-opening to give the three substituted σ-complexes in a product determining step (mechanism 45).



(44)



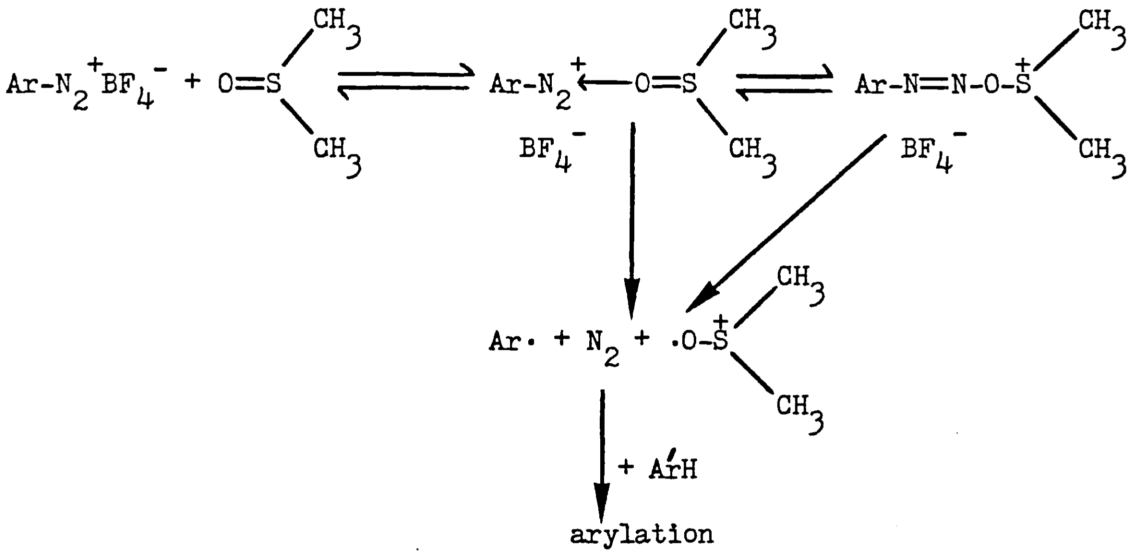
(45)

Kobayashi, in an experiment using ring deuturated aromatic substrates[108], demonstrated that since there was no kinetic isotope effect, the loss of a proton from the aromatic substrate could not be the rate limiting step. Although Kobayashi had no conclusive evidence to choose between mechanism 44 and 45, the author regards the biradical mechanism 45 as being extremely unlikely in the light of Swain's experimental[71-74] and theoretical[73] work together with the theoretical calculations of others[134-137].

Zollinger[107] in 1972 investigated arylations of benzene and nitrobenzene with benzenediazonium and p-nitrobenzenediazonium tetrafluoroborate in dimethylsulphoxide. Zollinger confirmed the results of Kobayashi[108] for the benzenediazonium ion arylations, concluding from the product isomer ratios that arylation of nitrobenzene was by the phenyl cation[107]. The percentages of o- and p-isomers in phenylation of nitrobenzene were however viewed as remarkably high for an electrophilic substitution. This was regarded as being indicative of (i) the extremely high reactivity and therefore low positional selectivity of the phenyl cation, or (ii) a concurrent homolytic and electrophilic substitution, or (iii) diradical type properties of the phenyl cation. The diradical explanation, although favoured by several[89,90,108] authors, was regarded by Zollinger as being improbable following theoretical calculations[134]. A minor decrease in phenylation yield on conducting the reaction under air was however not matched by a change in the isomer ratio, and a two pathway mechanism, involving superposition of a homolytic and electrophilic substitution, was therefore regarded as highly unlikely.

The arylation of benzene and nitrobenzene with p-nitrobenzenediazonium tetrafluoroborate in dimethylsulphoxide was shown by Zollinger[107] to proceed differently to the arylations with the benzenediazonium salt under nitrogen. High yields of the biphenyl products, viz 62-68% with benzene and 55-61% with nitrobenzene were obtained under a nitrogen atmosphere, and these dropped significantly when the reaction was conducted under air. At 80° the p-nitrophenylation of nitrobenzene gave a slightly lower yield but essentially the same isomer distribution as Hambling[138] had obtained using di-p-nitrobenzoylperoxide as the radical source at the same temperature. The biphenyl isomer ratios were therefore consistent with a radical mechanism involving the p-nitrophenyl radical and, although the yield of biphenyl decreased, the constancy of the isomer ratio under air was consistent with a homolytic mechanism in which oxygen acted as a radical scavenger. Spectroscopic evidence[139] indicated that the p-nitrobenzenediazonium ion was forming a charge-transfer complex with dimethylsulphoxide and scheme 1.6.2.1-1 was given to explain the p-nitrophenyl radical formation.

Scheme 1.6.2.1-1



This homolytic mechanism includes two possibilities of aryl radical formation; by a simple electron transfer, or via a covalent sulphonium adduct. Zollinger could not discriminate between these two processes.

1.6.2.2 Dediazoniation of p-nitrobenzenediazonium tetrafluoroborate

After conducting the work on arylations, Zollinger[140] decided to return to the problem of dediazoniation of p-nitrobenzenediazonium tetrafluoroborate in dimethylsulphoxide since there was some interest at the time in interactions of solvents with diazonium ions[42]. Since reaction products of p-nitrobenzenediazonium tetrafluoroborate with dimethylsulphoxide had previously been detected accompanying arylation reactions, Zollinger[140] investigated the dediazoniation of this salt with dimethylsulphoxide in the absence of aromatic substrates. It was found that in dilute solutions of the diazonium salt (2.0×10^{-2} mol dm^{-3}) p-nitrophenol was the main product. Since the origin of the phenolic oxygen atom was important in a mechanistic interpretation of the results ^{18}O-DMSO (26.2 ± 0.2% ^{18}O) was synthesized and used as the solvent. The p-nitrophenol obtained after dediazoniation also had an ^{18}O-content of 26.2%, showing that dimethylsulphoxide was the oxygen source. At a twenty fold increase of diazonium salt concentration the yield of p-nitrophenol however decreased substantially from 90% to 10% but being accompanied by large quantities of"polymeric diazo tars".

The rates of dediazoniation and formation of products were measured in dimethylsulphoxide containing low concentrations of the aryl radical scavenger[141], iodobenzene. Relative to pure dimethylsulphoxide, there was observed a large decrease in the yield of p-nitrophenol, and an increase in yields of nitrobenzene and tar. Also the formation of p-nitroiodobenzene, a product typical of a reaction involving p-nitrophenyl radicals[142], was significant. The formation of p-nitroiodobenzene was favoured by a higher concentration of iodobenzene and/or diazonium salt. The rate of formation of p-nitrophenol in dimethylsulphoxide at 50° was about eight times faster than that in acidic water at the same temperature, both reactions being first order in the diazonium ion. The dediazoniation reaction also gave good first order kinetics in dimethylsulphoxide/benzene mixtures, where the arylation product predominates even though the rate constant is not significantly different. The rate of formation of p-nitrophenol was also unaffected by small amounts of iodobenzene or the presence of oxygen. Zollinger[140, 143] however, observed a sharp contrast in the kinetics of dediazoniation on the addition of small quantities of pyridine. With pyridine a reciprocal optical density vs. time plot was linear, indicating second-order kinetics, and the rate of dediazoniation was strongly increased.

The straight-forward first-order kinetics of this hydroxydediazoniation in dimethylsulphoxide, and the absence of an effect on the rate of production of p-nitrophenol under oxygen, suggest a heterolytic mechanism. The existence of competitive arylation had however previously been shown to be homolytic[107] and to not influence the rate of dediazoniation. The production of p-nitroiodobenzene in the presence of iodobenzene confirmed a homolytic mechanism. Small amounts of by-products together with polymeric "diazo tars" can also be explained as the result of a radical mechanism. Table 1.6.2.2-1 shows the dediazoniation products of p-nitrobenzenediazonium tetrafluoroborate in dimethylsulphoxide at 50° as determined by Zollinger[140].

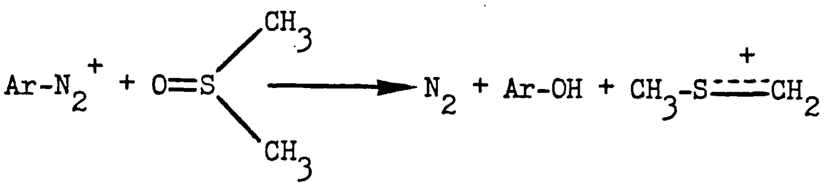
Table 1.6.2.2-1 Dediazoniation products of p-nitrobenzenediazonium tetrafluoroborate in DMSO at 50°

Concentration mol dm^{-3}	Yield expressed as % of the diazonium salt						
	Ar-OH	Ar-H	Ar-F	$Ar\text{-}SOCH_3$	$Ar\text{-}CH_2SOCH_3$	$Ar\text{-}SCH_3$	CH_3SCH_3
1.7×10^{-2}	89	0.5	< 0.1	< 0.1	< 0.1	Trace	0.1
2.0×10^{-2}	90	1	< 0.1	< 0.1	< 0.1	0	4.9
2.0×10^{-2}	88	2	< 0.1	< 0.1	< 0.1	Trace	3.8
40×10^{-2}	10	10	0.7	< 0.1	< 0.1	< 0.1	< 5 b)
40×10^{-2}	a)	11	0.5	Trace	< 0.1	Trace	< 2 b)
40×10^{-2}	10	6	0.1	Trace	< 0.1	Trace	a)

a) not determined

b) not quantitative

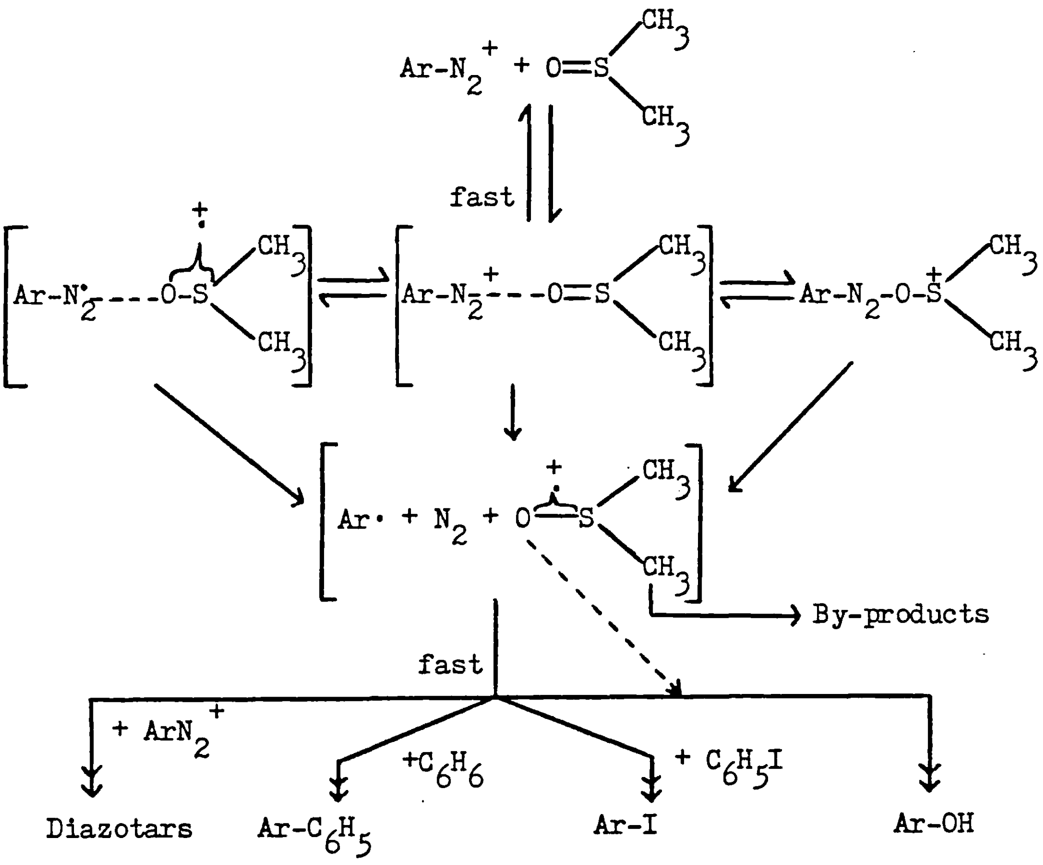
Nitrobenzene, which was formed, is known to be formed easily from p-nitrophenyl radicals in non-aromatic solvents free of halogen substituents[126]. The small quantities of p-nitrophenylmethylsulphoxide were not attributed to formation via the respective sulphide (also found), since no oxidation of the latter occurred when deliberately added to the system. Homolytic substitution at the methyl group in dimethyl sulphoxide by p-nitrophenyl radicals was thought to be a feasible explanation for its formation. A similar mechanism was thought likely for p-nitrophenylmethylsulphide formation. A major question not answered by Zollinger was the fate of the rest of the dimethylsulphoxide molecule which is the source of the oxygen atom in the major product, p-nitrophenol. The formation of a methyl methylene sulphoxonium cation (46), postulated as a steady-state intermediate by others[144,145], was rejected by Zollinger since it seemed to be too simple to interpret the results.



$$\mathrm{Ar{-}N_2^+} + \mathrm{O{=}S(CH_3)_2} \longrightarrow \mathrm{N_2} + \mathrm{Ar{-}OH} + \mathrm{CH_3{-}\overset{+}{S}{\cdots}CH_2} \qquad (46)$$

The kinetic results were consistent with a mechanism in which the formation of aryl radicals occurs in the rate determining step, and previously observed UV spectroscopic data indicated the formation of a charge-transfer complex formed [139] between the diazonium ion and dimethylsulphoxide, which is almost as good an electron donor as pyridine[146]. The mechanistic scheme 1.6.2.2-1 was accordingly proposed by Zollinger[140] to explain these results.

Scheme 1.6.2.2-1



Scheme 1.6.2.2-1 shows the rapid formation of the charge-transfer complex which decomposes slowly in the rate-determining step into a nitro-

gen molecule and a p-nitrophenyl radical and a dimethylsulphoxide radical cation. A slow diffusion of nitrogen and recombination of the two radicals in a cage was ruled out as the rate-determining step, since the formations of p-nitrophenyl, p-nitrobiphenyl, p-nitroiodobenzene and "diazo tars" were shown to be formed by competitive parallel reactions after the rate-limiting step. The decrease of p-nitrophenol yield at higher concentrations of the diazonium ion was explained by the increased equilibrium concentration of radicals, which initiate radical chain reactions of diazonium ions.

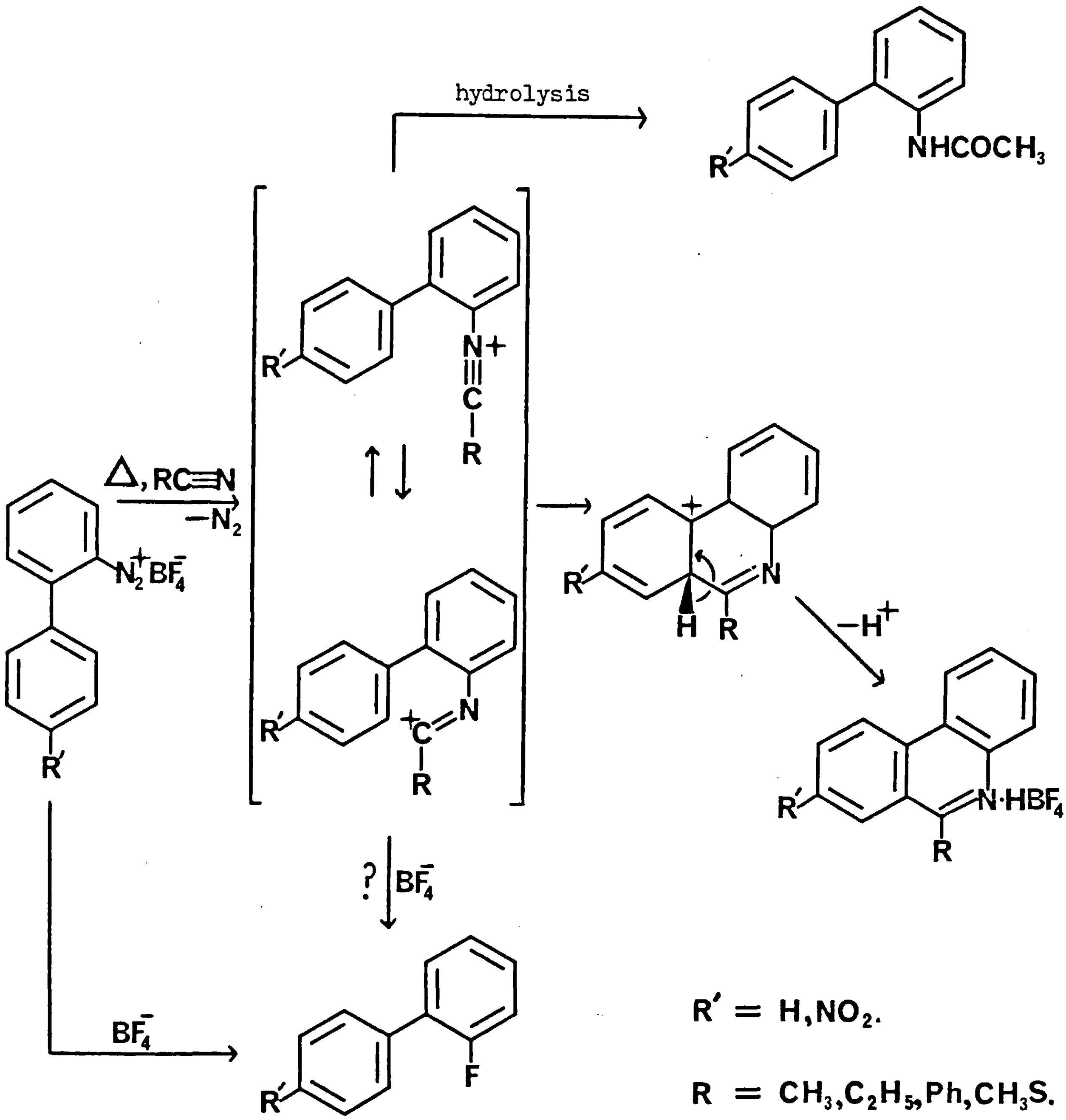
1.6.3 Dediazoniations in acetonitrile

The thermal dediazoniation of aryldiazonium tetrafluoroborates in the presence of organic nitriles can result in the formation of N-arylnitrilium tetrafluoroborate salts (47).

$$ArN_2^+BF_4^- + RC{\equiv}N \longrightarrow Ar\overset{+}{N}{\equiv}CRBF_4^- + N_2 \qquad (47)$$

In several cases the nitrilium salts have been isolated and characterized[147,148]. It is more usual, however, with aryldiazonium salt dediazoniations in acetonitrile, to either isolate an amide as the hydrolysis product of the nitrilium salt or else to utilize the nitrilium intermediate in a synthetic scheme[149,150]. Petterson[149] in 1974 showed that the thermal dediazoniation of 2-biphenyldiazonium tetrafluoroborates in the presence of aliphatic or aromatic nitriles afforded phenanthridines. Little competition was observed from the Schiemann reaction (fluoro-dediazoniation), and mechanistic scheme 1.6.3-1 was presented to explain these results. The formation of the phenanthridines, as outlined in scheme 1.6.3-1 was viewed as a two-step process. The first step was considered to be the replacement of the diazonium group by the nitrile, leading to the formation of the nitrilium salt. This first step was presumed to be fast, since evolution of the theoretical quantity

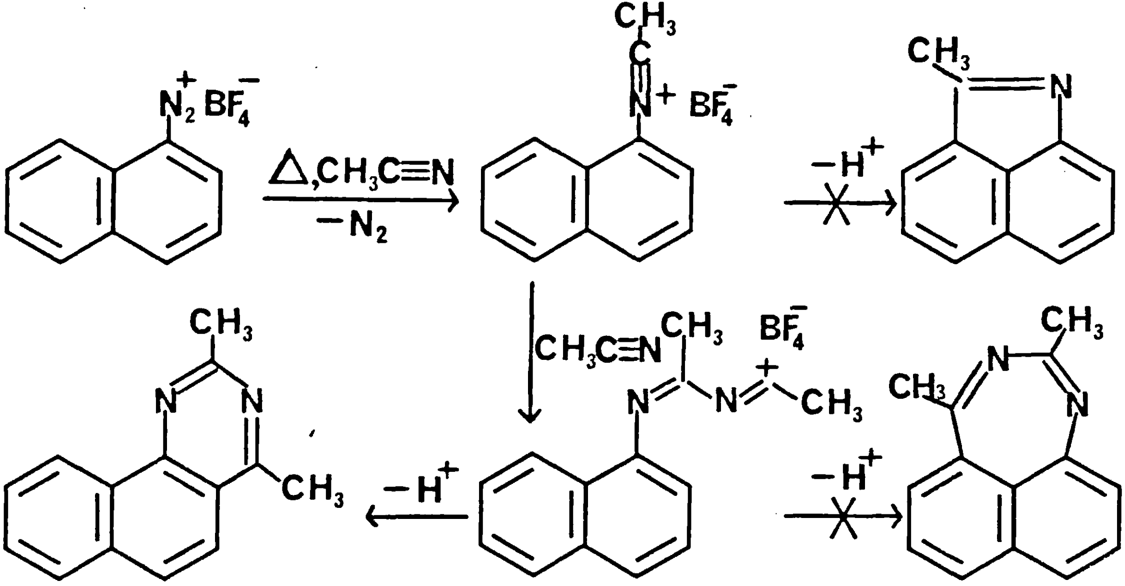
Scheme 1.6.3-1



of nitrogen was usually complete within a few minutes. A slower second step, which subsequently affords the phenanthridine, was demonstrated by the fact that higher yields of phenanthridine were obtained relative to the amide with longer reaction times prior to the addition of water. The amide must therefore result from the hydrolysis of the unreacted nitrilium ion. The small quantities of 2-fluorobiphenyls were accounted for by competition of the tetrafluoroborate anion with the nitrile in the first step, although reaction of the anion with the nitrilium ion was not ruled out.

The thermal dediazoniation of 1-naphthalenediazonium tetrafluoroborate in acetonitrile was also investigated by Petterson[149] and the major product was assigned the structure 2,4-dimethylbenzo[h]quinazoline, the formation of which was explained by scheme 1.6.3-2

Scheme 1.6.3-2



Scheme 1.6.3-2 accounts for the formation of the quinazoline by reaction of the initial nitrilium salt with a second molecule of acetonitrile to give a salt, which then intramolecularly attacks the 2 position of the naphthalene ring to give the quinazoline. The other cyclization products shown in scheme 1.6.3-2 were not detected by Petterson[149].

A kinetic study of the thermal dediazoniation of benzenediazonium tetrafluoroborate in aprotic polar solvents by Kobayashi[151], included acetonitrile as one of the solvents studied. The other solvents investigated were dimethylsulphoxide, dimethylformamide, nitromethane, and acetone. The decomposition of benzenediazonium tetrafluoroborate in all five solvents gave very similar first-order rate constants. These results were explained by the monomolecular dediazoniation of the diazonium ion to give the phenyl cation and nitrogen[71]. The decomposition in these aprotic polar solvents was contrasted to that in methanol[116,152] or pyridine[153], where it has been demonstrated that decomposition occurs homolytically. The nucleophilicity of these solvents was said to be insufficient to cause a combination with the diazonium ion*, as with diazonium ions and pyridine[140,143]. The polarity of the solvents was large enough, however, to assist in the formation of a phenyl cation stabilized by solvation.

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* Although the author does not dispute the formation of the phenyl cation in these aprotic polar solvents the mechanism of electron transfer, favoured later by Bunnett[122] in methanol dediazoniations and with the p-nitrobenzenediazonium ion in dimethylsulphoxide, should also be considered here.

1.7 PHOTOLYTIC DEDIAZONIATIONS

1.7.1 Competitive homolytic and heterolytic dediazoniations

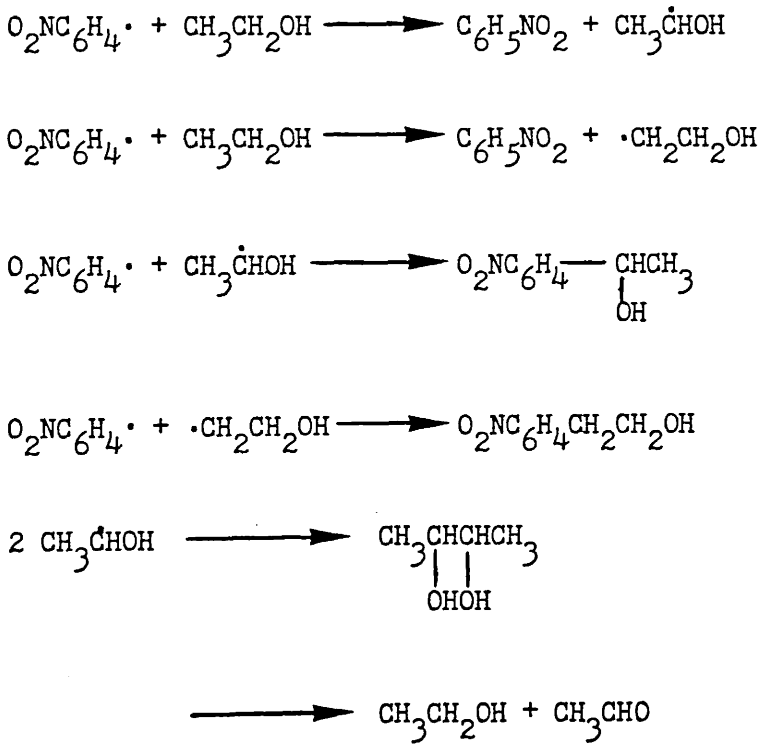
In 1961 Lee, Calvert, and Malmberg[154] studied the photodecomposition of p- and m-nitrobenzenediazonium salts in ethanol solutions, using a polychromatic medium pressure mercury arc lamp. The dominant primary process of the photochemical dediazoniations in ethanol was concluded to be the homolytic scission of the (C-1)-N_α bond (48).

$$O_2NC_6H_4N_2^+X^- \xrightarrow{h\nu} O_2NC_6H_4\cdot + N_2 + X\cdot \tag{48}$$

X^- = Cl^-, $SnCl_5^-$ or ion solvent dipole complexes.

The nitrophenyl radicals so produced were responsible for the formation of nitrobenzene, α and β arylethanol acetaldehyde and butanediol by the secondary reactions in scheme 1.7.1-1. Formation of the nitroso derivative, in the presence of nitric oxide, the high degree of halogenated nitrobenzenes formed in the presence of halogens, and the

Scheme 1.7.1-1



$$O_2NC_6H_4\cdot + CH_3CH_2OH \longrightarrow C_6H_5NO_2 + CH_3\dot{C}HOH$$

$$O_2NC_6H_4\cdot + CH_3CH_2OH \longrightarrow C_6H_5NO_2 + \cdot CH_2CH_2OH$$

$$O_2NC_6H_4\cdot + CH_3\dot{C}HOH \longrightarrow O_2NC_6H_4-\underset{OH}{\underset{|}{C}}HCH_3$$

$$O_2NC_6H_4\cdot + \cdot CH_2CH_2OH \longrightarrow O_2NC_6H_4CH_2CH_2OH$$

$$2\ CH_3\dot{C}HOH \longrightarrow CH_3\underset{OH}{\underset{|}{C}}H\underset{OH}{\underset{|}{C}}HCH_3$$

$$\longrightarrow CH_3CH_2OH + CH_3CHO$$

Scheme 1.7.1-1 continued

$$O_2NC_6H_4\cdot + CH_3\dot{C}HOH \longrightarrow C_6H_5NO_2 + CH_3CHO$$

$$O_2NC_6H_4\cdot + \cdot CH_2CH_2OH \longrightarrow C_6H_5NO_2 + \underset{\begin{array}{c}\downarrow \\ CH_3CHO\end{array}}{CH_2{=}CHOH}$$

decrease in concentration of added 2,2-diphenylpicrylhydrazyl on photolysis, all pointed to the importance of nitrophenyl radicals in the photochemical dediazoniation reaction. However all of the products could not be explained by a single primary process, and the formation of aryl ethers was attributed to a second primary process of lower probability, involving the heterolytic scission of the $(C\text{-}1)\text{-}N_\alpha$ bond, to form an aryl cation (49), and subsequent formation of the aryl ether (50).

$$O_2NC_6H_4N_2{}^+X^- \xrightarrow{h\nu} O_2NC_6H_4{}^+ + N_2 + X^- \qquad (49)$$

$$O_2NC_6H_4{}^+ + CH_3CH_2OH \longrightarrow O_2NC_6H_4OCH_2CH_3 + H^+ \qquad (50)$$

The idea of competitive homolytic and heterolytic photochemical dediazoniations was tested by analysis of the product distribution on addition of iodine. On addition of iodine to the p-nitrobenzenediazonium salt photolysis solution the amount of aryl ether produced did not significantly change, but the high yield of p-iodonitrobenzene was found at the cost of nitrobenzene formation. This was attributed to the competing fast reaction of the p-nitrophenyl radical with iodine (51).

$$O_2NC_6H_4\cdot + I_2 \longrightarrow O_2NC_6H_4I + I\cdot \qquad (51)$$

The contrast[154] between the photolysis products of p-nitrobenzenediazonium chloride in alcohol and in aqueous solution is striking.

Nitrobenzene, the major product in ethanol, was not detected in aqueous solution while p-nitrophenol and p-chloronitrobenzene dominated the reaction products in water. These results, coupled with product studies with nitric oxide, indicated that free radical formation in the photolysis of the diazonium salts in aqueous solutions was unimportant, and was consistent with a single heterolytic primary process forming the aryl cation (49). The product distributions in solutions with added chloride ion concentrations were seen as the result of competition between the chloride ion and water for the aryl cation (scheme 1.7.1-2)

Scheme 1.7.1-2

$$O_2NC_6H_4^+ + Cl^- \longrightarrow O_2NC_6H_4Cl$$

$$O_2NC_6H_4^+ + H_2O \longrightarrow O_2NC_6H_4OH + H^+$$

A search for radicals in the photolysis of p-dimethylaminobenzenediazonium chloride was previously conducted by Boudreaux and Boulet[155], who suggested that the observed magnetism was due to the chlorine radical and an aryl radical. These results were however strongly disputed by Zandstra and Evleth[156], who credited these results to the presence of the p-dimethylaminophenoxy radical through their ESR experiments.

In 1969, as part of his investigations into the mechanism of aryl diazonium salt dediazoniations in aqueous solution[83,157,158] by photochemical and thermal routes, Lewis[158] conducted isotopic labelling experiments on α-^{15}N labelled aryl diazonium salts. When α-^{15}N p-methylbenzenediazonium or α-^{15}N p-methoxybenzenediazonium salts were exposed to light, for insufficient time to complete the photolysis, the residual diazonium salt was in part rearranged to the β-^{15}N-aryl diazonium salt but significantly more than in the corresponding dark reaction. Lewis[158] rejected that the aryl cation was the only species involved as a common intermediate in photochemical and thermal dediazoniations in aqueous solution, and proposed mechanistic scheme 1.7.1-3 for the photochemical reaction. The intermediate D^*, formed on the absorption of light, was considered to be stable enough to undergo bimolecular reactions with nucleophiles. Lewis[158] also speculated that D^* may have a spiro diazirine structure, analogous with the species observed by Lee, Calvert and Malmberg[154] in the low temperature (77K)irradiation of p-dimethylaminobenzenediazonium hexachlorostannate, whose structure[159] was tentatively suggested as XXV.

Scheme 1.7.1-3

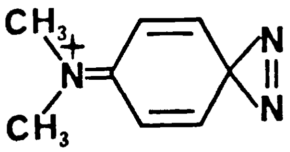
$$Ar-{}^{15}\overset{+}{N}\equiv N \xrightarrow{h\nu} D^*$$

$$D^* \longrightarrow Ar-{}^{15}\overset{+}{N}\equiv N$$

$$D^* \longrightarrow Ar-\overset{+}{N}\equiv {}^{15}N$$

$$D^* + H_2O \longrightarrow ArOH + N_2 + H^+$$

$$D^* + Cl^- \longrightarrow ArCl + N_2$$



XXV

1.7.2 The wavelength dependence of photochemical dediazoniations

Becker[160] in 1977 investigated the photolysis of benzenediazonium tetrafluoroborate, together with a number of its p-substituted derivatives. The photolyses were conducted at various wavelengths, in methanol and ethanol/acetonitrile solutions, under argon. The arylethers and arylfluorides were regarded as being formed by an SN1 type ionic path (52).

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N} \longrightarrow \mathrm{N_2} + \mathrm{Ar^+} \xrightarrow[\mathrm{BF_4^-}]{\mathrm{ROH}} \mathrm{ArOR,\ ArF} \qquad \mathrm{SN1} \qquad (52)$$

The production of aromatic hydrocarbons was thought to occur by an electron transfer mechanism (53).

$$\mathrm{Ar{-}\overset{+}{N}{\equiv}N} + \mathrm{{:}D} \longrightarrow \mathrm{D^+} + \mathrm{Ar{-}N{=}N\cdot} \longrightarrow \mathrm{N_2} + \mathrm{Ar\cdot} \xrightarrow{\mathrm{RH}} \mathrm{ArH} \qquad (53)$$

Both of these paths had been shown to be in competition from previous work[161,162]. The radical reaction (53) shows the transference of an electron from an electron donor (:D) to the diazonium salt, and the donor may be the solvent or in some cases the anion. The reduction reaction had previously been shown to be the preferred reaction in thermolysis argued on the basis of the larger decrease in the Gibbs Free Energy (ΔG)[161,163]. The same change was true of the Gibbs Free Energy of the photolysis reaction (ΔG^*).

$$\Delta G = E^{\mathrm{OX}}_{\frac{1}{2}(\mathrm{Donor})} - E^{\mathrm{Red}}_{\frac{1}{2}(\mathrm{ArN_2^+})} \qquad \text{(Thermolysis)}$$

$$\Delta G^* = E^{\mathrm{OX}}_{\frac{1}{2}(\mathrm{Donor})} - E^{\mathrm{Red}}_{\frac{1}{2}(\mathrm{ArN_2^+})} - E^{h\nu} \qquad \text{(Photolysis)}$$

The ΔG relationship however only says whether the reaction is feasible on a thermodynamic basis and does not guarantee a reaction[164,165].

When the nucleophile is a relatively better donor, as with thiols[166] (see reaction scheme 1.7.2-1) then a two stage process may occur.

Scheme 1.7.2-1

$$\mathrm{Ar\text{-}\overset{+}{N}{\equiv}N + R\text{-}S\text{-}H \rightleftharpoons Ar\text{-}N{=}N\text{-}S\text{-}R + H^{+}}$$

$$\mathrm{Ar\text{-}N{=}N\text{-}S\text{-}R \longrightarrow Ar\text{-}N{=}N\cdot + \cdot S\text{-}R}$$

$$\mathrm{Ar\text{-}N{=}N\cdot \longrightarrow Ar\cdot + N_2}$$

A similar course may also occur with other nucleophiles (HO^-, RO^-, amines, phosphines, etc), but the relationship between electron pair donation and electron transfer leading to reduction for various nucleophiles is not entirely clear at present[167,168].

Becker[160] found that the amount of reduction product obtained from the photolysis of various p-substituted aryldiazonium salts, in methanol and ethanol, was dependent on the wavelength of irradiation. Pyrene was also added as an electron donor during some experiments. The yields of products obtained in all of Becker's experiments are given in table 1.7.2-1.

Table 1.7.2-1 Photochemical and thermal dediazoniation product distributions for some para substituted benzenediazonium tetrafluoroborates in alcoholic solutions

p-X	Products in MeOH, under Argon					in EtOH/MeCN[d] under		
						Argon	+ pyrene	
		A	B	C	D	E	F	G
		313 nm	$\Delta(50^{o})$	>330 nm	Hg-MP[b]	313 nm	313 nm	365 nm
NO_2	% ArH	87	95		94			
	% ArOR	0	0		3			
	% ArF	0	0		1			
Cl	% ArH	87	100(69[c])	91(74[c])	87(54[c])	97	85	79
	% ArOR	7	0(16[c])	0(4[c])	9(17[c])			
H	% ArOH	52	2		80			
	% ArOR	36	94		13			
	% ArF	2	3		1			
Me	% ArH	11	7	23[a]	82	35	69	72
	% ArOR	80	82	73[a]	12	36	10	5
	% ArF	5	3	4[a]	1	7	1	1
MeO	% ArH	12	1	78	88	9	46	81
	% ArOR	80	18	9	9	45	23	0
	% ArF	5	47	1	1	7	0	0
NMe_2	% ArH			24[a]	6	31[a]	37	33
	% ArOR			62[a]	86			
	% ArF			4[a]	1			

a) At 365 nm

b) Hg-medium pressure lamp

c) In the presence of 0.5 mol dm^{-3} 2-Methyl-2-nitrosopropane

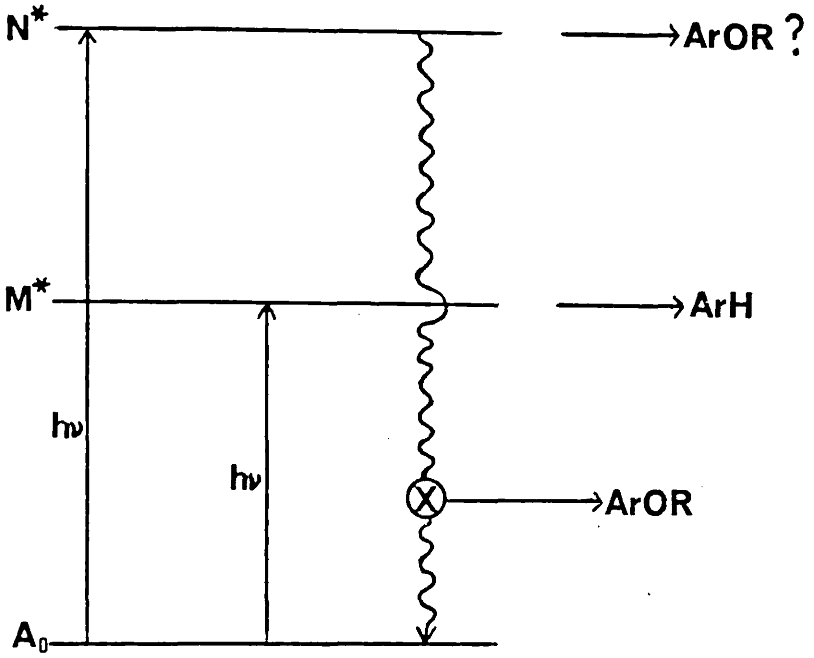
d) EtOH/MeCN 4:1 v/v

In view of arguments based upon the value[162] for ΔG^* in dediazoniations with methanol and ethanol one would expect that the radical reaction should be favoured. In the photochemical dediazoniation of p-methyl and p-methoxyphenyldiazonium salts, irradiated < 313 nm, only relatively small amounts of reduction product (ArH) were obtained, while the yield of (ArOR + ArF) was high (see table 1.7.2-1 A and E). With the unsubstituted benzenediazonium salt, and its p-chloro and p-nitro derivatives, this effect was said to be masked by the presence of a thermal chain reaction, which causes exceptional yields of the reduction product. The presence of the radical scavenger 2-methyl-2-nitroso propane during photolysis was however seen to partially inhibit this thermal chain reaction (see table 1.7.2-1 D).

At irradiation > 330 nm, at which most of the diazonium salts still absorb, although weakly, the formation of reduction product was seen to be more favourable (see table 1.7.2-1 C). When, for comparison, the irradiation was conducted in the absorption region of the electron donor or the electron donor acceptor complex, as with pyrene (see table 1.7.2-1 F and G), high yields of reduction products are found and so accord with the ΔG^* relationship. The p-dimethylaminobenzene diazonium salt however shows no significant difference on addition of pyrene, possibly because its absorption band is then irradiated (~ 380 nm) and the electron transfer and ionic cleavages occur with similar facility.

The wavelength dependence of the photochemical reactions was explained by Becker[160], as being due to competing reactions of excited states (see diagram 1.7.2-1).

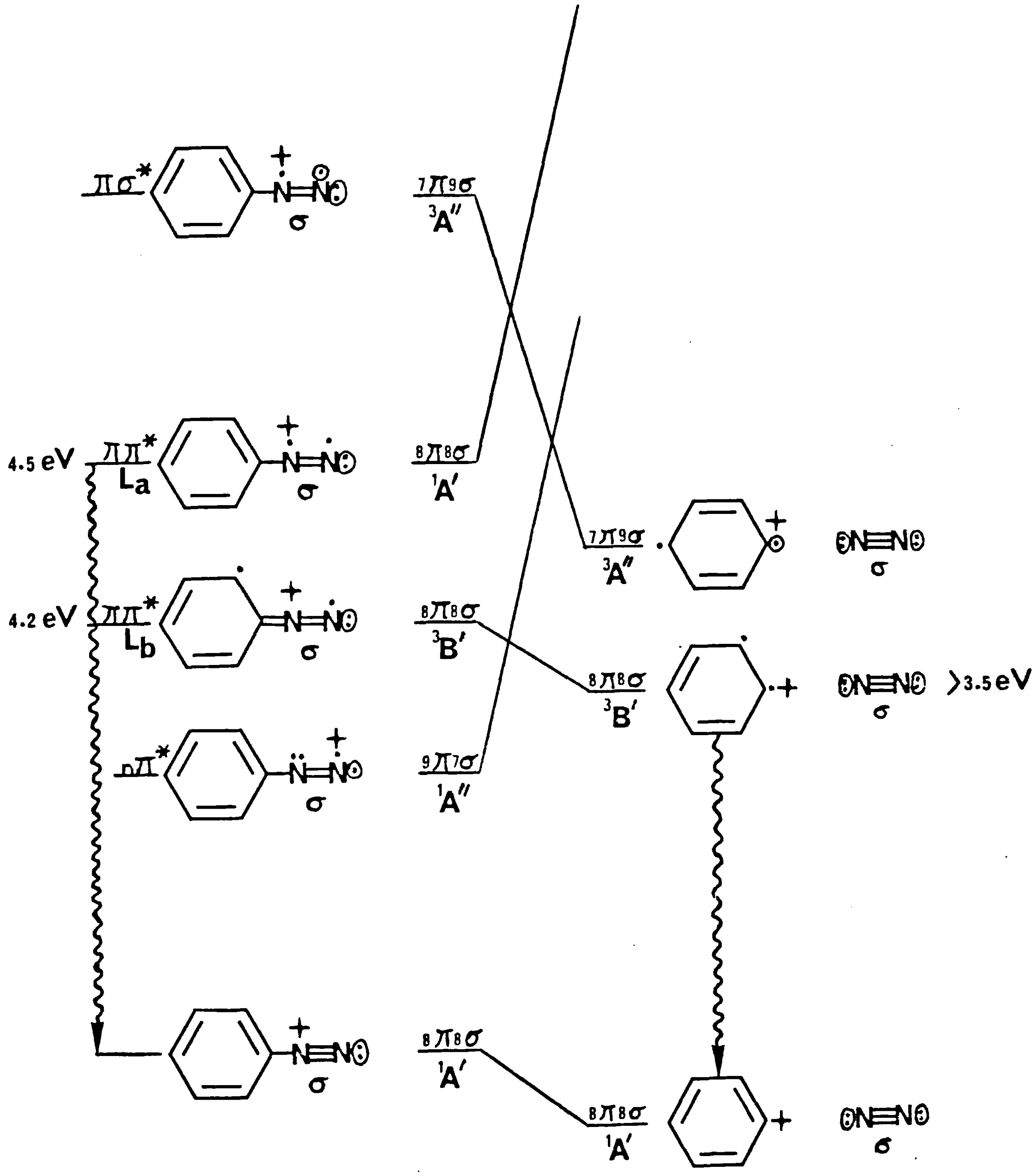
Diagram 1.7.2-1 Wavelength dependence for photochemical dediazoniations



He proposed that the higher energy state N^* (from absorption of light at lower wavelengths) to be responsible for the formation of products via the ionic pathway while the lower energy excited state M^* (from absorption of light at higher wavelengths) leads to the formation of reduction products by the electron transfer reaction. This picture seems however too simple to explain the product distributions obtained. An internal conversion from the N^* excited state to the M^* state may occur, and application of symmetry criteria of photochemical reactions must be used to explain this[169,170]. The Woodward-Hoffmann treatment[171] was not employed by Becker since it was regarded as too simple a treatment. Electrons in σ and π planes are perpendicular to one another. A doubly occupied state with π symmetry is always symmetrical with reference to the symmetry plane, while a single occupancy is antisymmetric. The state with σ -symmetry lies in the symmetry plane and therefore affords no contribution to the total symmetry.

A symmetry correlation diagram was constructed by Becker for the benzenediazonium salt ionic dediazoniation (diagram 1.7.2-2).

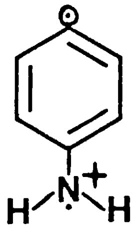
Diagram 1.7.2-2 Symmetry diagram for the ionic dediazoniation of the benzenediazonium salt



For the phenyl cation, INDO calculations[172] give the singlet σ-cation ($^1A'$) as the most stable species, and at much higher energy ($>$ 3.5 eV) the triplet σ-cation ($^3B'$) with the "Taft cation"[89] ($^3A''$) at even higher energy. Diagram 1.7.2-2 shows that the ground state of the diazonium salt ($^1A'$) correlates with the σ ground state of the aryl cation ($^1A'$), and so explains how easily the thermal dediazoniations proceed. The high lying "Taft cation" correlates with a high $\pi\sigma^*$ state of the diazonium salt, while the nπ^* and the $\pi\pi^*$ state of $^1A'$ symmetry do not correlate with any lower lying aryl cationic species. The two most important electronic transitions, L_a and L_b, are shown in diagram 1.7.2-2 and correspond to the assignments given by Evleth[173]. The highest energy transition, L_a, (lower wavelength absorption), is shown as a transition from the groundstate of the diazonium ion to the $^1A'$ symmetric $\pi\pi^*$ state and which deexcites to a high vibrational energy level of the groundstate $^1A'$. Reactions may then proceed to the singlet aryl cation $^1A'$, as in the thermal reaction. The lower energy electronic transition, L_b, (higher wavelength absorption), is shown as a transition from the groundstate of the diazonium ion to the $^3B'$ symmetric $\pi\pi^*$ state, which correlates with the $^3B'$ symmetric triplet aryl σ-cation. Deexcitation of the $^3B'$ symmetric triplet aryl σ-cation to the $^1A'$ singlet aryl σ-cation is also shown in the diagram. The lack of experimental evidence, particularly for other p-substituted diazonium salts, and differing relative stabilities of their excited states means that this picture may only be, at best, of use for the benzenediazonium ion. The extreme case for this difference in stabilities of excited states is the p-aminobenzenediazonium ion, or its analogues for which theoretical calculations make the triplet aryl cation[136,172] more stable than the singlet aryl cation.

1.7.3 Theoretical calculations of singlet and triplet aryl cations

Evleth and Horowitz[172] in 1971 performed INDO calculations on the electronic structures of the phenyl cation and the p-aminophenyl cation, finding that the filled-shell singlet and open-shell triplet forms were strongly substituent dependent. The relative stabilities of the phenyl cation species are given in the right hand side of diagram 1.7.2-2. In contrast with the phenyl cation results the calculations for the p-aminophenyl cation (XXVI) predicted a near degeneracy of the π-cation triplet state ($^3A''$) and the σ filled-shell cation singlet ($^1A'$). The triplet state was predicted to be slightly more stable than the lowest filled-shell singlet in this case. Examination of the spin and electron densities of the triplet state p-aminophenyl cation showed that the π-electronic structure can be approximated to the valence-bond structure XXVI.



XXVI

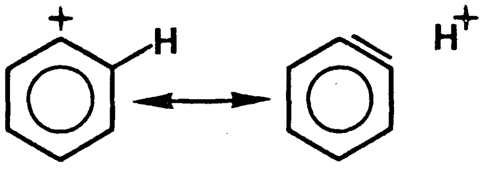
Pople[136] in 1977, made a more extensive set of ab initio Gaussian 70 calculations of substituted phenyl cations, using an STO-3G minimal basis set with standard geometry for both open (triplet) and closed-shell (singlet) calculations.

Stabilization energies of the various substituted singlet phenyl cations, obtained by Pople[136], are given in table 1.7.3-1.

Table 1.7.3-1 Singlet stabilization energies

X		[Stabilization energy, kJ mol^{-1}]		
		Ortho	Meta	Para
Li		237	158	130
HBe		48.5	28.5	15.5
H_2B	(coplanar)	8.4	8.8	-8.4
	(orthogonal)	20.5	15.1	16.7
H_3C	(syn)	14.6	16.7	17.6
	(anti)	16.3	15.9	17.6
H_2N	(coplanar)	20.1	20.5	47.3
	(orthogonal)	15.5	28.0	13.4
HO	(syn)	-31.0	-5.4	11.3
	(anti)	-1.7	-9.6	11.3
F		-36.0	-25.5	-14.6

Conformational and positional preferences were explained in terms of σ, π, and steric effects. The σ effects include all interactions implying a movement of electrons symmetric with respect to the ring plane. These interactions included inductive effects as well as in-plane hyperconjugation, illustrated by XXVII and XXVIII. Based on the electron withdrawal from the ring hydrogens in the singlet phenyl



XXVII XXVIII

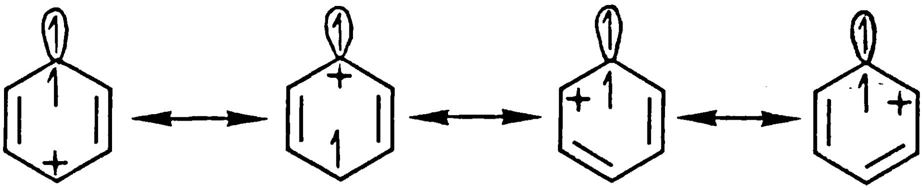
cation, the electronic demands in the σ system were expected to be severe. The stabilization energies in table 1.7.3-1 clearly demonstrate that substituents which are σ donors, Li and HBe, provide strong stabilization while σ withdrawing substituents, like OH and F, are poor, (fluorine destabilizes in every position around the ring). The π effects towards stabilization of substituted singlet phenyl cations were not so strong. In summary, the singlet phenyl cation was stabilized most strongly by σ donors, $o > m > p$, but π donors were also effective $(p > o > m)$.

Stabilization energies of the various substituted triplet phenyl cations, obtained by Pople[136], are given in table 1.7.3-2.

Table 1.7.3-2 Triplet stabilization energies

		[Stabilization energy, kJ mol^{-1}]		
X		Ortho	Meta	Para
Li		203	160	194
HBe		27.2	22.6	12.6
H_2B	(coplanar)	-4.2	12.1	-19.7
	(orthogonal)	49.8	36.0	54.4
H_3C		20.9	39.7	55.2
H_2N	(coplanar)	235	152	236
	(orthogonal)	31.0	32.6	22.6
HO	(syn)	125	63.2	127
	(anti)	123	55.2	127
F		31.4	12.1	41.0

Since there is no vacant orbital in the σ system of the triplet, σ-effects were not expected to be as important as in the singlet cases. Population analysis did not however bear this out. Although triplet σ transfer values were unchanged relative to singlets with electropositive substituents, they were considerably increased with electronegative substituents. The latter was attributed to an increase in π donation which enhanced σ withdrawal by a "push-pull" mechanism. Fluorine was found to stabilize the triplet and this indicated that inductive effects are less important than π effects in triplet states. The triplet states under consideration have five π-electrons with the desire to obtain a sixth to increase aromaticity. The triplet stabilization energies, in table 1.7.3-2 bore this out by following the positional preferences expected of the $^3B'$ resonance forms XXIX.



XXIX

The major π-donating substituents NH_2 and OH show the stabilizing trend implied by the $^3B'$ resonance forms XXIX all being stabilized, especially NH_2, in order of effectiveness $o \sim p > m$. Rotation of the amino group from planarity with the ring reduced the π-donation to the ring and was thereby costly energetically.

Pople[136] calculated the relative differences in energies between the most favourable conformations of singlet and triplet substituted phenyl cations, and these results are given in table 1.7.3-3. These values were corrected for gross geometrical and theoretical errors in singlet-triplet separations.

Table 1.7.3-3 Calculated singlet-triplet separations

X	Favoured isomer singlet	Favoured isomer triplet	E(singlet) - E(triplet) kJ mol^{-1}
H			-84.1
Li	ortho	ortho	-119
HBe	ortho	ortho	-106
H_2B	meta.copl	para.orth	-68.6
H_3C	para	para	-46.4
H_2N	para.copl	para.copl	104
HO	para	para	31.8
F	para	para	-28.5

The singlet-triplet separations showed that the phenyl cation and derivatives with π acceptor substituents have singlet ground states. Triplets become increasingly favourable as substituents become π donating, so that in agreement with the INDO calculations of Evleth[172], the p-aminophenyl cation ground state was predicted to be a triplet. Although the p-hydroxyphenyl cation was also predicted to have a triplet ground state, the uncertainty in the calculations was too great to make a definite decision in this case.

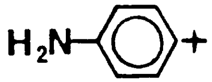
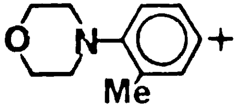
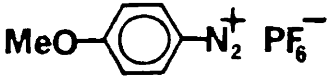
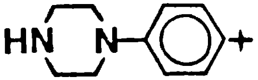
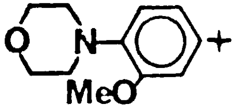
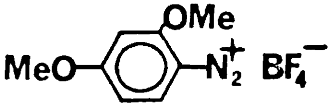
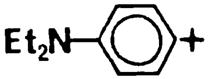
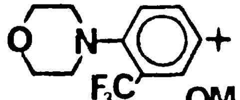
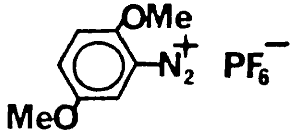
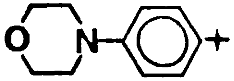
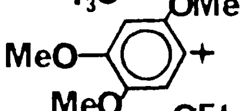
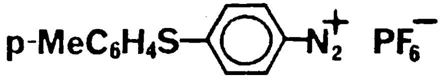
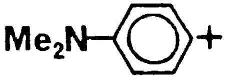
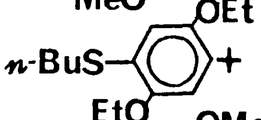
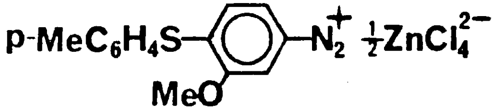
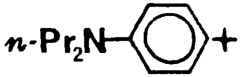
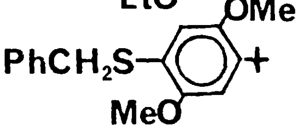
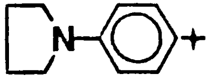
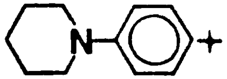
1.7.4 ESR spectroscopic evidence for triplet aryl cations

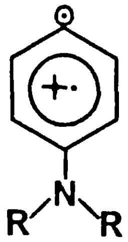
Kemp[174] in 1976 presented ESR spectroscopic evidence for the existence of ground state triplet aryl cations, produced on photolysis of suitably substituted aryl diazonium salts at 77K. In this and further papers Kemp presented his data obtained from the irradiation of the diazonium salts in cellulose acetate films[174-176], lithium chloride aqueous glasses[175-177], and the microcrystalline state[176], with light of wavelength > 300 nm. The typical ESR triplet spectra so obtained, were analysed by the method outlined by Kottis and Lefebvre[178] in terms of D and R parameters. The related D and R parameters give an important insight into the stability and electronic structure of the triplets. The D parameter gives a measure of the stability of the triplet state with respect to the singlet state, while the R parameter measures the spin separation distance between the unpaired electrons.

Kemp found, in agreement with theoretical calculations[136,172], that aryl cations suitably substituted with good π-donors had triplet ground states. A list of some important aryl diazonium salts which gave triplet ground state spectra, together with their D and R parameters, are compiled in table 1.7.4-1. Also listed in table 1.7.4-1 are some important aryl diazonium salts which failed to produce triplet spectra.

The p-aminophenyl cation, as predicted by Pople[136], was observed as a triplet with a D parameter of 0.2967 cm^{-1}, which was the largest value measured. This confirmed a previous generalisation[176] that the D parameter increases with the π electron donor ability of the substituent. The larger the D value then the more stable is the triplet form relative to the singlet. Therefore the order of stabilization of triplets with amine groups is amino > piperazinyl > diethylamino> morpholino > dimethylamino > dipropylamino > pyrrolidino > piperidino. This indicates the special π-donor effect of the amino group[179], that it decreases systematically with an increase in the number of carbon atoms bonded to the donor nitrogen, (with the exception of the dimethylamino group). The spin separations (R) of the amino substituted compounds imply a structure based on XXX (ie (π^5) $(sp^2)^1$ configuration) , with one electron localized in a sp^2 hybrid orbital and the other present in the π system.

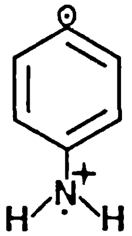
Table 1.7.4-1 Some triplet state parameters of aryl cations as measured by ESR spectroscopy

aryl cation	D(cm^{-1})	R(Å)	aryl cation	D(cm^{-1})	R(Å)	Diazonium salts not giving triplet spectra
	0.2967	2.062		0.2227	2.268	
	0.2563	2.165		0.1998	2.352	
	0.2549	2.169		0.2062	2.327	
	0.2531	2.174		0.1779	2.45	
	0.2522	2.176		0.1684	2.49	
	0.2518	2.177		0.1728	2.47	
	0.2515	2.178				
	0.2474	2.190				



XXX

The structure XXVI proposed by Evleth[172] was not supported by the



XXVI

spin separation values. Further[176] substitutions into the 3 position of 4-amino containing aryl cations were all seen to destabilize the parent aryl cation, presumably by steric interaction and therefore loss of π donation from the nitrogen.

The presence of a 4-alkoxy group was not sufficient to stabilize the triplet state, and even dimethoxylated aryl cations failed to give a triplet resonance. The 2,4,5-trimethoxyphenyl cation was however seen to give a triplet resonance. Mercapto substituted aryl cations[176] were also seen to give triplet spectra with the 2,4,5-trisubstitution pattern, the mercapto group being at the 4-position.

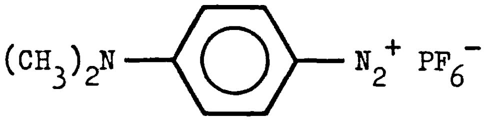
Kemp[176], in summary, thought that substituent effects promoting stabilization of the triplet, as opposed to the singlet state of the aryl cation, operate in a subtle way. While a 4-dialkylamino group produces a ground state triplet, further substitutions in the 3 position, complicated by a steric effect, do not change the D parameter following a simple trend. The stabilizing effect of a given substituent is positionally dependent (4 > 2 ≫ 3 substitution) while for a given site of substitution the stabilization is $NR_2 > OR \sim SR \sim SAr$.

2 RESULTS AND DISCUSSION

2.1 PHOTODEDIAZONIATION OF p-N,N-DIMETHYLAMINOBENZENEDIAZONIUM HEXAFLUOROPHOSPHATE IN THE SOLID STATE

2.1.1 Introduction

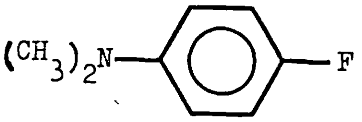
Industrial research[18] has shown that the photolysis of aryl diazonium salts in diazo emulsions yields considerably larger amounts of aryl halides than photolyses conducted in solution. Therefore, it was appropriate to study the photodediazoniation of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb) in the solid state. Very little work has been undertaken on photodediazoniations in the solid state, although Swain[75] investigated the mechanism of aryl fluoride formation from tetrafluoroborate diazonium salts in methylene chloride. Petterson[68] studied the synthetic use of aryl diazonium salt fluorodediazoniations, and photolysed samples as crystalline films coated on the inside of flasks by using a 350 nm UV light source. One of the photolyses studied by Petterson[68] was that of p-N,N-diethylaminobenzenediazonium hexafluorophosphate, from which the recovery of p-N,N-diethylfluoroaniline was 74%, after treating the crude product with aqueous sodium hydroxide followed by steam distillation.



IIb

2.1.2 Determination of products

The photodediazoniation of IIb was conducted in the solid state with a high pressure mercury lamp. The sample was kept at ~0° in a vacuum desiccator during the photolysis, and the product so obtained was a viscous red liquid (XXXI). Unlike p-N,N-dimethylfluoroaniline (XXXII), viz. the expected photochemical[68] or thermal[61] (Schiemann) product of the solid state dediazoniation of IIb, XXXI was found to be insoluble in carbon tetrachloride.



XXXII

The ^1H NMR spectrum of XXXI was therefore recorded in d_3-acetonitrile solution, and compared with that of XXXII (fig. 2.1.2-1 and 2.1.2-2 respectively).

Treating XXXI with aqueous sodium hydroxide, followed by extraction with carbon tetrachloride, gave a product having identical ^1H NMR and IR spectra to those of XXXII. Further, GLC chromatography showed that XXXII was the only detectable product, and also the absence of any N,N-dimethylaniline.

The assignment of the absorption bands for the ^1H NMR spectra of XXXI and XXXII, from these experiments, are given in table 2.1.2-1. The spectrum of XXXII shows a large singlet absorption at $\delta = 2.82$ ppm which was assigned to the six equivalent hydrogens of the dimethylamino substituent. The four aromatic hydrogens of XXXII show a complex splitting pattern. The presence of the fluoro substituent complicates the usually simple characteristic para substitution signal by coupling with the ortho, ($J_{2,F} = J_{6,F} = 9.0$ Hz) and the meta hydrogens, ($J_{3,F} = J_{5,F} = 5.0$ Hz). The meta hydrogens, H (3,5), therefore appear as a doublet of doublets at $\delta = 6.67$ ppm. The ortho hydrogens, H (2,6), appear as a triplet at 6.95ppm, since the value of the coupling constant of the ortho hydrogens with the fluoro substituent is approximately the same as that for the ortho hydrogens with the meta hydrogens ($J_{2,3} = J_{6,5} = 9.0$ Hz).

The complex coupling pattern of the ^{1}H NMR spectrum of XXXI may be intepreted in the same way as that of XXXII, while the vast differences in chemical shifts of the absorption signals may be interpreted in terms of a change in the electronic effect of the dimethylamino substituent from powerfully electron donating in XXXII to powerfully electron withdrawing in XXXI. The singlet at $\delta = 3.60$ ppm in the spectrum of XXXI, assigned as the absorption of the dimethylamino hydrogens, shows a chemical shift of + 0.78 ppm with respect to the corresponding absorption in the spectrum of XXXII. The aromatic hydrogens adjacent to the dimethylamino substituent, H (3,5) which give rise to a doublet of doublets signal, show a change in chemical shift of + 1.43 ppm while the hydrogens adjacent to the fluoro substituent show a smaller shift of + 0.61 ppm each with respect to the spectrum of XXXII. Such a change in the electronic effect of the dimethylamino substituent would be expected upon its protonation. The addition of hydrochloric acid to a sample of XXXII in d_3-acetonitrile solution was observed to qualitatively change the ^{1}H NMR spectrum from that of XXXII to a spectrum which more closely resembled that of XXXI. The ^{1}H NMR spectrum of XXXI does not however show the presence of an acid proton and could therefore not represent the spectrum of this type of acid salt.

By considering the stoichiometry for the fluorodediazoniation of aryldiazonium hexafluorophosphates by thermal[61] or photochemical[68] routes in the solid state eqn (54), one would expect the evolution of one mole of

$$ArN_2{}^+PF_6{}^- \xrightarrow{\Delta \text{ or } h\nu} ArF + N_2\uparrow + PF_5\uparrow \qquad (54)$$

phosphorus pentafluoride to accompany the formation of one mole of aryl fluoride.

Fig. 2.1.2-1 60 MHz ^1H NMR spectrum of the solid state photolysis product of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb), assigned as the addition compound p-N,N-dimethylfluoroaniline phosphorus pentafluoride (XXXIII).

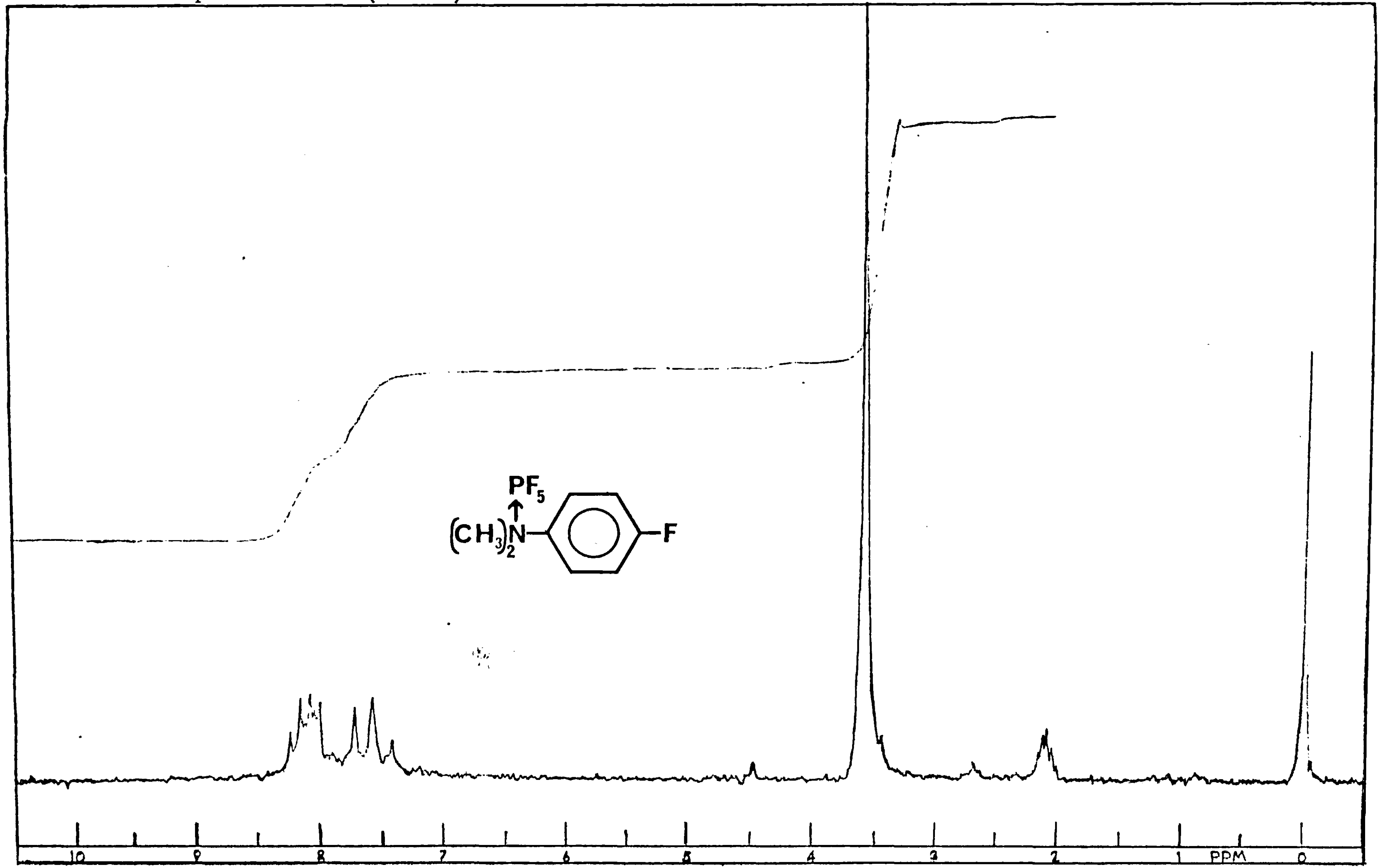


Fig. 2.1.2-2 60 MHz ^{1}H NMR spectrum of p-N,N-dimethylfluoroaniline (XXXII)

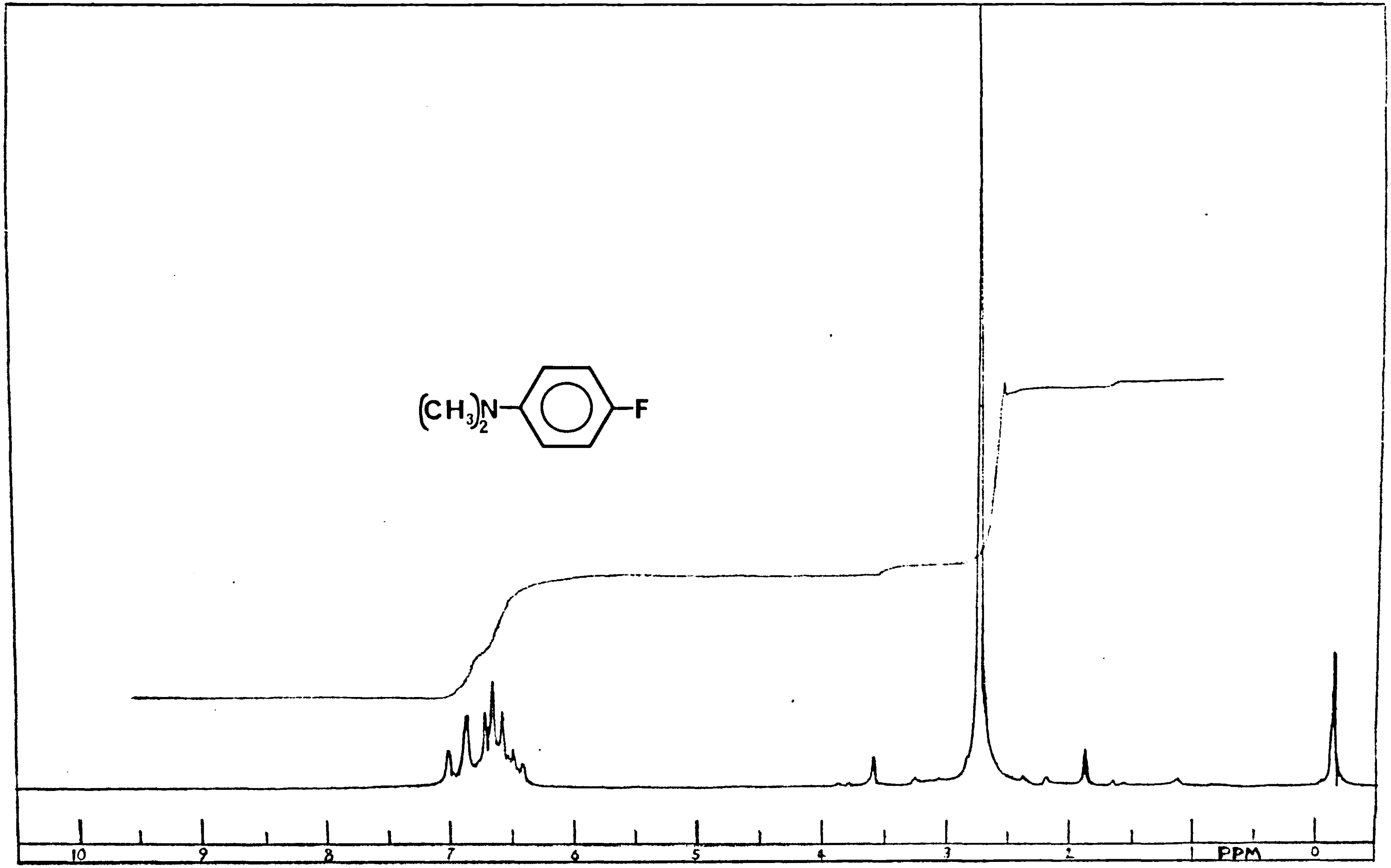


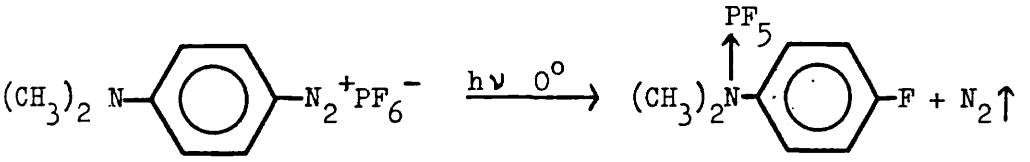
Table 2.1.2-1 ^1H NMR absorptions of the solid state photolysis product of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (XXXI), p-N,N-dimethylfluoroaniline (XXXII) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
XXXI	CD_3CN					
		s	3.60	$\overset{\overset{PF_5}{\uparrow}}{-N}(CH_3)_2$ (4)		6
		t	7.56	H (2,6)	J 2,3 = J 6,5 = 9.0 J 2,F = J 6,F = 9.0	2
		quad	8.10	H (3,5)	J 2,3 = J 6,5 = 9.0 J 3,F = J 5,F = 5.0	2
XXXII	CCl_4	s	2.82	$-N(CH_3)_2$ (4)		6
		quad	6.67	H (3,5)	J 2,3 = J 6,5 = 9.0 J 3,F = J 5,F = 5.0	2
		t	6.95	H (2,6)	J 2,3 = J 6,5 = 9.0 J 2,F = J 6,F = 9.0	2

The Lewis acid phosphorus pentafluoride is however known to form addition compounds with tertiary amines[180] of the general form :-

$$R_3N \longrightarrow PF_5$$

In particular, Johnson[181] describes the formation of such addition compounds between either N,N-dimethylaniline, or N,N-diethylaniline and phosphorus pentafluoride, which he prepared by introducing a measured volume of gaseous phosphorus pentafluoride into a known quantity of the amine in a vacuum system. It was therefore suggested that in the low temperature photodediazoniation of IIb, the product XXXI was the addition compound p-N,N-dimethylfluoroaniline phosphorus pentafluoride (XXXIII), and the equation for its formation is given below, eqn (55).



(55)

IIb XXXIII

2.1.3 Weight loss, phosphorus analysis, and ^{31}P NMR spectroscopy

Further experiments were conducted to establish the stoichiometry of eqn (55). The weight loss accompanying the solid state photodediazoniation of IIb was calculated by photolysing a known amount and reweighing after photolysis. The results of the weight loss experiment (table 2.1.3-1a) indicate that $<3\%$ of the theoretical amount of phosphorus pentafluoride is evolved as a gas during the photolysis. The quantitative determination of phosphorus in XXXI was estimated by the formation and volumetric analysis of ammonium molybdophosphate. These results (table 2.1.3-1b) also indicate, within experimental error, that phosphorus is not lost as gaseous phosphorus pentafluoride during the photolysis. Both the results of the weight loss and phosphorus determination experiments were therefore consistent with eqn (55) rather than eqn (54).

By analogy with ^{31}P NMR spectroscopic investigations[182], XXXIII is predicted to show a characteristic phosphorus resonance of a quintuplet, arising from coupling of the phosphorus with four equivalent equatorial fluorine ligands, each resonance of which is further split into a doublet, arising from the coupling of the phosphorus with the one axial fluorine. The amine is coordinated to the phosphorus in the one remaining axial position. The ^{31}P NMR spectrum of uncomplexed phosphorus pentafluoride on the other hand shows a sextuplet resonance signal,[183] despite having a square pyrimidal structure, since the four equatorial fluorines exchange position rapidly with the axial fluorine even at low temperatures. The ^{31}P NMR spectrum of XXXI was obtained (table 2.1.3-2), which did not however correspond to the characteristic spectrum of a phosphorus pentafluoride amine addition compound. The spectrum obtained showed a septuplet signal at δ = -145 ppm, assigned as hexafluorophosphoric acid (XXXIV, -148 ppm lit.[184]), and a triplet signal at δ =-19 ppm, assigned as difluorophosphoric acid (XXXV, -21 ppm lit[184]). The septuplet to triplet integration ratio obtained for the ^{31}P NMR spectrum was 3:1, in accord with eqn (56), representing the hydrolysis of phosphorus pentafluoride to give a mixture of the hexafluorophosphoric and difluorophosphoric acids.

$$4PF_5 + 2H_2O \longrightarrow \underset{XXXIV}{3HPF_6} + \underset{XXXV}{HPO_2F_2} \qquad (56)$$

Confirmation of the presence of the acidic protons in this particular spectroscopic sample was obtained by the subsequent recording of its ^{1}H NMR spectrum. Vide supra absence of acidic protons in NMR of freshly prepared solution. The ease of hydrolysis of phosphorus pentafluoride adducts to form fluorophosphorus acids is well known.[185] Difficulty in preparing samples of the photolysis product of IIb (0.3 g) i.e. for ^{31}PNMR spectroscopy after manipulation, and transportation, is demonstrated by the small quantity of water ($\sim$0.01 g) required to completely hydrolyse the sample in accordance with eqn. (56).

Further evidence indicating the highly hydroscopic nature of XXXI was obtained from the weight loss experiment, and IR spectroscopy. After recording the weight of a photolysed sample, if the flask was unstoppered and exposed to the atmosphere, a steady increase in weight was observed. This increase in weight was also accompanied by changes in the IR spectrum of the sample (XXXIa $\longrightarrow$ XXXIb, table 2.1.3-3), corresponding to the increase in intensity of the absorption bands at 3450 and 1300 cm^{-1}, assigned as O-H str and $P=O$ str frequencies respectively. Strong absorption bands, assigned as P-F str, appearing at $\sim$840 cm^{-1} in the spectra of XXXIa and XXXIb provides further evidence for the presence of phosphorus in XXXI.

Table 2.1.3-1a The weight loss in the solid state photodediazoniation of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb).

Initial mass (g)	After photolysis (g)	Loss of mass (g)	Corrected for loss of nitrogen (g)	PF_5 retained (%)
1.2607	1.1281	0.1326	0.0121	97.77
1.2489	1.1181	0.1308	0.0115	97.86
1.2576	1.1256	0.1320	0.0118	97.82

Table 2.1.3-1b The quantitative phosphorus determination of the solid state photolysis product of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (XXXI).

Quantity of diazonium salt (mol)	Quantity of phosphorus after photolysis (mol)	Phosphorus retained (%)
$6.164\ 10^{-4}$	$6.411\ 10^{-4}$	104
$6.608\ 10^{-4}$	$6.542\ 10^{-4}$	99

Table 2.1.3-2 The ^{31}P NMR spectrum of the solid state photolysis product of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (XXXI)

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
XXXI	CH_3CN					
		t	-19.07	${}^{\diagdown}_{/\!/}PF_2$	$J_{P-F} = 957$	1.0
		Sept.	-145.26	PF_6^-	$J_{P-F} = 708$	3.0
HPO_2F_2[184]	H_2O	t	-21.0	${}^{\diagdown}_{/\!/}PF_2$	$J_{P-F} = 984$	
HPF_6 [184]	H_2O					
		Sept.	-148	PF_6^-	$J_{P-F} = 708$	

Table 2.1.3-3 The major IR absorption bands of the solid state photolysis products of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate, (XXXI) and p-N,N-dimethylfluoroaniline (XXXII) in cm^{-1} and their assignments.

Compound	O-H Str	CH_3(C-H) Str	Aromatic ring modes	P = O str.	C-N str	P-F str	C-H Aromatic ring modes
XXXIa	3450 br, vw	2960 w-mlt	1518 s	1300 w		840 vs	
XXXIb+	3450 br, m	2960 w-mlt	1518 s	1300 s		848 vs	
XXXII		2940 w-mlt	1518 s		1250 s		820 m

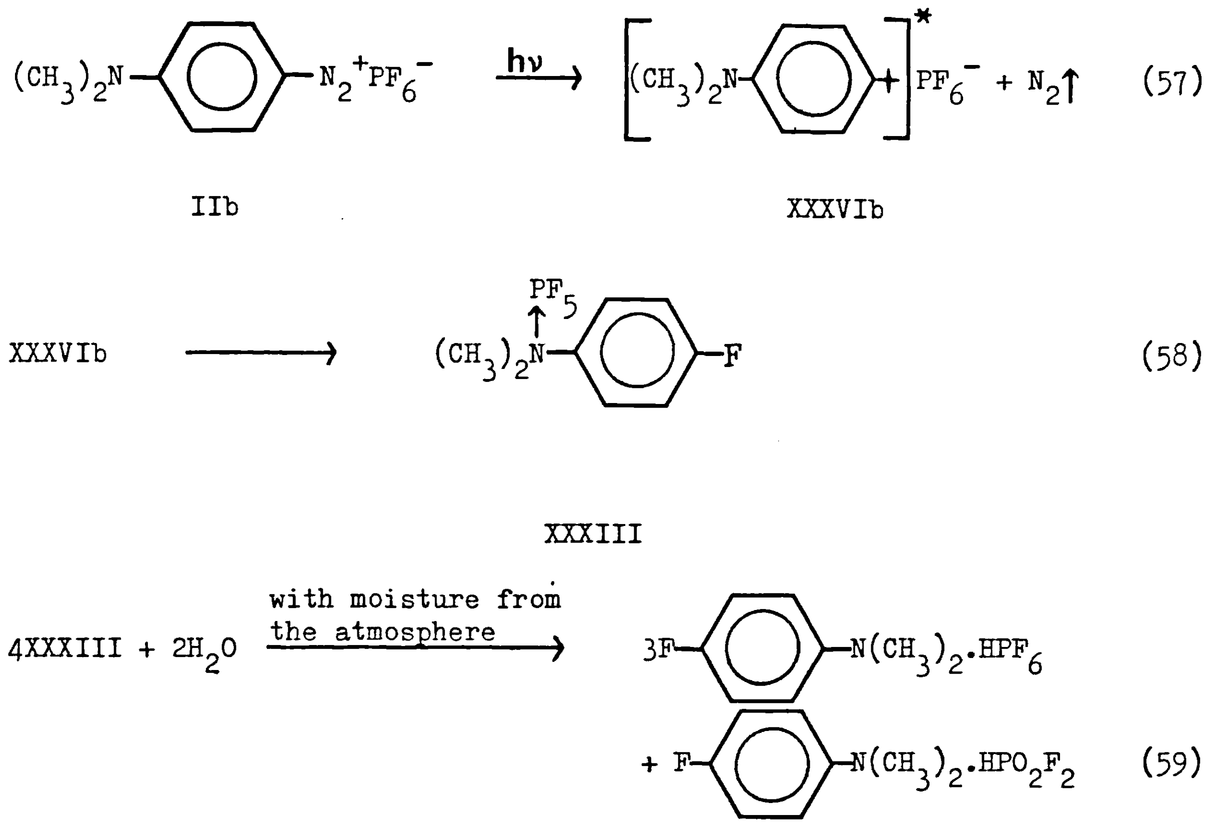
+ Sample having been exposed to the atmosphere for several hours.

2.1.4 Mechanistic interpretation

The photodediazoniation of IIb in the solid state was shown to lead to fluorination of the aromatic nucleus, and not to the formation of N,N-dimethylaniline. This immediately suggests that the dediazoniation did not proceed by a homolytic mechanism with the formation of aryl radicals since, in the presence of the dimethylaminoalkyl hydrogens, no hydrogen abstraction occured. A heterolytic mechanism via the aryl cation XXXVIb is therefore proposed for the photodediazonation of IIb in the solid state (scheme 2.1.4-1).

Scheme 2.1.4-1 shows that after the initial absorption of light IIb undergoes heterolytic dediazonation,eqn (57), to form an aryl cation, the aryl cation and hexafluorophosphate anion existing as an ion pair.[56] In accord with the heterolytic thermal dediazoniation of tetrafluoroborate diazonium salts by Swain,[75] the hexafluorophosphate anion is considered as the fluorinating agent rather than the fluoride anion, eqn (58). Although a fundamentally different mechanism of fluorination with hexafluorophosphate diazonium salts is considered unlikely, the effect of changes in the complex polyfluoro anion on the product distribution obtained in dediazonations in 2,2,2-trifluoroethanol solution is examined in ch. 2.2.4. The question whether the formation of XXXIII is a concerted rather than step-wise reaction, with donation of the nitrogen lone pair to the phosphorus commencing before the formation of the carbon fluorine bond is complete, is discussed after calculations of energies of p-N,N-dimethylaminophenyl cation electronic structures are considered (ch. 2.5.1).

Scheme 2.1.4-1 Mechanism proposed for the photodediazoniation of IIb in the solid state.

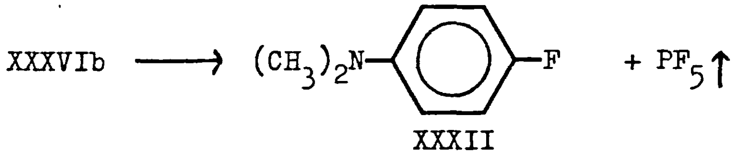


(57) IIb XXXVIb

XXXVIb (58) XXXIII

(59)

The alternative formation of XXXIII by reaction of the aryl cation with the hexafluorophosphate anion eqn (60), followed by reaction of XXXII with free phosphorus pentafluoride, eqn (61), is shown below. However, especially since under conditions of reduced pressure all the phosphorus is retained duri the photolysis of IIb, the alternative formation of XXXIII by eqn (60) and (61) is not favoured. The complete reaction of such a small equimolar amount of phosphorus pentafluoride with XXXII to yield XXXIII is considered improbable.



XXXII (60)

$$\text{XXXII} + PF_5 \longrightarrow \text{XXXIII} \qquad (61)$$

2.2 PHOTODEDIAZONIATION OF p-N,N-DIMETHYLAMINOBENZENEDIAZONIUM SALTS IN ACETONE, ACETONITRILE, and 2,2,2-TRIFLUOROETHANOL SOLUTIONS

2.2.1 Introduction

The photodediazoniation studies of the p-N,N-dimethylaminobenzenediazonium ion in organic solvents were initially conducted as the hexafluorophosphate salt (IIb), although later the hexafluoroantimonate (IIc) and tetrafluoroborate (IId) salts were also photolysed in 2,2,2-trifluoroethanol (TFE) solutions. A high pressure mercury lamp was used in all the photochemical studies and, with the exception of some temperature dependence studies in TFE, all solutions were photolysed at $\sim 0^{\circ}$.

The most important factor in making the selection of solvents was that the diazonium salts, and in particular IIb, should have a reasonable solubility in them. Both acetonitrile and TFE had the extra merit of being used previously as a solvent in thermal dediazoniation studies by other workers,[40, 109-113] while their use in photodediazoniations is not well investigated. Most photodediazoniations of aryl diazonium salts have been undertaken in alcohol[154,160] or aqueous solutions,[158] but the solubility of IIb in these solvents is very poor.

Acetone was selected for study since, apart from being a reasonable solvent, ketones are used industrially as solvents for coating solutions in the semi wet diazo process. Methylethylketone (MEK) is the most frequently used coating solvent, and is known to be inefficiently evaporated during the coating process, leaving considerable amounts of MEK in the coated emulsion. The carbonyl group is also a common feature in many polymers used as the resin in the emulsions. The use of acetone, or other carbonylic solvents, in both thermal and photodediazoniations has been little studied, and therefore had a special industrial importance in the investigation of possible mechanisms leading to the "yellowing" of diazotypes.

2.2.2 Photolyses in acetone solutions

2.2.2.1 Determination of products

It was observed, by ^{1}H NMR spectroscopy that during the photolysis of IIb in d_6-acetone solution, two major para substituted products were formed (fig. 2.2.2.1-1). Further, the relative proportion of these two products was dependent on the presence of water. The product, designated as XXXVII was the only observed photolysis product when a recently purchased sample of d_6-acetone (stored over molecular sieves) was used. The second product, XXXVIII, was observed and increased in relative proportions to XXXVII when the experiment was repeated several times over a period of four weeks, after which time the two products were formed in almost equal amounts. When a trace of D_2O was added to the solvent prior to the photolysis, only the product XXXVIII was formed. Two further samples of IIb were photolysed under the conditions which produced, in each case, XXXVII and XXXVIII in similar amounts. When a drop of D_2O was added to each of the photolysed mixtures, the immediate conversion of XXXVII to XXXVIII was not observed. One sample was now irradiated while the other was kept in the dark at the same temperature.

In both cases, a slow conversion of XXXVII to XXXVIII was observed, but was complete after 18 hr. A summary of all the above conversions is represented below (scheme 2.2.2.1-1).

Scheme 2.2.2.1-1 Summary of the photolysis of IIb in d_6-acetone

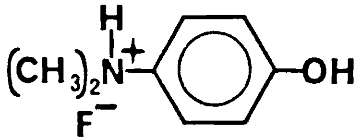
$$\text{IIb} \xrightarrow{h\nu \text{ (dry } d_6\text{-acetone)}} \text{XXXVII}$$

$$\text{IIb} \xrightarrow{h\nu \text{ (after prolonged storage of the solvent)}} \text{XXXVII + XXXVIII}$$

$$\text{IIb} \xrightarrow{h\nu \text{ (wet solvent)}} \text{XXXVIII}$$

$$\text{XXXVII} \xrightarrow[\text{slow}]{h\nu \text{ or dark (wet solvent)}} \text{XXXVIII}$$

The photolysis of a sample of IIb dissolved in wet acetone, on standing, produced a white precipitate. This precipitate was identified as the hydrofluoric acid salt of p-N,N-dimethylaminophenol (XXXIX), by comparison with the ^1H NMR and IR spectra of an authentic sample. The assignments for the ^1H NMR and IR spectra of XXXIX are given in table 2.2.2.2-1,

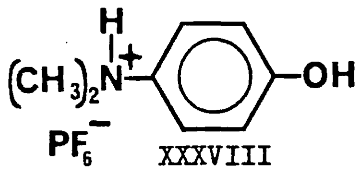


XXXIX

and table 2.2.2.2-2a respectively.

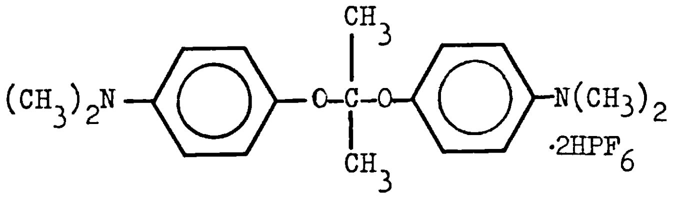
GLC analysis of the product distribution from the photodediazoniation of IIb (4.322 10^{-4} mol) in wet acetone (0.10 g H_2O/10.00 g of solvent) was determined, and the results are given in table 2.2.2.2-3. These GLC results show that the yield of p-N,N-dimethylaminophenol was ~96.5%, that of p-N,N-dimethylfluoroaniline was ~3.5%, while the yield of N,N-dimethylaniline was < 0.5%.

The rotary evaporation of a freshly photolysed sample of IIb in wet acetone produced a viscous brown liquid with an identical ^1H NMR spectrum to that of XXXVIII and an IR spectrum (table 2.2.2.2-2a), apart from showing a strong characteristic P-F str band at ~840 cm^{-1}, the same as that obtained for XXXIX. The structure of XXXVIII was therefore assigned as the hexafluorophosphoric acid salt of p-N,N-dimethylaminophenol.

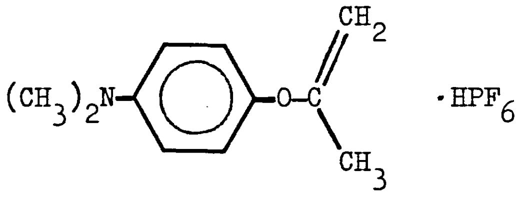


XXXVIII

The isolation of XXXVII from a photolysed solution of IIb in acetone was attempted. A white solid XL was isolated from the solution, on reducing the volume. This was shown by ^1H NMR spectroscopy (fig. 2.2.2.2-1) not to be either XXXVII or XXXVIII. Further attempts to isolate XXXVII were unsuccessful. The ^1H NMR spectrum of XL slowly changed to that of XXXVIII and acetone over a period of a week. The product XL was now assigned to be the hexafluorophosphoric acid salt of the ketal 2,2-bis(p-N,N-dimethylaminophenoxy)propane, while XXXVII was assigned to be the hexafluorophosphoric acid salt of 2-(p-N,N-dimethylaminophenoxy)propene. The independent synthesis of XL from p-N,N-dimethylaminophenol and 2,2-dibromopropane was unsuccessful. The assignments of the ^1H NMR absorption data for XXXVII, XXXVIII and XL are given in table 2.2.2.2-4, while the assignments of the major IR absorption bands of XL are given in table 2.2.2.2-2a.

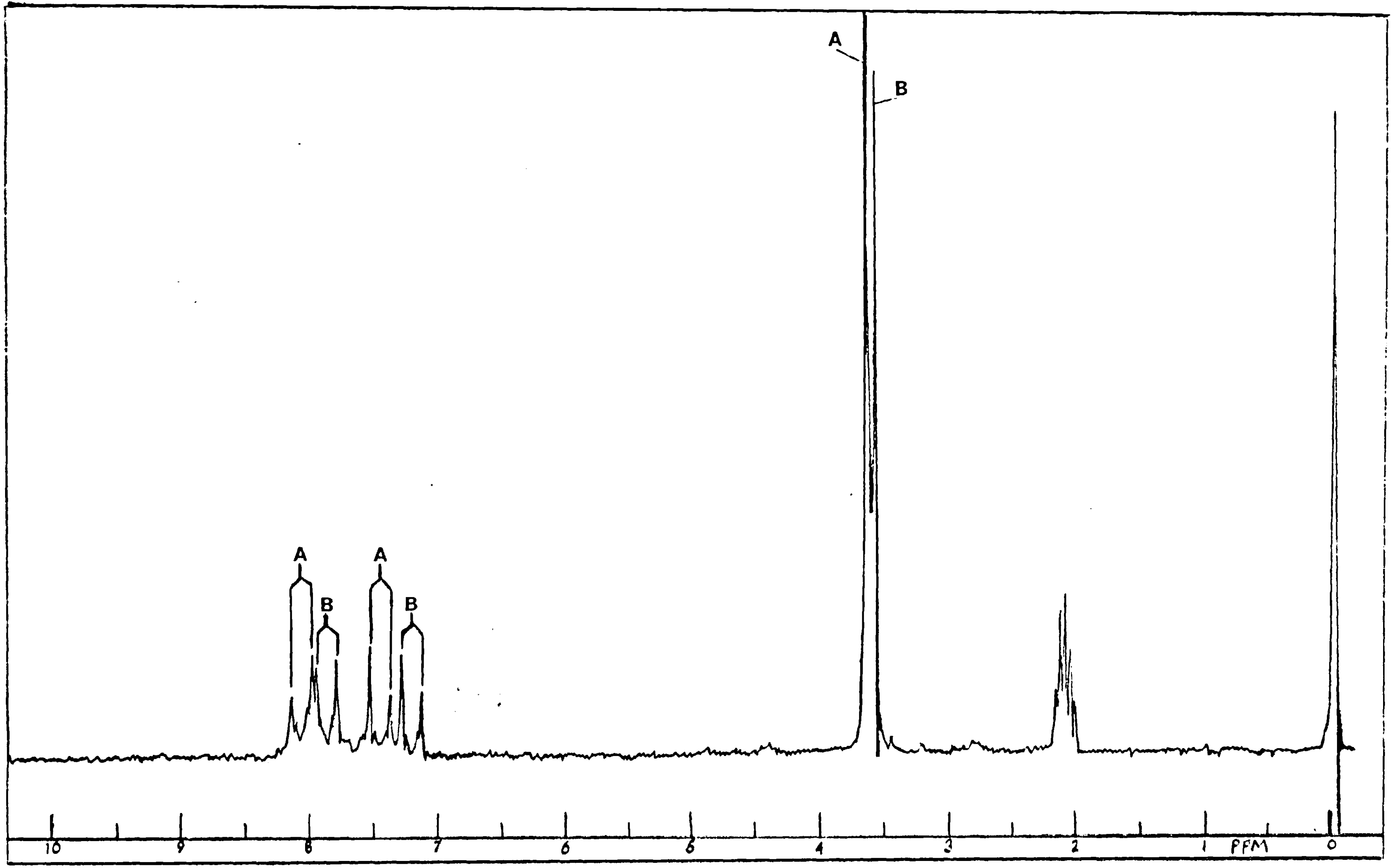


XL



XXXVII

Fig. 2.2.2.1-1 60 MHz ^1H NMR spectrum of XXXVII(A) and XXXVIII(B) formed on the photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb) in d_6-acetone solution[+]

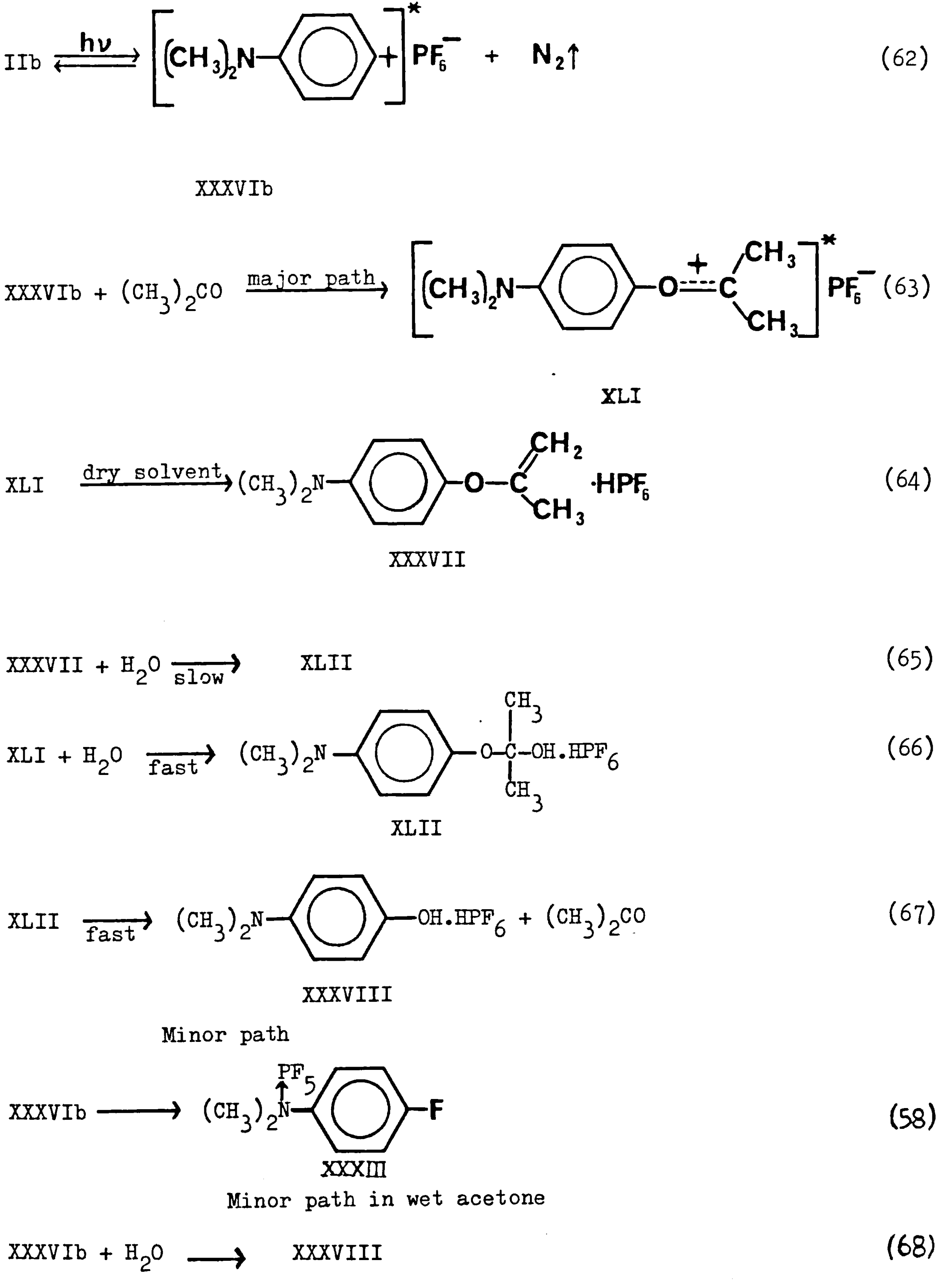


[+] The d_6-acetone was stored for four weeks over molecular sieves prior to use.

2.2.2.2 Mechanistic interpretation

A mechanistic scheme, which is consistent with all the above data, is proposed for the photochemical heterolytic dediazoniation of IIb in acetone (scheme 2.2.2.2-1).

Scheme 2.2.2.2-1 Mechanism proposed for the photolysis of IIb in acetone



The formation of phenols or arylethers is usually thought to be characteristic of heterolytic dediazoniations,[122] while formation of arenes is characteristic of a homolytic path via aryl radicals.[123] Even though the solutions were flushed with nitrogen prior to photolysis, to avoid quenching of radical chain reactions by dissolved oxygen, the GLC analysis for the dediazoniation of IIb in wet acetone shows a high yield of the phenol, and only trace quantities of the arene. Although a heterolytic mechanism is thus preferred a homolytic path cannot be ruled out at this stage. Thermal dediazoniations in dimethylsulphoxide solutions yield high quantities of phenols by a heterolytic mechanism with the benzenediazonium ion,[108,151] and by a homolytic mechanism with the p-nitrobenzenediazonium ion.[140]

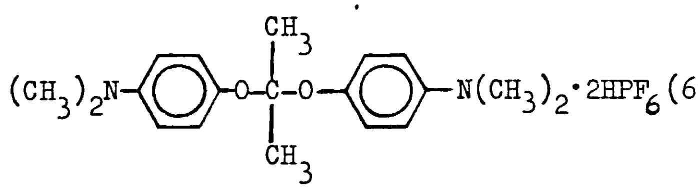
Scheme 2.2.2.2-1 shows the initial formation of an aryl cation (XXXVIb) after the absorption of light eqn. (62). This step probably conceals a complex process analogous with that proposed by Zollinger[109-113] for thermal heterolytic dediazoniations in TFE, or implied by Lewis[158] in his aqueous photochemical studies. By ^{15}N isotopic labelling experiments the formation of aryl cations was shown to be reversible by Zollinger[109-113] and Lewis,[158] and therefore eqn. (62) is also suggested to be reversible. The major path of the reaction of the aryl cation XXXVIb proceeds via the formation of the carbonylic adduct XLI eqn. (63), while the reaction with the hexafluorophosphate anion is shown as the minor path eqn. (58). Formation of XXXVIII in wet acetone is proposed to occur predominantly by the rapid reaction of XLI with water eqn. (66) to produce the hemi-ketal XLII which subsequently decomposes rapidly eqn. (67) to give XXXVIII and acetone. The formation of XXXVIII by the reaction of XXXVIb with water eqn. (68) is regarded as a minor path, in accord with Zollinger's[56] observations for the thermal dediazoniation of benzenediazonium tetrafluoroborate in aqueous TFE solutions. In TFE the phenyl cation, already shown by Lewis[85,92] and Swain[71-75] to be a highly reactive and unselective cation, was shown by Zollinger to react with TFE in preference to water.

Scheme 2.2.2.2-1 shows that in dry acetone XLI undergoes deprotonation to form XXXVII eqn. (64) which only slowly reacts with water eqn. (65) to form XLII. XLII is then shown to rapidly decompose eqn. (67) forming XXXVIII and acetone.

Scheme 2.2.2.2-2 below, is proposed for the formation of the hexafluorophosphoric acid salt of 2,2-bis(p-N,N-dimethylaminophenoxy)propane (XL) from the reaction of XXXVIII with XXXVII, eqn. (69), and its subsequent hydrolysis via XLII, eqn. (70) and (67), to give XXXVIII and acetone.

Scheme 2.2.2.2-2 Mechanism proposed for the formation and hydrolysis of the hexafluorophosphoric acid salt of 2,2-bis(p-N,N-dimethylaminophenoxy) propane (XL)

XXXVII + XXXVIII ⟶



(69)

XL

$$XL + H_2O \longrightarrow XLII + XXXVIII \qquad (70)$$

$$XLII \xrightarrow[\text{fast}]{} XXXVIII + (CH_3)_2CO \qquad (67)$$

Schemes 2.2.2.2-1 and 2.2.2.2-2 are highly speculative and are only proposed because they are consistent with all the data presented. Their speculative nature is highlighted by the failure both to isolate XXXVII and independently synthesize XL. The most speculative proposal is however the existence of the highly unstable and reactive intermediate carbonylic adduct XLI, for which we present no direct evidence. The industrial importance of these photodediazonation studies in acetone is clearly demonstrated by the high yield of the phenolic product, since industrial research[18] has shown that the "yellowing" of diazotypes is associated with phenols. Scheme 2.2.2.2-1 also indicates a possible route which ultimately yields such phenolic products in emulsions, by heterolytic photodediazonation in the presence of carbonyl groups.

Fig. 2.2.2.2-1 60 MHz ^{1}H NMR spectrum of XL, assigned as the hexafluorophosphoric acid salt of of 2,2-bis(p-N,N-dimethylaminophenoxy)propane.

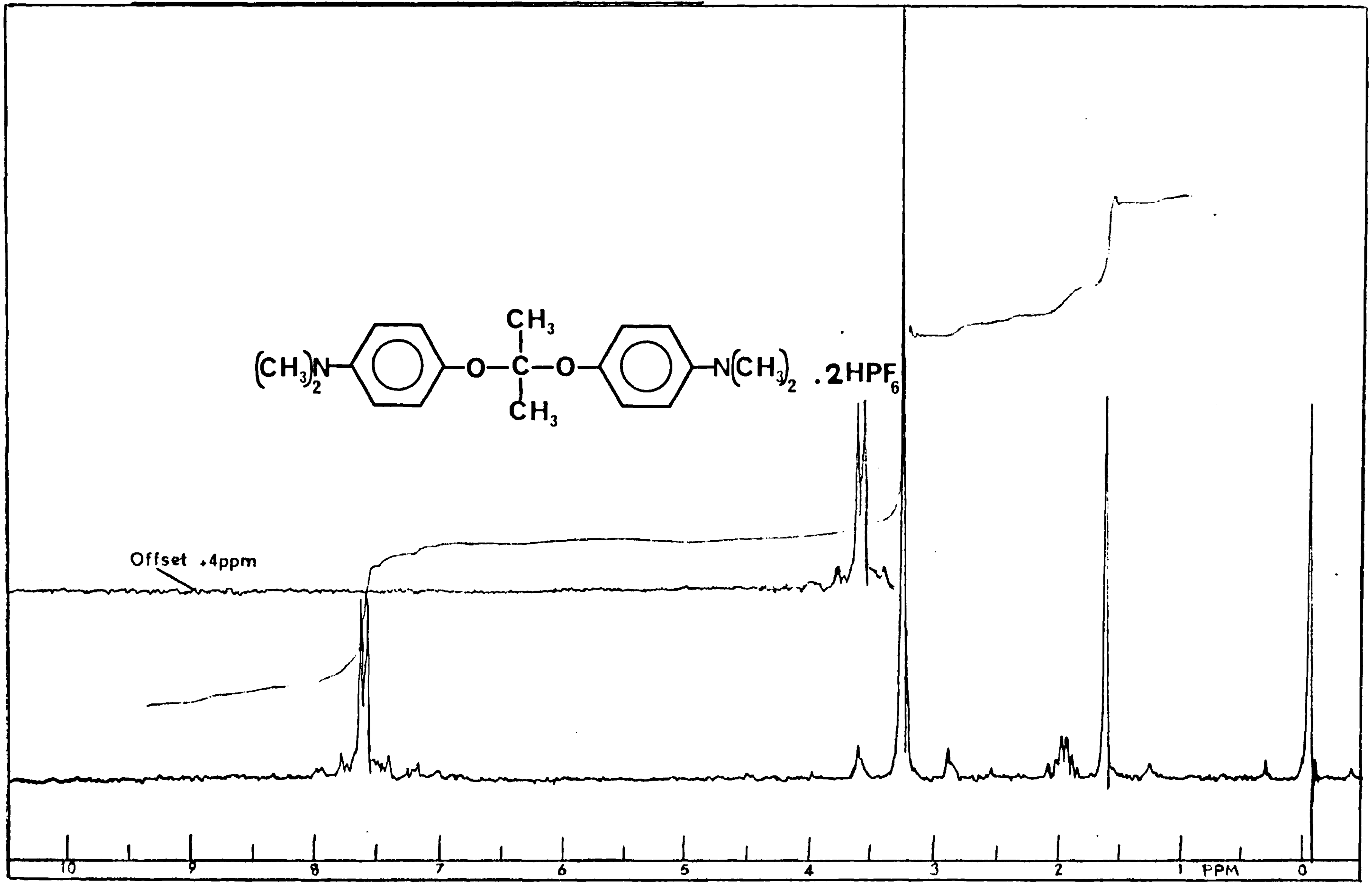


Table 2.2.2.2-1 The ^{1}H NMR absorptions of the major products isolated from the photolysis of p-N,N-dimethylaminobenzenediazonium salts (II): a) XXXIX from wet acetone; b) XLIII from wet acetonitrile; and c) XLVII from 2,2,2-trifluoroethanol solution and their assignments.

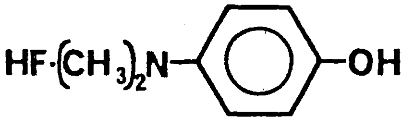
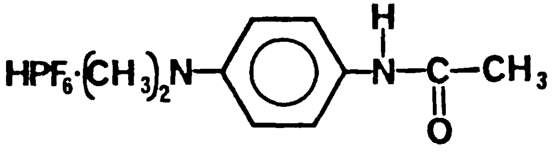
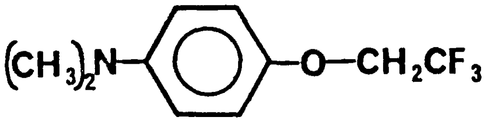
Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
 XXXIX	D_2O	s	3.75	$-N(CH_3)_2$ (4)		6
		d	7.63	H (2,6)	J 2,3 = J 6,5 = 9.0	2
		d	8.17	H (3,5)	J 2,3 = J 6,5 = 9.0	2
 XLIII	CD_3CN	s	2.16	$-\underset{\underset{O}{\|}}{C}-CH_3$		3
		s	3.30	$-N(CH_3)_2(4)$		6
		d	7.68	H (2,6)	J 2,3 = J 6,5 = 10.0	2
		d	7.95	H (3,5)	J 2,3 = J 6,5 = 10.0	2
		s	8.87	$\overset{+}{N}H_2$		2
 XLVII	CCl_4	s	2.90	$-N(CH_3)_2(4)$		6
		quart	4.23	$-OCH_2CF_3(1)$	JH,F = 8.0	2
		d	6.70	H (3,5)	J 2,3 = J 6,5 = 9.0	2
		d	6.92	H (2,6)	J 2,3 = J 6,5 = 9.0	2

Table 2.2.2.2-2a The assignments of the major IR absorptions (cm^{-1}) for the photolysis products of p,N,N-dimethylaminobenzenediazonium hexafluorophosphate(IIb) in wet acetone; XXXVIII, XXXIX, and XL.

Compound	$R_3\overset{+}{N}$-H str	C-H str.(Arom)	CH_3(C-H) str	Aromatic ring modes	Aryl-OH str	Aryl ether str	P-F str	ν C-H Aromatic ring modes
XXXVIII	3260 s	3120 m-mlt	2920 w-mlt	1618 m 1527 s 1478 m	1288 m 1242 m		840 vs	
XXXIX	3260 s	3120 m-mlt	2920 w-mlt	1618 m 1527 s 1478 m	1288 m 1242 m			852 s
XL	3225 s	3100 w-mlt	2950 w-mlt	1614 w 1515 s 1480 m		1260 s	840 vs	

Table 2.2.2.2-2b The assignments of the major IR absorptions (cm^{-1}) for the photolysis product (XLIII) of IIb in wet acetonitrile solution.

Compound	$R_3\overset{+}{N}$-H str	C-H str (Arom)	CH_3(C-H) str	Amide bands (C =O) str	Aromatic ring modes	P-F str
XLIII	3405 s	3025 m-mlt	2950 w-mlt	1670 s 1560 s	1622 m 1522 s	840 vs

Table 2.2.2.2-2c The assignments of the major IR adsorptions (cm^{-1}) for the photolysis product (XLVII) of IIb in 2,2,2-trifluoroethanol solution.

Compound	C-H str (Arom)	CH_3(C-H) str	Aromatic ring	Arylether str	C-H Aromatic ring modes
XLVII	3005 w-mlt	2896 m-mlt	1615 w 1512 s 1462 w	1247 s	820 s

Table 2.2.2.2-3 GLC analysis of the product distribution for the photodediazoniation of p-N,N-dimethylaminobenzene diazonium salts (II) at 0°C in 2,2,2-trifluoroethanol, wet acetone, wet acetonitrile and 1:1 aqueous acetonitrile solutions.

Diazonium salt[a]	2,2,2-trifluoroethanol products			Wet acetone products			Wet acetonitrile products			
	$ArOCH_2CF_3$	ArF	ArH	ArOH	ArF	ArH	$ArNHCOCH_3$	ArOH	ArF	ArH
IIb	92.6	7.0	<0.5	$96.9^{b)}$	$3.5^{b)}$	$<0.5^{b)}$	$98.2^{b)}$	$<1.0^{b)}$	$1.2^{b)}$	$<0.5^{b)}$
	91.7	7.1	<0.5	96.3	3.4	<0.5	97.6	<1.0	1.3	<0.5
IIc	92.1	7.3	<0.5							
	90.0	8.1	<0.5							
IId	93.8	6.5	<0.5							
	94.2	6.1	<0.5							
IIb	$92.4^{d)}$	$7.2^{d)}$	$<0.5^{d)}$				$57.5^{c)}$	$41.5^{c)}$	$0.8^{c)}$	$<0.5^{c)}$
	92.2	7.1	<0.5				56.9	41.9	0.9	<0.5
IIb	$92.1^{e)}$	$7.0^{e)}$	$<0.5^{e)}$							
	92.4	7.2	<0.5							

a) $4.322\ 10^{-4}$ mol of either the hexafluorophosphate (IIb), hexafluoroantimonate (IIc), or tetrafluoroborate (IId) diazonium salt in 10.00 g of solvent.

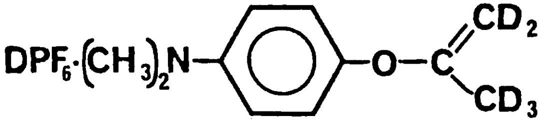
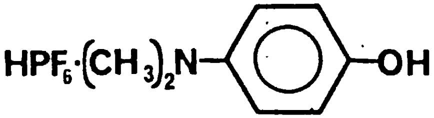
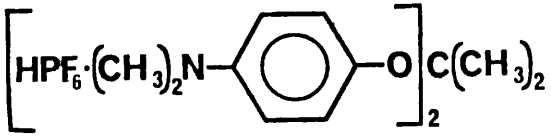
b) 0.10 g of water in 10.00 g of solvent.

c) 1:1 aqueous acetonitrile solution.

d) Photolysed at 30°C.

e) Photolysed at 60°C.

Table 2.2.2.2-4 The proposed structure and ^1H NMR adsorptions for XXXVII-d_6, XXXVIII, and XL together with their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
	$(CD_3)_2CO$					
		s	3.65	$-N(CH_3)_2(4)$		6
		d	7.45	H (2,6)	J 2,3 = J 6,5 = 9.0	2
XXXVII-d_6		d	8.05	H (3,5)		2
	$(CD_3)_2CO$	s	3.57	$-N(CH_3)_2(4)$		6
		d	7.20	H (2,6)	J 2,3 = J 6,5 = 9.0	2
		d	7.85	H (3,5)		2
XXXVIII		s	10.72	$-OH(1),\overset{+}{H}NR_3(4)$		2
	CD_3CN					
		s	1.67	CH_3 (1,3)		6
		s	3.30	$-N(CH_3)_2(4')$		12
		d	7.53	H (2',6')	J 2',3' = J 6',5' =9.0	4
		s	overlap	$\overset{+}{H}NR_3$ (4')		2
XL		d	7.73	H (3',5')	J 2',3' = J 6',5'= 9.0	4

2.2.3 Photolyses in acetonitrile solutions

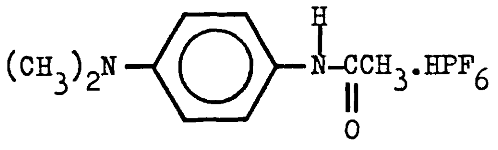
2.2.3.1 Introduction

After the initial photochemical investigations in acetone solution, for which a heterolytic mechanism (scheme 2.2.2.2-1) is proposed, it was thought likely that a similar heterolytic mechanism might occur under photochemical conditions in acetonitrile solution. It has already been accepted that acetonitrile can support heterolytic thermal dediazoniations.[151] After the initial formation of an aryl cation, an aryl nitrilium ion[147,148] is produced which ultimately captures water giving an arylamide.[151]

2.2.3.2 Determination of products

It was observed, by ^1H NMR spectroscopy, that during the photolysis of IIb in d_3-acetonitrile solution a mixture of at least three different para-substituted products was formed when using a freshly purchased solvent that had been stored over molecular sieve. However, as with d_6-acetone solutions, when wet d_3-acetonitrile was used a single para-substituted product was observed.

A product (XLIII) was isolated from the photolysed solution of IIb in wet non-deuterated acetonitrile, and its ^1H NMR spectrum (table2.2.2.2-1), with the exception of an extra singlet absorption at $\delta = 2.16$ ppm, was identical with that observed in wet d_3-acetonitrile. The product, XLIII, was proposed to be the hexafluorophosphoric acid salt of p-N,N-dimethylaminoacetanilide, which was independently synthesized and found to have an identical mp, ^1H NMR and IR spectrum (table 2.2.2.2-2b) to that obtained for XLIII. The singlet absorption at $\delta = 2.16$ ppm, observed in



XLIII

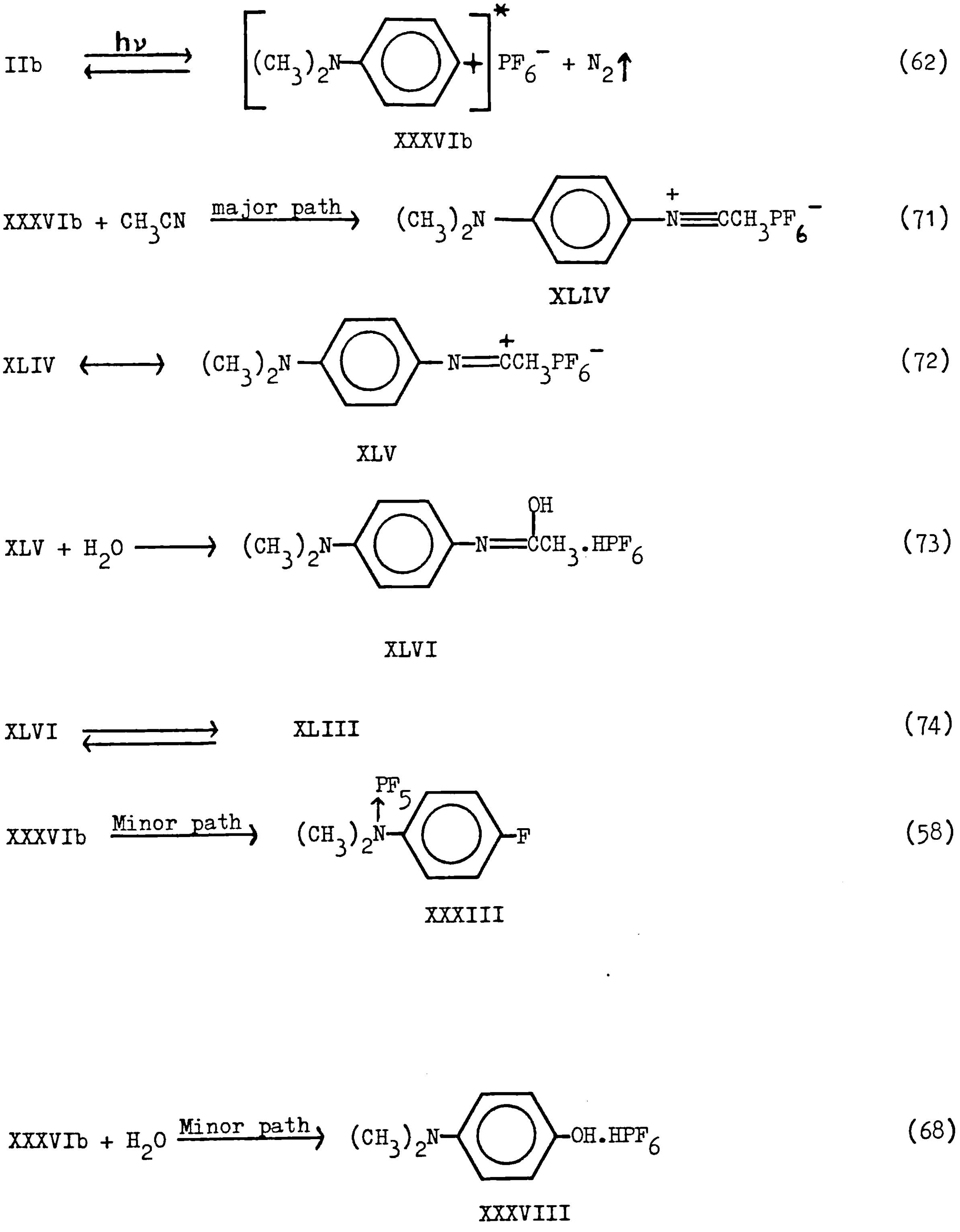
the ^1H NMR spectrum of XLIII but absent in the sample photolysed in wet d_3-acetonitrile was now assigned to the hydrogens of the α-methyl group to the carbonyl function of the arylamide, and correspond to those originally in acetonitrile.

The GLC analysis (table 2.2.2.2-3) of the product distribution from the photodediazonation of IIb ($4.322\ 10^{-4}$ mol) in wet acetonitrile (0.10 g H_2O/10.00 g of solvent) was determined, and showed that the yield of XLIII was ~ 98%, p-N,N-dimethylfluoroaniline ~ 1.3%, p-N,N-dimethylaminophenol < 1.0%, and N,N-dimethylaniline < 0.5%. The GLC analysis of the product distribution on changing to a 1:1 aqueous acetonitrile solution (table 2.2.2.2-3) showed that the yield of XLIII decreased to ~ 57%, p-N,N-dimethylaminophenol increased to ~ 42%, while that of p-N,N-dimethylfluoroaniline slightly decreased to ~ 0.9%.

2.2.3.3 Mechanistic interpretation

The photolysis of IIb in wet acetonitrile yielded the products characteristic of a heterolytic mechanism. Even though the solutions were flushed with nitrogen prior to photolysis, to avoid quenching of radical chain reactions by dissolved oxygen, the GLC analyses show only trace quantities of the arene and therefore a homolytic path via aryl radicals was thought to be highly unlikely. A heterolytic mechanism (scheme 2.2.3.3-1) was therefore proposed for the photodediazoniation of IIb in wet acetonitrile solution similar to that accepted for the thermal dediazonation of many aryl diazonium salts.[151]

Scheme 2.2.3.3-1 Mechanism proposed for the photolysis of IIb in wet acetonitrile



Scheme 2.2.3.3-1 shows the initial formation of an aryl cation XXXVIb after the absorption of light eqn. (62) as proposed for the photodediazoniation of IIb in acetone solution (scheme 2.2.2.2-1). The major path of the reaction of the aryl cation XXXVIb proceeds via the formation of the aryl nitrilium ion XLIV eqn. (71), while the reaction with the hexafluorophosphate anion or water are shown as the minor paths eqn. (58) and (68) respectively. A resonance structure of the nitrilium ion XLIV is the carbonium ion XLV, with which the subsequent reaction with water proceeds to give XLVI eqn. (73). Finally, XLVI through tautomerism affords the aryl amide, XLIII.

Kobayashi[151] in studying the thermal dediazoniation of benzenediazonium tetrafluoroborate in a range of aprotic polar organic solvents, including acetonitrile, acetone, and dimethylsulphoxide, found similar first-order rate constants and concluded that the rate limiting process was the monomolecular dediazoniation to give the phenyl cation in each of these solvents. The polarity of these solvents was considered to be large enough to assist in the formation of the solvated phenyl cation[151]. The nucleophilicity was regarded as being insufficient to cause interaction prior to the dediazoniation, as with pyridine[140,143] which forms a charge-transfer complex that subsequently decomposes by a homolytic path. The anomalous finding by Zollinger[140] that p-nitrobenzenediazonium tetrafluoroborate probably undergoes homolytic thermal dediazoniation in dimethylsulphoxide by the formation of a charge-transfer complex, is viewed by the author as being primarily due to the strongly electron-withdrawing property of the nitro substituent facilitating charge-transfer complex formation. The presence of the powerfully electron donating dimethylamino substituent in IIb would therefore suggest that charge-transfer complex formation of this diazonium salt is unimportant with the range of solvents studied by Kobayashi.[151] From the photochemical studies of Becker[160-162] in alcoholic solutions the formation of a charge-transfer complex by IIb with acetonitrile or acetone would also not be expected, even from a photochemically activated state of the diazonium salt, since in the presence of pyrene (a much better electron donor than acetonitrile or acetone) he observed no significant increase in arene formation.

An alternative homolytic mechanism in acetonitrile or acetone, similar to that proposed by Bunnett[122,123] (ch. 1.6.1) involving electron transfer from the solvent, is also highly unlikely in view of Becker's[160] work. Becker, after photolysing ethanolic solutions of p-N,N-dimethylaminobenzenediazonium tetrafluoroborate at wavelengths comparable to the present studies (365 nm), found that the heterolytic path predominated in the dediazoniation even though ethanol is a fairly good electron donor.

The formation of a nitrilium ion in acetonitrile solution, proposed here for the photodediazoniation of IIb (scheme 2.2.3.3-1), is suggested to be analogous to the formation of a carbonylic adduct in acetone solution as proposed previously (scheme 2.2.2.2-1). A high yield of XLIII with respect to that of XXXVIII in wet acetonitrile clearly demonstrates that the formation of the nitrilium ion, eqn. (71), is a major path whereas the reaction of the aryl cation with water, eqn. (68), is a minor path. In contrast the distinction between the formation of a carbonylic adduct of acetone, eqn. (63), or reaction of the aryl cation with water, eqn. (68), in wet acetone could not be made by GLC analysis, since both paths ultimately yield the same phenolic product. The suggestion that carbonylic adduct formation is the major path in wet acetone is however supported by these results.

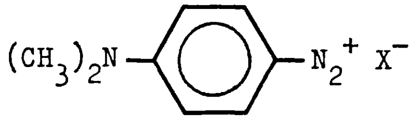
The close similarity of the product distributions for the photolysis of IIb in wet acetonitrile and wet acetone also suggests a similarity in the mechanisms. Both reactions yield trace amounts of N,N-dimethylaniline, the yield of p-N,N-dimethylaminophenol in wet acetone (~96.5%) is close to that obtained for p-N,N-dimethylaminophenol + p-N,N-dimethylaminoacetanilide in wet acetonitrile (~98.5%), and the yield of p-N,N-dimethylfluoroaniline in wet acetone (~3.5%) is similar to that obtained in wet acetonitrile (~1.3%).

The product distribution obtained for the photolysis of IIb in 1:1 aqueous acetonitrile solution seems at first sight to be puzzling since, despite water being much more nucleophilic than acetonitrile, the yield of p-N,N-dimethylaminoacetanilide was ~57%, p-N,N-dimethylaminophenol ~42%, and p-N,N-dimethylfluoroaniline ~ 0.9%. This behaviour is however consistent with that observed by Zollinger[56] for the heterolytic thermal dediazoniation of benzenediazonium tetrafluoroborate in aqueous TFE solutions. Zollinger found that the rate of dediazoniation was higher in pure TFE than in pure water and, after measuring the rates and product distributions obtained in aqueous TFE over the range 100% TFE ⟶ 100% water, concluded that neither TFE or water were involved in the rate-limiting step as nucleophiles. The differences in solvation between TFE and water were seen as affecting the rate-limiting formation of the aryl cation, while the nucleophilic attack upon the aryl cation was seen as a fast product-determining step. Zollinger also concluded that the fluorodediazoniation was not a reaction between free aryl cations and the tetrafluoroborate anion, but a reaction within an ion pair. This was substantiated by the fact that the aryl fluoride was not formed in pure water, where ion pairs are unlikely, but was increasingly formed as the proportion of TFE increased. It seems reasonable to propose that in the photolysis of IIb, after the initial absorption of light, the participation of the solvent is in the rate-limiting formation of a solvated aryl cation and that, as with TFE, acetonitrile and acetone assist this process more effectively than water. Subsequent to the formation of this solvated aryl cation the acetonitrile or water participate in the product-determining step of the mechanism as nucleophiles.

2.2.4 Photolyses in 2,2,2-trifluoroethanol solutions

2.2.4.1 Introduction

Following the photochemical investigations in acetone and acetonitrile solutions further photodediazoniations were conducted in 2,2,2-trifluoroethanol (TFE) solutions. TFE is an unusual solvent since it is highly polar and yet possesses extremely low nucleophilicity. These properties have prompted its use as a solvent by Zollinger[40,56,109-111,113,114] in several investigations of heterolytic thermal dediazoniations. The high polarity of TFE assists in the formation of ionic intermediates which it stabilises by solvation, while its low nucleophilicity disfavours the formation of charge-transfer complexes or electron transfer processes. Because of the lower nucleophilicity of TFE, than acetonitrile or acetone, the proportion of aryl fluoride should increase in dediazoniations conducted in TFE with respect to those in acetonitrile or acetone solutions. With this in mind photodediazoniation studies of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb), hexafluoroantimonate (IIc), and tetrafluoroborate (IId) salts were undertaken in TFE solutions, so that the affect of the change in anion on the product distribution could be investigated.



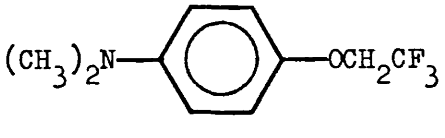
$X^- = PF_6^-$ (IIb), SbF_6^- (IIc), BF_4^- (IId)

The photodediazoniation of IIb in TFE solutions at different temperatures was also investigated to see what affect, if any, this had on the product distribution.

2.2.4.2 Determination of products

From the photolysed solution of IId in TFE; after neutralization, extraction with diethylether, and rotary evaporation of the ether layer, a solid XLVII was isolated by recrystallization of the residue. The ^1H NMR and IR spectra of the solid XLVII were recorded and their assignments are given in table 2.2.2.2-1 and table 2.2.2.2-2c respectively.

The ^1H NMR spectrum of XLVII shows a singlet absorption at $\delta = 2.90$ ppm assigned to the dimethylamino group, a pair of doublets centred at $\delta = 6.70$ and 6.92 ppm ($J = 9.0$ Hz), characteristic of para-substituted benzenes, and a quartet signal centred at $\delta = 4.23$ ppm. The quartet signal, not being coupled with any other observed resonance, was assigned to the methylene hydrogens of the 2,2,2-trifluoroethyl group ($J_{HF} = 8.0$ Hz). The above data, together with the observed integration ratios, was consistent with XLVII being assigned the structure p-N,N-dimethylamino(2',2',2'-trifluoroethoxy)benzene. Observation of an absorption band at 1247 cm^{-1}, in



XLVII

the IR spectrum of XLVII, assigned as the aryl ether str. frequency, was also in accord with the above structure.

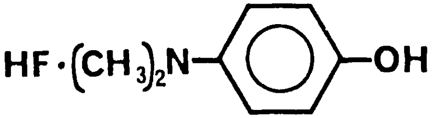
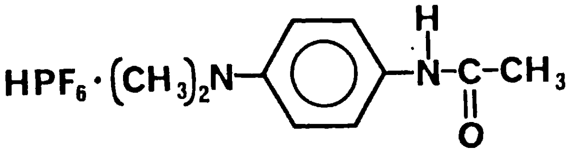
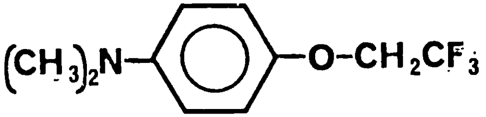
The structure, mp, crude yield, and yield after recrystallization of the major products isolated from the photolysis of p-N,N-dimethylaminobenzenediazonium salts (II) in wet acetone (XXXIX), wet acetonitrile (XLIII) and TFE (XLVII) are given in table 2.2.4.3-1.

The results of the GLC analyses of photolysed solutions of IIb, IIc, and IId ($4.322\ 10^{-4}$ mol) in TFE at ~0° are given in table 2.2.2.2-3. In all cases the amount of N,N-dimethylaniline detected was $< 0.5\%$ while yields of XLVII were ~92%, ~91%, and ~94% for IIb, IIc, and IId respectively. The yields of p-N,N-dimethylfluoroaniline were ~7%, ~ 8%, and ~6% for IIb, IIc, and IId respectively. Photolyses of IIb solutions at higher temperatures (30° and 60°) gave no observable differences in the product distributions (also table 2.2.2.2-3).

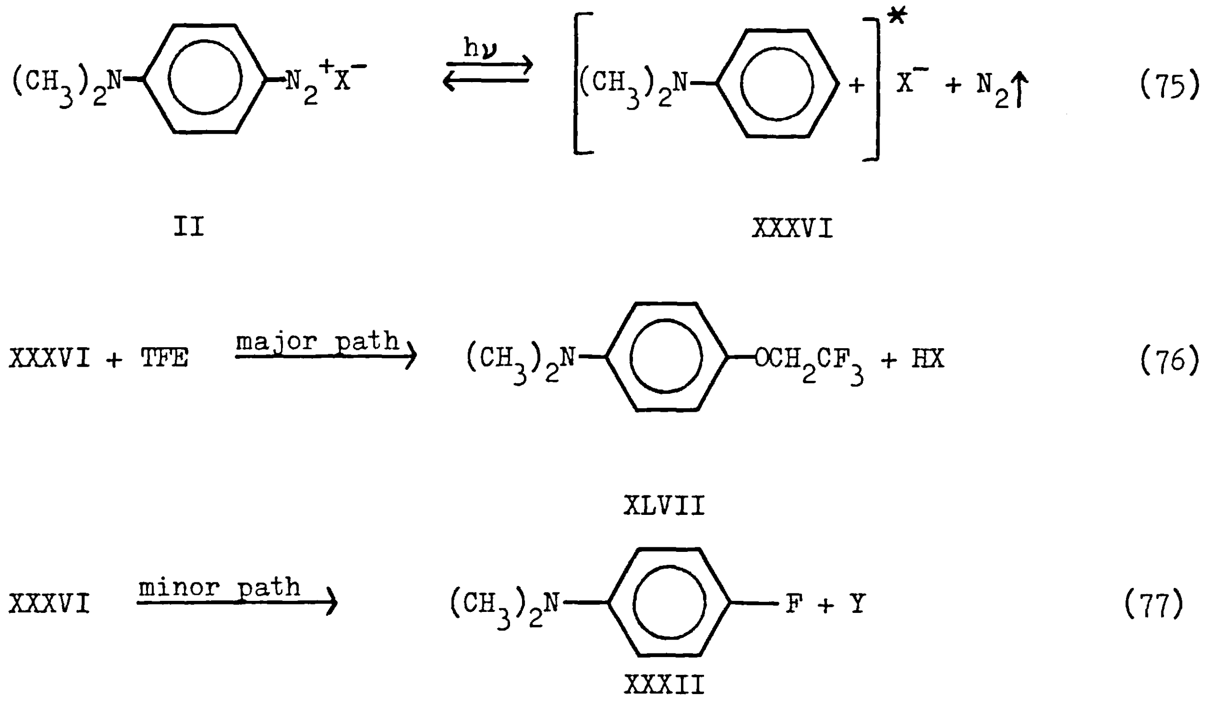
2.2.4.3 Mechanistic interpretation

The product distributions obtained for the photolyses of IIb, IIc and IId in TFE solution, yielding the aryl ether XLVII and the aryl fluoride XXXII are characteristic of heterolytic processes. As observed previously for the photolysis of IIb in acetone and acetonitrile solutions, only trace quantities of the arene N,N-dimethylaniline were detected, although as before the solutions were flushed with nitrogen prior to the photolyses, to avoid quenching of any radical chain processes by dissolved oxygen. A heterolytic mechanism (scheme 2.2.4.3-1) is therefore proposed for the photolyses of IIb, IIc and IId in TFE solution.

Table 2.2.4.3-1 The structure, mp, crude recovery and recovery after recrystallization for the major product isolated from the photolysis of p-N,N-dimethylaminobenzenediazonium salts (II); in wet acetone (XXXIX), wet acetonitrile (XLIII), and 2,2,2-trifluoroethanol (XLVII).

Compound	Structure	mp	Crude recovery	After recrystallization (yield and solvent)
XXXIX		211.5 - 3.5	1.78 g	1.10 g (51%, H_2O)
XLIII		203.5 - 5.0	4.07 g	2.65 g (60%, EtOH)
XLVII		74.5 - 5.0	2.76 g	2.15 g (58%, Et_2O)

Scheme 2.2.4.3-1 Mechanism proposed for the photolyses of IIb, IIc and IId in TFE solution



(b); $X^- = PF_6^-$, $Y = PF_5$

(c); SbF_6^-, SbF_5

(d); BF_4^- , BF_3

Scheme 2.2.4.3-1 shows that after the initial absorption of light, the p-N,N-dimethylaminobenzenediazonium salts (II) undergo a reversible heterolytic dediazoniation to form the aryl cation eqn. (75), that then reacts giving the aryl ether eqn. (76) or aryl fluoride eqn. (77).

A heterolytic process has already been observed and extensively studied by Zollinger[40,56,109-111,113,114] (ch. 1.5.3) for the thermal dediazoniation of other aryl diazonium salts in TFE solution. A heterolytic mechanism for the photolyses of IIb, IIc and IId in TFE is also in accord with the proposed mechanisms for the photodediazoniation of IIb in acetone (scheme 2.2.2.2-1), acetonitrile (scheme 2.2.3.3-1), and in the solid state.

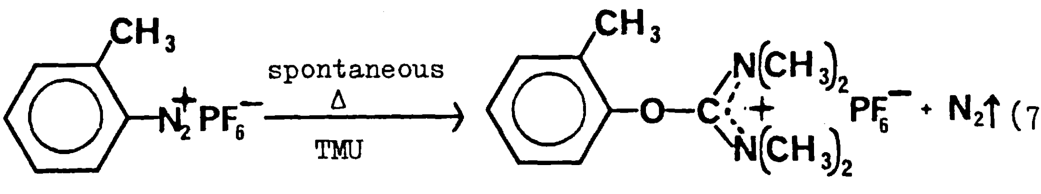
Zollinger[56] observed that the product distribution obtained for the thermal dediazoniation of benzenediazonium tetrafluoroborate in TFE solution was independent of temperature. Our observation that the product distribution obtained for the photolysis of IIb in TFE is also independent of temperature (range 0° – 60°), demonstrates again the similarity between these thermal and photochemical processes. The relatively small changes in the yield of aryl fluoride obtained by changing the polyfluoro anion suggests a common mechanism for these reactions. These fluorodediazoniations, are suggested to occur within an ion pair formed between the aryl cation and the polyfluoro anion.

2.3 FURTHER ARYL DIAZONIUM SALT DEDIAZONIATIONS IN CARBONYLIC SOLVENTS

2.3.1 Introduction

In our photolytic studies of IIb in acetone solutions (ch. 2.2.2) the high yield of phenolic product demonstrated the industrial importance[18] of these investigations. The most speculative proposal embodied in the heterolytic mechanism (scheme 2.2.2.2-1), suggested for the above process, was the formation of a carbonylic adduct as an intermediate for which no direct evidence of its existence was presented.

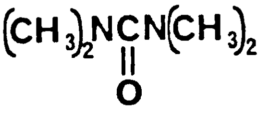
Rutherford[67] investigating the spontaneous thermal dediazoniation of aryl diazonium hexafluorophosphates in the carbonylic solvent 1,1,3,3-tetramethylurea (TMU), using 2-methylbenzenediazonium hexafluorophosphate (XLVIIIb) isolated the carbonylic adduct, 2-(2'-methylphenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (LIIb) as the major reaction product. Rutherford obtained no arene product from



(78)

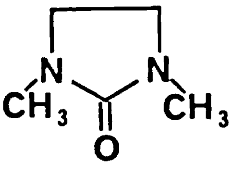
XLVIIIb LIIb

the dediazoniation of XLVIIIb in TMU but with other diazonium salts, especially those with electron withdrawing substituents, the major product was the arene. It was therefore proposed to investigate the thermal dediazoniation of other aryl diazonium salts with methyl substituents ortho to the diazonium group, with a view to the isolation of their carbonylic adducts from TMU solutions. The range of thermal dediazoniations in carbonylic solvents was also extended to include the solvents;1,3-dimethyl-2-imidazolidinone (DMI), 1-methyl-2-pyridone (MPY), and cyclohepta-2,4,6-triene-1-one (tropone).

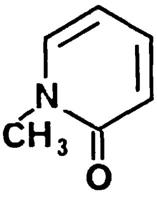


$(CH_3)_2NC(=O)N(CH_3)_2$

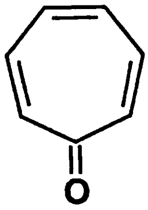
TMU



DMI



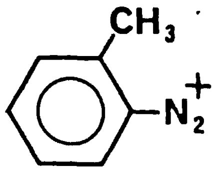
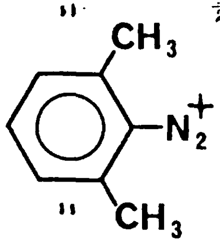
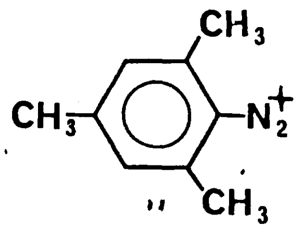
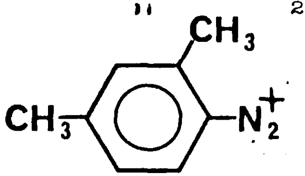
MPY



tropone

The scope of the thermal dediazoniation studies was further widened to include aryl diazonium hexafluoroantimonates and hexachlorostannates. Table 2.3.1-1 gives the structure, mp, crude yield, and reprecipitation recovery of all diazonium salts used in thermolytic studies.

Table 2.3.1-1 Table of structure, mp, crude yield, and reprecipitation recovery of the diazonium salts used in thermal dediazoniations.

Compound	Structure	mp	Crude yield %	% recovery from purification by reprecipitation
XLVIIIb	 PF_6^-	116 - 7 dec.	95	83
XLVIIIc	" SbF_6^-	63.5 - 4.5 dec	75	65
XLVIIIe	" $\frac{1}{2}SnCl_6^{2-}$	83 - 4 dec	87	
XLIXb	 PF_6^-	94.5 - 5.5 dec	86	71
XLIXc	" SbF_6^-	59.5 - 60.0 dec	81	62
XLIXe	" $\frac{1}{2}SnCl_6^{2-}$	67.5 - 8.5 dec	89	
Lb	 PF_6^-	125 - 6 dec	81	74
Lc	" SbF_6^-	78.5 - 9.0 dec	78	63
Le	" $\frac{1}{2}SnCl_6^{2-}$	83.5 - 4.0 dec	80	
LIb	 PF_6^-	121 - 2 dec	84	78

2.3.2 Thermal dediazoniations in 1,1,3,3-tetramethylurea, 1,3-dimethyl-2-imidazolidinone, 1-methyl-2-pyridone and cyclohepta-2,4,6-triene-1-one solutions

2.3.2.1 Isolation of products

Owing to the large number of experiments undertaken, reactions in TMU, DMI, MPY and tropone solutions were conducted on a much smaller scale than those of Rutherford.[67] The 2-methyl (XLVIIIb), 2,6-dimethyl (XLIXb), 2,4-dimethyl (LIb), and 2,4,6-trimethylbenzenediazonium hexafluorophosphate (Lb), were all observed to spontaneously decompose at room temperature in TMU and MPY solutions. The spontaneous thermal dediazoniation of XLIXb was also observed in DMI solution. The reaction products were isolated in all cases by the method of Rutherford.[67]

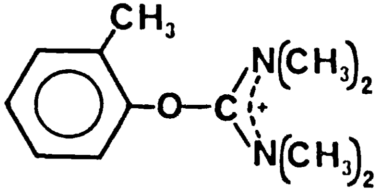
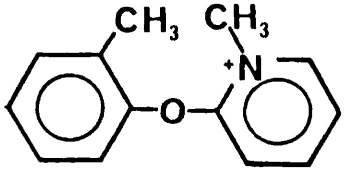
The spontaneous thermal dediazoniation of 2,6-dimethylbenzenediazonium hexafluorophosphate (XLIXb) in tropone solution was not observed, but this may be attributed to its low solubility in this solvent at room temperature. The thermal dediazoniation of XLIXb in tropone solution at 50°, and the subsequent isolation of the reaction product, was effected by the method described in ch. 4.6.2.

The 2-methyl (XLVIIIc), 2,6-dimethyl (XLIXc), and 2,4,6-trimethylbenzenediazonium hexafluoroantimonate (Lc), were also observed to decompose spontaneously at room temperature in TMU and MPY solutions, but the method employed for hexafluorophosphate salts failed to isolate their products. An alternative method of isolation was therefore developed for these products and is described in ch. 4.6.1.

The 2-methyl (XLVIIIe), 2,6-dimethyl (XLIXe), and 2,4,6-trimethylbenzenediazonium hexachlorostannate (Le) have only low solubilities in TMU and MPY solutions and so were maintained at 50° throughout their reactions. As with the hexafluoroantimonate products, the original method of Rutherford[67] failed to isolate the hexachlorostannate products, so the method of isolation described in ch. 4.6.1 was also employed here.

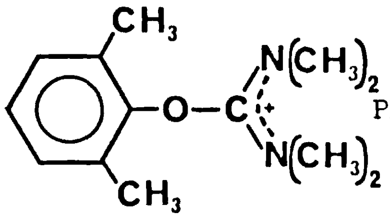
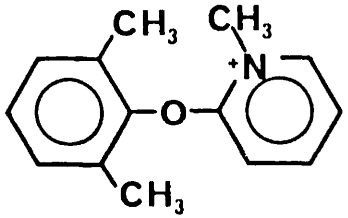
All of the products isolated from the thermal dediazoniations in TMU, DMI, and MPY solutions were recrystallized. Tables 2.3.2.1-1a—2.3.2.1-1d give the subsequently assigned structure of all the isolated products together with the mp, crude yield, yield after recrystallization, and also the elemental analysis for several of the products.

Table 2.3.2.1-1a The structure, mp, crude yield, yield after recrystallization, and elemental analysis of the carbonylic adducts isolated from thermal dediazoniations of 2-methylbenzenediazonium salts (XLVIII) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.+

Compound	Structure	mp	Crude yield	After recrystallization (yield, solvent)	Elemental analysis%
LIIb	 PF_6^-	144 - 5	1.56 g	1.12 g (42%, EtOH)	
LIIc	" SbF_6^-	141 - 2	1.09 g	0.82 g (33%, EtOH/nPrOH)	
LIIe	" $\frac{1}{2}SnCl_6^{2-}$	245 - 7	1.24 g	0.91 g (35%, MeOH)	
LIIIb	 PF_6^-	155 - 6	0.85 g	0.65 g (25%, EtOH)	C H N PF_6^- Calc. 45.23 4.09 4.06 41.99 Found 45.28 3.83 4.08 42.24 45.35 4.05 4.14 42.19
LIIIc	" SbF_6^-	142 - 3.5	0.87 g	0.64 g (26%, EtOH)	
LIIIe	" $\frac{1}{2}SnCl_6^{2-}$	227 - 8	1.03 g	0.74 g (29%, MeOH)	

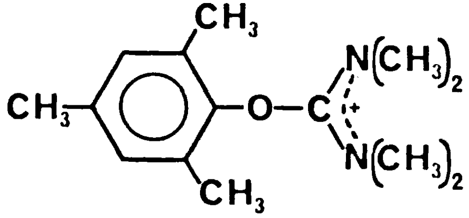
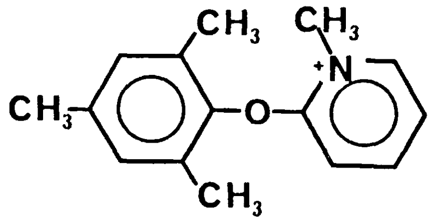
+ 2.0 g of diazonium salt in 5.0 g of either TMU or MPY solution.

Table 2.3.2.1-1b The structure, mp, crude yield, yield after recrystallization, and elemental analysis of the carbonylic adducts isolated from thermal dediazoniations of 2,6-dimethylbenzenediazonium salts (XLIX) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.+

Compound	Structure		mp	Crude yield	After recrystallization (yield, solvent)	Elemental analysis %				
							C	H	N	PF_6^-
LIVb		PF_6^-	194-4.5	1.23 g	0.90 g (34%, EtOH)	Calc.	42.63	5.78	7.65	39.58
						Found	42.54	6.14	7.64	39.69
							42.74	6.19	7.64	39.86
LIVc	"	SbF_6^-	173.5-4	0.82 g	0.63 g (26%, EtOH/nPrOH)					
LIVe	"	$\frac{1}{2}SnCl_6^{2-}$	214-6	0.96 g	0.70 g (27%, MeOH)					
							C	H	N	PF_6^-
LVb		PF_6^-	192-3	1.03 g	0.75 g (29%, EtOH)	Calc.	46.81	4.49	3.90	40.35
						Found	46.95	4.87	3.95	40.91
							46.89	4.72	3.93	40.87
LVc	"	SbF_6^-	174-5.5	0.85 g	0.69 g (28%, EtOH/nPrOH)					
LVe	"	$\frac{1}{2}SnCl_6^{2-}$	274-6	1.27 g	0.84 g (33%, MeOH)					

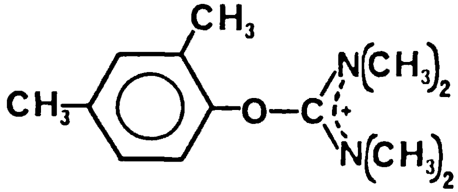
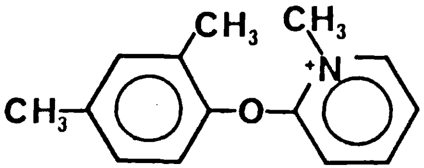
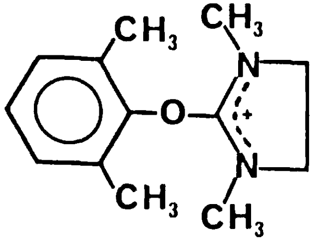
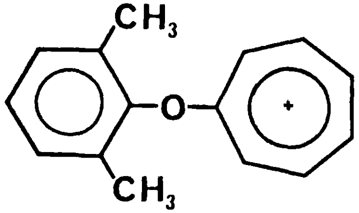
+ 2.0 g of diazonium salt in 5.0 g of either TMU or MPY solution.

Table 2.3.2.1-1c The structure, mp, crude yield, yield after recrystallization, and elemental analysis of the carbonylic adducts isolated from thermal dediazoniations of 2,4,6-trimethylbenzenediazonium salts (L) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.+

Compound	Structure	mp	Crude yield	After recrystallization (yield, solvent)	Elemental analysis %
LVIb	 PF_6^-	135-6	1.42 g	1.15 g (44%, EtOH)	PF_6^- Calc. 38.12 Found 38.99
LVIc	" SbF_6^-	119-20	0.96 g	0.76 g (31%, EtOH)	
LVIe	" $\frac{1}{2}SnCl_6^{2-}$	220-2	1.28 g	0.90 g (35%, MeOH)	
LVIIb	 PF_6^-	189-90	0.98 g	0.73 g (29%, EtOH)	
LVIIc	" SbF_6^-	176-7	1.01 g	0.74 g (31%, EtOH)	
LVIIe	" $\frac{1}{2}SnCl_6^{2-}$	265-7	1.31 g	0.96 (38%, MeOH)	

+ 2.0 g of diazonium salt in 5.0 g of either TMU or MPY solution.

Table 2.3.2.1-1d The structure, mp, crude yield, yield after recrystallization and elemental analysis of miscellaneous carbonylic adducts isolated from thermal dediazoniations+

Compound	Structure	mp	Crude yield	After recrystalliation (yield, solvent)	Elemental analysis %
LVIIIb		PF_6^- 123.5 - 4.5	1.05 g	0.79 g (30%, EtOH)	PF_6^- Calc. 39.58 Found 39.70
LIXb		PF_6^- 154 - 5	0.89 g	0.67 g (26%, EtOH)	PF_6^- Calc. 40.35 Found 40.90
LXb		PF_6^- 159.5 - 60.5	0.96 g	0.68 g (26%, EtOH)	C H N PF_6^- Calc. 42.86 5.36 7.69 40.02 Found 42.88 5.50 7.64 40.07 42.99 5.52 7.66 40.16
LXIb		PF_6^- 162 - 4	0.22 g (9%)		C H PF_6^- Calc. 50.57 4.24 40.69 Found 50.19 4.60 39.69 50.24 4.63

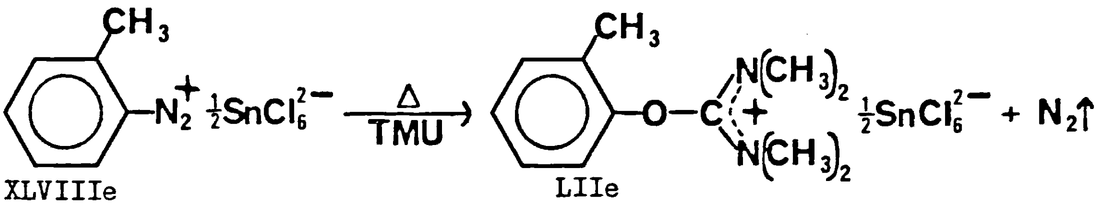
+ 2.0 g of diazonium salt in 5.0 g of TMU, MPY, or DMI solution, while 6.0 g of tropone was used.

2.3.2.2 Identification of products

The products isolated from thermal dediazoniations in TMU, DMI and MPY solutions were assigned structures on the basis of their ^{1}H NMR spectra, IR spectra and, for several products, their elemental analyses which were consistent with the assigned carbonylic adduct structures shown in tables 2.3.2.1-1a — 2.3.2.1-1d. The assignments of the ^{1}H NMR absorption bands for all these thermal dediazoniation products are given in tables 2.3.2.2-1a — 2.3.2.2-1g, while the assignments of their major IR absorption bands are given in tables 2.3.2.2-2a — 2.3.2.2-2d.

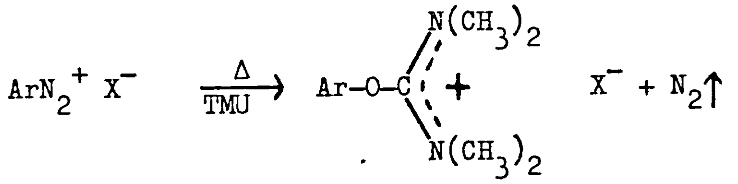
Four products chosen as being representative of all the products obtained in these thermal dediazoniation studies are those products obtained from the thermolysis of XLVIIIe in TMU, XLIXb in DMI, Lc in MPY, and XLIXb in tropone solution.

The product isolated from the thermolysis of XLVIIIe in TMU was thought to be 2-(2'-methylphenoxy)-1,1,3,3-tetramethylamidinium hexachlorostannate (LIIe). Fig. 2.3.2.2-2 shows the ^{1}H NMR spectrum of



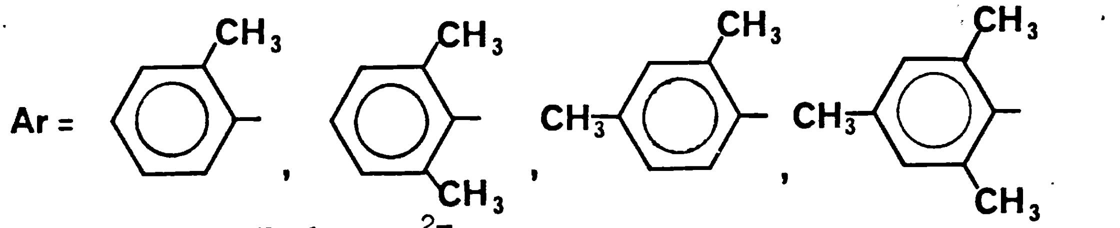
(79)

this product which is consistent with structure LIIe, and whose assignment of bands is given in table 2.3.2.2-1a. The ^{1}H NMR spectrum of LIIe has a singlet absorption of $\delta = 2.45$ ppm corresponding to the three hydrogens of the ortho methyl substituent, a large singlet at $\delta = 3.32$ ppm, corresponding to the twelve equivalent hydrogens of the two dimethylamino groups, while the complex multiplet absorption at $\delta = 6.9 - 7.7$ ppm arises from the four non-equivalent aromatic hydrogens. An inspection of the assignments for the ^1H NMR spectra of other isolated products (tables 2.3.2.2-1a — 2.3.2.2-1g) shows that all assignments of aromatic methyl substituents are in the range $\delta = 2.12 - 2.45$ ppm, while all assignments for the hydrogens of the two dimethylamino groups in adducts isolated from TMU solution, fall in the range $\delta = 3.05 - 3.32$ ppm. The most important feature in the IR spectrum of LIIe (table 2.3.2.2-2a) is the strong absorption band at 1670 cm^{-1} correlating with the $C{=}N$ stretching vibration in accord with the amidinium structure proposed for LIIb by Rutherford.[67] Indeed a strong absorption band in the region 1655 - 70 cm^{-1} is a common feature of all the IR spectra for products isolated from TMU solution and is indicative of a common amidinium type structure (LXII). A summary of the products isolated from the thermal dediazoniation of aryldiazonium salts in TMU solution is given below, eqn. (80).



$$ArN_2^+ X^- \xrightarrow[TMU]{\Delta} Ar{-}O{-}\overset{N(CH_3)_2}{\underset{N(CH_3)_2}{C}}{}^{+} \quad X^- + N_2\uparrow \qquad (80)$$

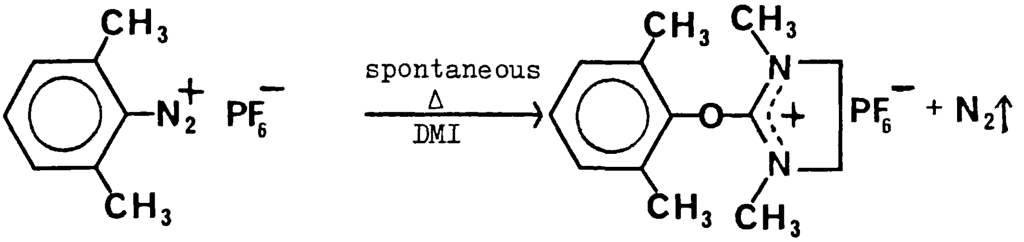
LXII



$X^- = PF_6^-, SbF_6^-, \frac{1}{2}\,SnCl_6^{2-}$

The product isolated from the thermolysis of XLIXb in DMI was regarded as 2-(2',6'-dimethylphenoxy)-1,3-dimethylimidazolidinium hexafluorophosphate (LXb).

The elemental analysis for LXb, see table 2.3.2.1-1d, was in agreement with this formula.

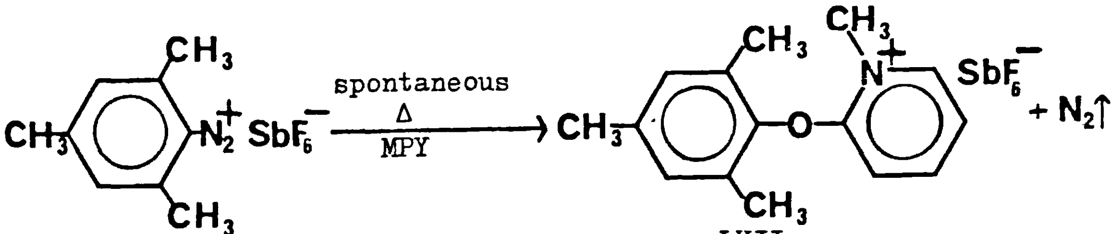


(81)

XLIXb LXb

Fig. 2.3.2.2-3 shows the ^{1}H NMR spectrum of this product which is consistent with the structure LXb and whose assignment of bands is given in table 2.3.2.2-1g. The ^{1}H NMR spectrum of LXb has a singlet absorption at $\delta = 2.33$ ppm resulting from the six hydrogens of the two equivalent aromatic methyl substituents, a singlet at $\delta = 2.83$ ppm that can be assigned to the six hydrogens of the two equivalent methylamino substituents while the singlet at $\delta = 3.90$ ppm corresponds to the four hydrogens of the two equivalent methylene groups. The singlet of $\delta = 7.35$ ppm was assigned to the three aromatic hydrogens, and is consistent with the appearance of a similar singlet in the ^{1}H NMR spectrum of all other carbonylic adducts derived from 2,6-dimethylbenzenediazonium salts. The most important features in the IR spectrum of LXb (table 2.3.2.2-2d) are the strong absorption bands at 1638 cm^{-1}, and 838 cm^{-1} that correlate with the C = N and the P-F stretching vibrations.

The product isolated from the thermolysis of Lc in MPY was assigned the structure 2-(2',4',6'-trimethylphenoxy)-1-methylpyridinium hexafluoroantimonate (LVIIc).



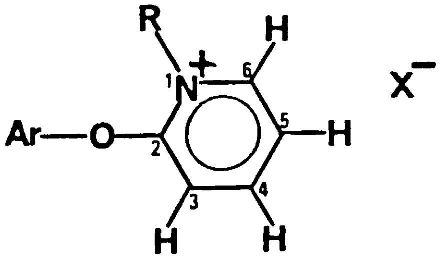
(82)

Lc LVIIc

Fig. 2.3.2.2-4 shows the ^{1}H NMR spectrum of this product which is consistent with the structure LVIIc, and whose assignment of bands is given in table 2.3.2.2-1f. The ^{1}H NMR spectrum of LVIIc has a singlet absorption of $\delta = 2.12$ ppm which may be assigned as the six hydrogens of the two equivalent aromatic methyl substituents, while the singlet absorption at $\delta = 2.36$ ppm arises from the three hydrogens of the other aromatic methyl substituent. The assignment of the above methyl substituents is consistent with all the other ^{1}H NMR spectra of carbonylic adducts derived from 2,4,6-trimethylbenzenediazonium salts. The singlet absorption at $\delta = 4.32$ ppm in the ^{1}H NMR spectrum of LVIIc corresponds to the three hydrogens of the N-methyl substituent of the pyridinium ring, and is consistent with the observation of a singlet in the range $\delta = 4.28 - 4.63$ ppm for all of the products isolated from MPY solutions.

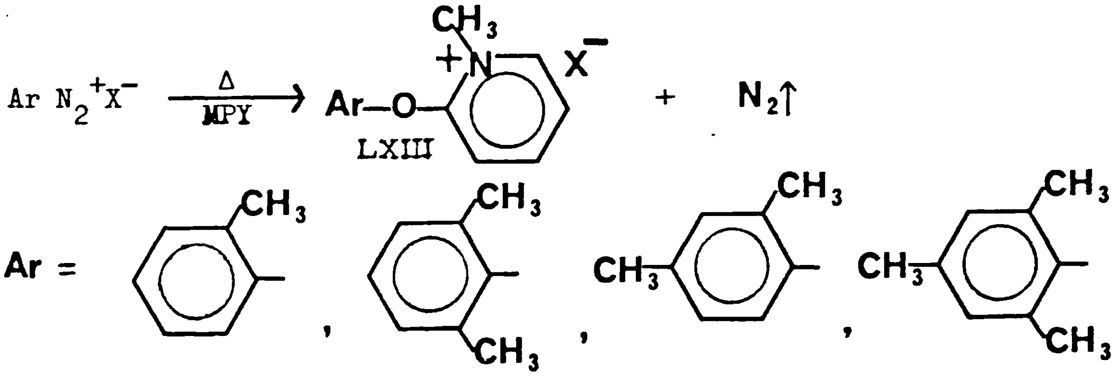
The aromatic region of fig. 2.3.2.2-4 appears to be quite complex but is fully consistent with that obtained for the other proposed pyridinium type carbonylic adducts. The singlet at $\delta = 7.26$ ppm may be assigned to the two equivalent aromatic hydrogens of the aryl ring, in accord with a similar singlet observed for all the carbonylic adducts derived from 2,4,6-trimethylbenzenediazonium salts. Fig. 2.3.2.2-1 below shows the numbering system employed in the assignment of the pyridinium ring hydrogens in the ^{1}H NMR data tables. In fig. 2.3.2.2-4 the doublet at $\delta = 7.03$ ppm (J = 8.0 Hz) was assigned as H(3), being the most shielded

<u>Fig. 2.3.2.2-1 Numbering of pyridinium ring hydrogens used in ^{1}H NMR tables of data</u>



since it is ortho to the electron donating aroxy substituent and should appear as a doublet being coupled only with H(4) in a first order interpretation. The triplet at δ = 7.70 ppm (J = 7.0 Hz) was assigned as H(5) since it is para to the electron donating aroxy substituent, and its appearance as a triplet is attributed to almost identical coupling with H(6) and H(4). The multiplet signal close to 8.6 ppm is proposed to be composed of a triplet at δ = 8.50 ppm (J = 8.0 Hz) assigned as H (4), and a doublet at δ = 8.62 ppm assigned as H(6) (J = 6.0 Hz). The electron withdrawing pyridinium nitrogen should heavily deshield the para hydrogen H(4) and its appearance as a triplet is attributed to almost identical coupling with H(3) and H(5). In addition the pyridinium nitrogen should deshield the H(6) hydrogen the most and appear as a doublet by coupling with H(5).

The most important features in the IR spectrum of LVIIc (table 2.3.2.2-2c) are the absorption bands at 1638 cm^{-1}, and 658 cm^{-1} corresponding to the C $=$ N stretching mode and the Sb–F stretching mode common to all the hexafluoroantimonate products. The absorption band at 1638 cm^{-1} is consistent with the observation of a band in the region 1642 – 35 cm^{-1} for all of the products isolated from MPY solutions, and is proposed to be indicative of a common pyridinium type structure (LXIII). A summary of the products isolated from the thermal dediazoniation of aryldiazonium salts in MPY solution is given below in eqn. (83).

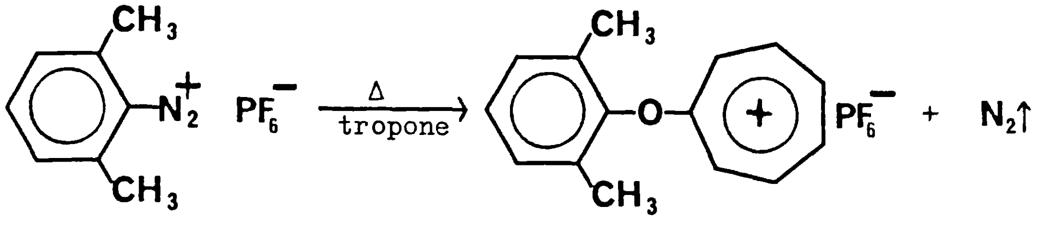


LXIII

(83)

$X^- = PF_6^-,\ SbF_6^-,\ \frac{1}{2}SnCl_6^{2-}$

The product isolated from the thermolysis of XLIXb in tropone was assigned the structure (2',6'-dimethylphenoxy)-tropylium hexafluorophosphate (LXIb). The elemental analysis for LXIb (see table 2.3.2.1-1d) was

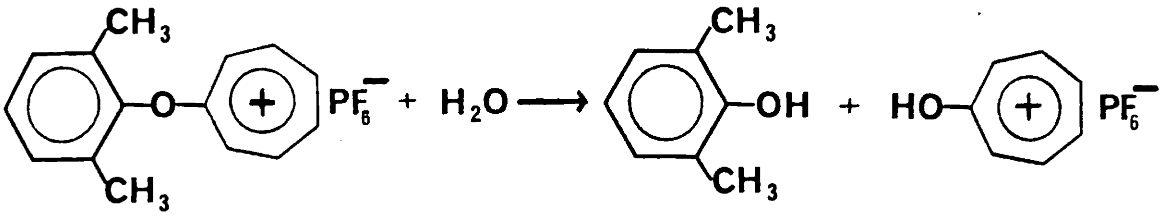


(84)

XLIXb LXIb

in agreement with this formula. Fig. 2.3.2.2-5 shows the ^{1}H NMR spectrum of this product and is consistent with the structure LXIb, and whose assignment of absorptions is given in table 2.3.2.2-1g. The ^{1}H NMR spectrum of LXIb has a singlet absorption at $\delta = 2.15$ ppm, assigned as the six hydrogens of the two equivalent aromatic methyl substituents, while the singlet at $\delta = 7.45$ ppm was assigned to the three aromatic hydrogens of the aryl ring, and is consistent with the appearance of a similar singlet in the ^{1}H NMR spectrum of all other carbonylic adducts derived from 2,6-dimethylbenzenediazonium salts. The multiplet absorption signal in the range 8.4 - 9.3 ppm which has an absorption maximum at $\delta = 8.95$ ppm was assigned to the six aromatic hydrogens of the tropylium ring. Fig. 2.3.2.2-5 includes the inset low temperature ^{1}H NMR spectrum of the reactive intermediate acetoxytropylium tetrafluoroborate obtained by Schenk[186] whose tropylium ring hydrogens have a similar absorption pattern to that observed for LXIb.

On the addition of D_2O (2 drops) to the ^{1}H NMR sample of LXIb there was observed a change in the spectrum (fig. 2.3.2.2-6 (a→ b) over a period of 24 hr. This change produced a spectrum (fig. 2.3.2.2-6 (b)) identified as a 1:1 mixture of 2,6-dimethylphenol (LXIV), and the hexafluorophosphoric acid salt of tropone (LXV) by comparison with spectra of authentic samples.



(85)

LXIb LXIV LXV

The most important feature in the IR spectrum of LXIb (table 2.3.2.2-2d) is the strongest band at 837 cm^{-1} (P - F str) common to all hexafluorophosphate salts. The strong or medium absorption band in the range 1677 - 1635 cm^{-1}, previously associated with the C = N stretching mode and a common feature of all the carbonylic adducts isolated from TMU, DMI and MPY solutions, is absent from the IR spectrum of LXIb.

Fig. 2.3.2.2-2 60 MHz ^{1}H NMR spectrum of LIIe, assigned the structure 2-(2'-methylphenoxy)-1,1,3,3-tetramethylamidinium hexachlorostannate.

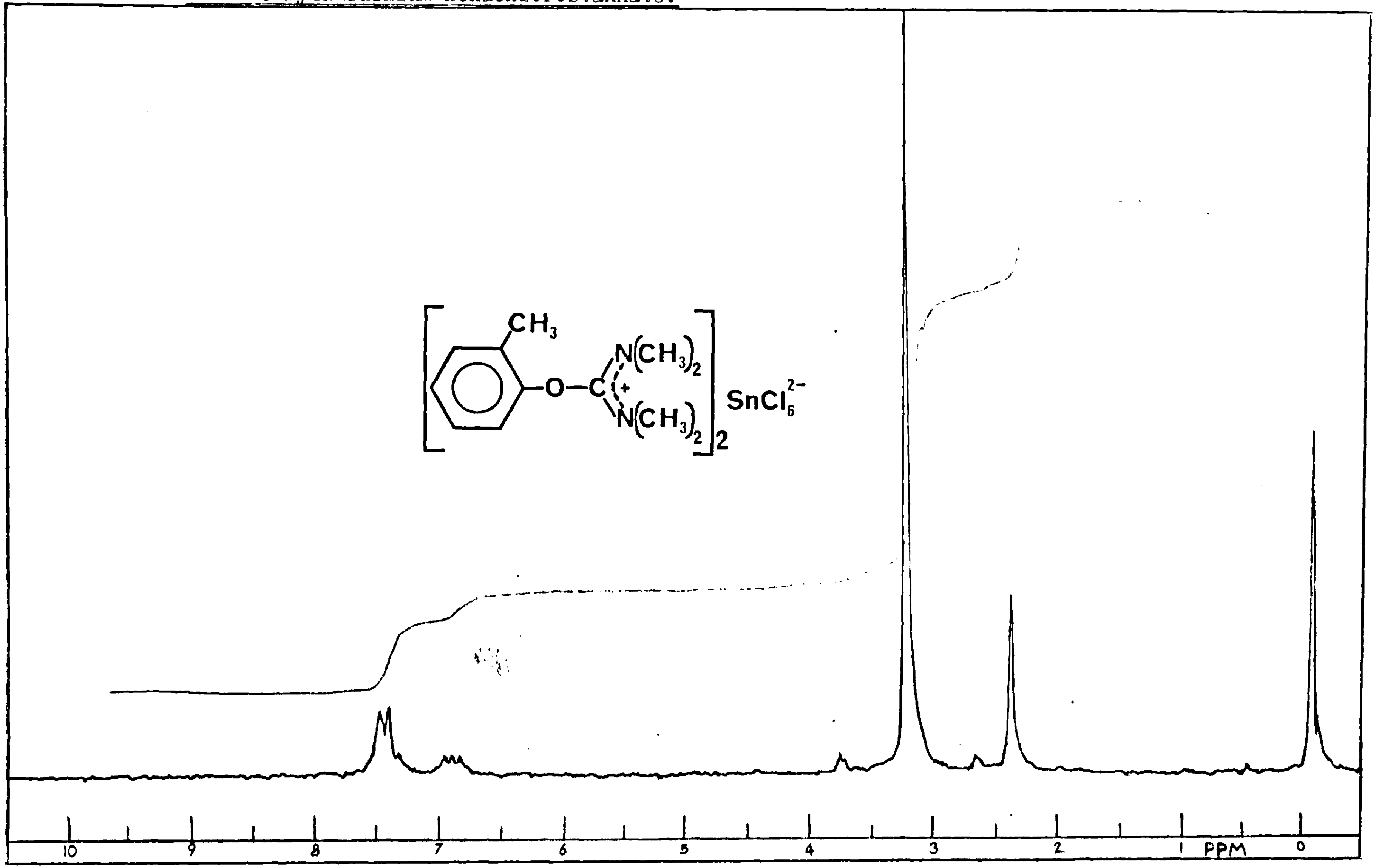


Fig. 2.3.2.2-3 60 MHz ^{1}H NMR spectrum of LXb, assigned the structure 2-(2',6'-dimethylphenoxy)-1,3-dimethylimidazolidinium hexafluorophosphate.

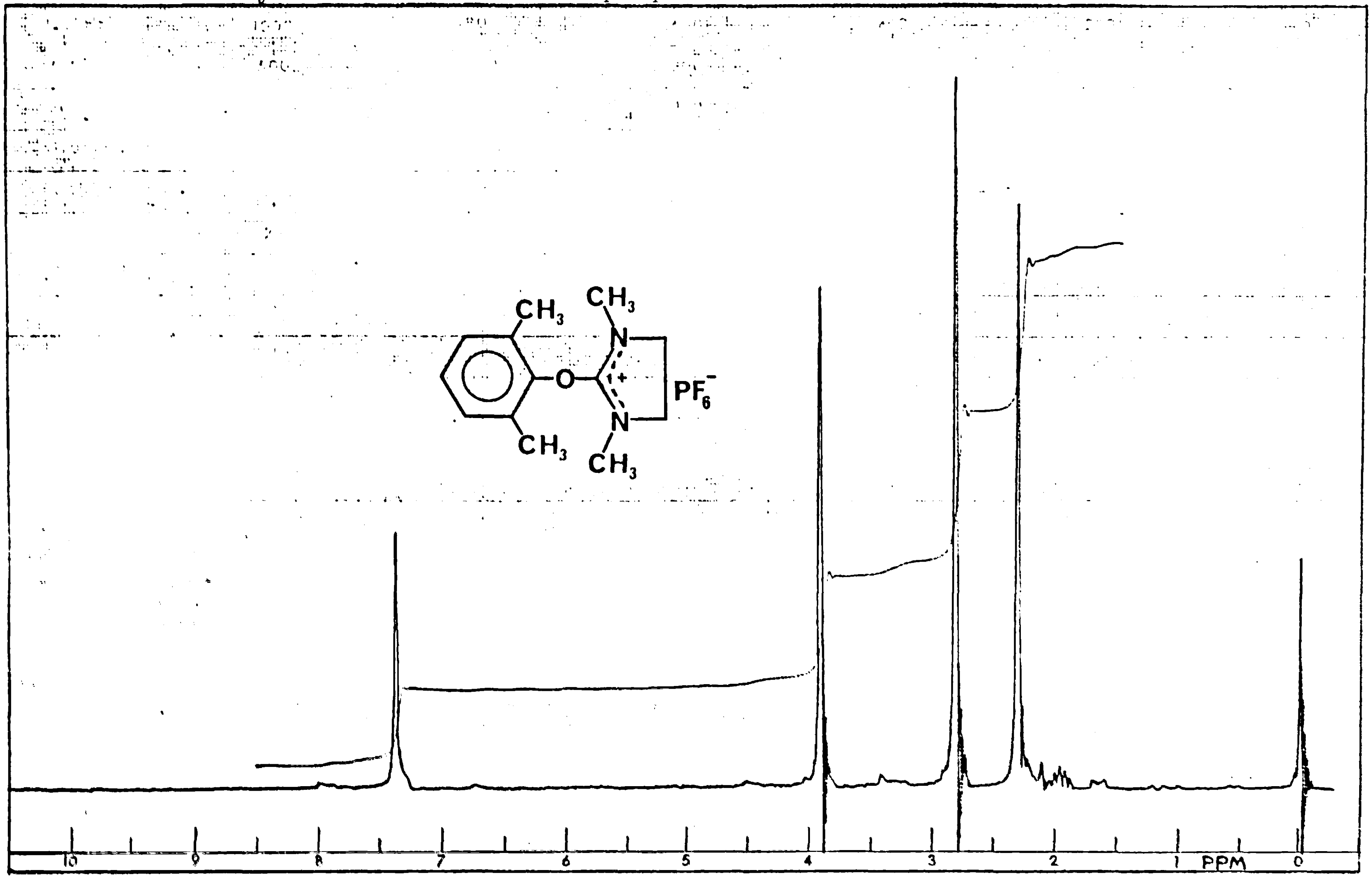


Fig. 2.3.2.2-4 60 MHz ^1H NMR spectrum of LVIIc, assigned the structure 2-(2',4',6'-trimethylphenoxy)-1-methylpyridinium hexafluoroantimonate.

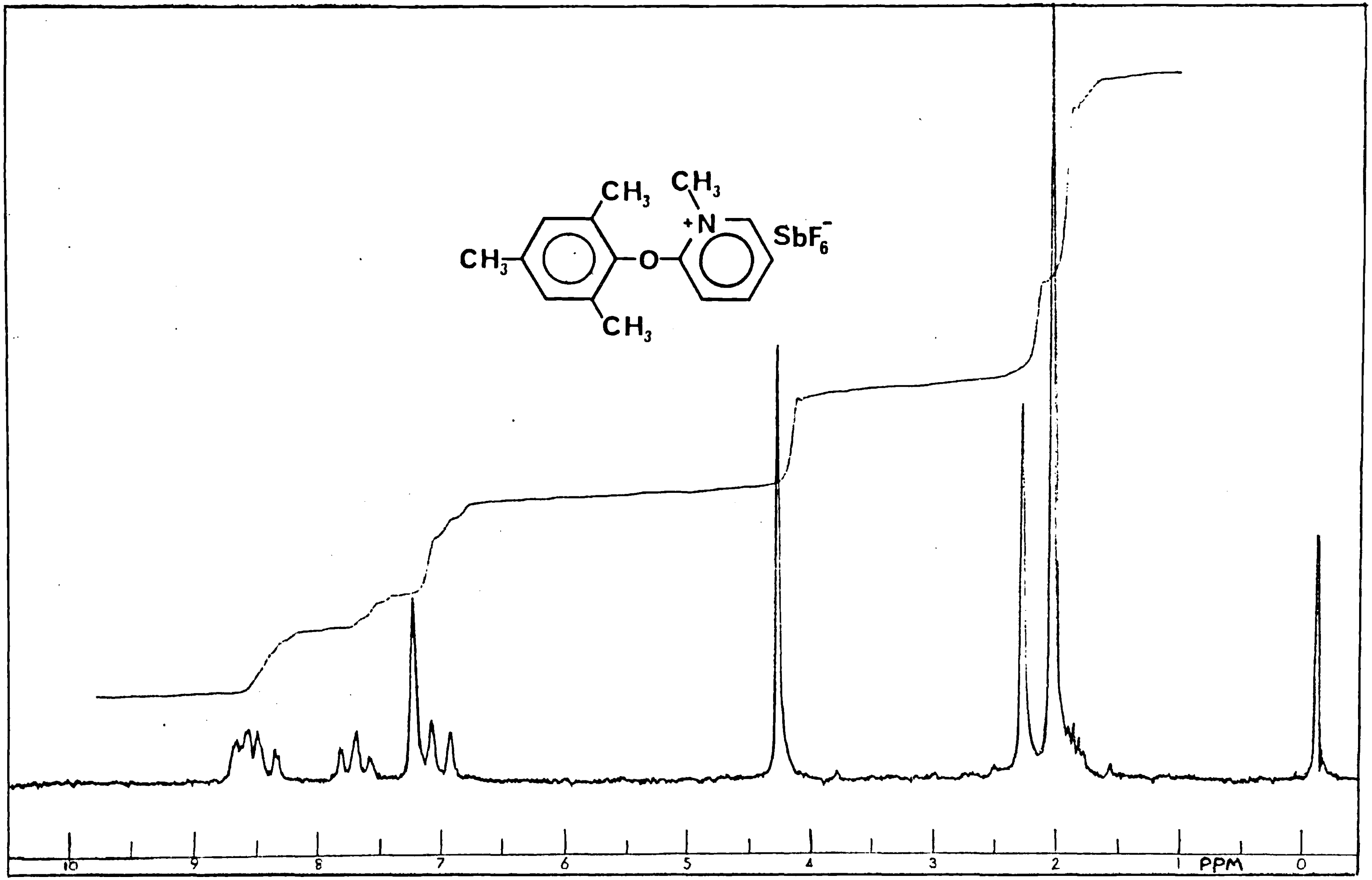


Fig. 2.3.2.2-5 60 MHz ^1H NMR spectrum of LXIb assigned the structure of (2',6'-dimethylphenoxy)-tropylium hexafluorophosphate, together with the inset spectrum of acetoxytropylium tetrafluoroborate.

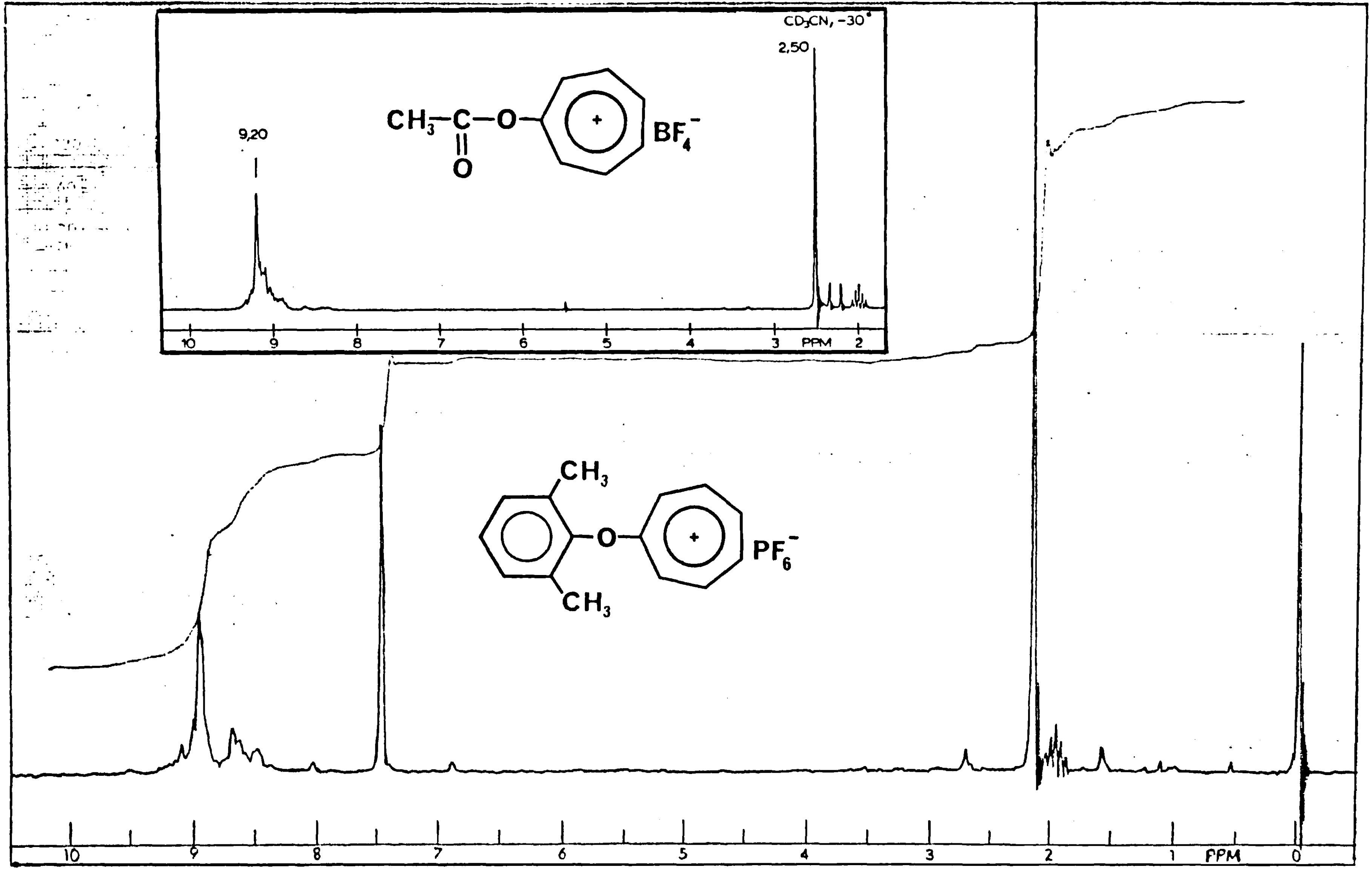


Fig. 2.3.2.2-6 Figure showing the change in the 60 MHz ^{1}H NMR spectrum of LXIb after the addition of D_2O (2 drops)

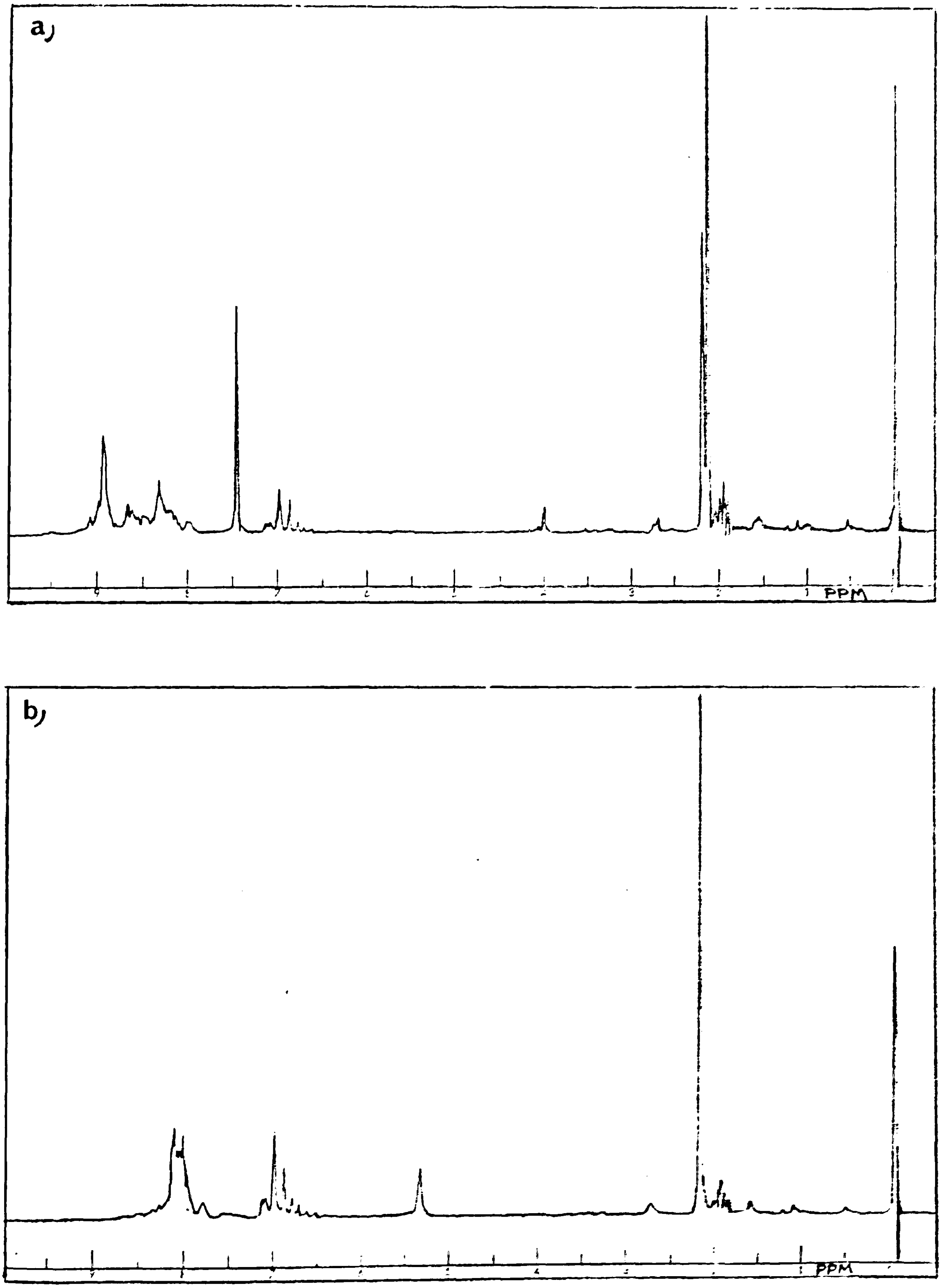


Table 2.3.2.2-1a ^1H NMR absorptions of carbonylic adducts[+] isolated from the thermal dediazoniation of 2-methylbenzenediazonium salts (XLVIII) in 1,1,3,3-tetramethylurea (TMU) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Integration
LIIb	CD_3CN	s	2.38	$CH_3(2')$	3
		s	3.10	$-N(CH_3)_2$ (1,3)	12
		mlt	6.9 - 7.7	H (3',4',5',6')	4
LIIc	CD_3CN	s	2.38	$CH_3(2')$	3
		s	3.12	$-N(CH_3)_2$ (1,3)	12
		mlt	6.9 - 7.7	H(3',4',5',6')	4
LIIe	CF_3CO_2D	s	2.45	$CH_3(2')$	3
		s	3.32	$-N(CH_3)_2(1,3)$	12
		mlt	6.9 - 7.7	H (3',4',5',6')	4

[+] Table 2.3.2.1-1a shows the proposed structure of these carbonylic adducts.

Table 2.3.2.2-1b ^{1}H NMR absorptions of carbonylic adducts^{+} isolated from the thermal dediazoniation of 2-methylbenzene diazonium salts (XLVIII) in 1-methyl-2-pyridone (MPY) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LIIIb	CD_3CN	s	2.25	CH_3 (2')		3
		s	4.28	$-NCH_3$ (1)		3
		d	7.07	H (3)	J 3,4 = 9.0	1
		mlt	7.25 - 7.80	H (3',4',5',6',5)		5
		mlt { t	8.45	H (4)	J 3,4 ≈ J 4,5 = 9.0	2
		d	8.57	H (6)	J 5,6 = 6.0	
LIIIc	CD_3CN	s	2.26	CH_3 (2')		3
		s	4.31	$-NCH_3$ (1)		3
		d	7.13	H (3)	J 3,4 = 9.0	1
		mlt	7.25 - 7.80	H (3',4',5',6',5)		5
		mlt { t	8.46	H (4)	J 3,4 ≈ J 4,5 = 9.0	2
		d	8.60	H (6)	J 5,6 = 6.0	
LIIIe	CF_3CO_2D	s	2.34	CH_3 (2')		3
		s	4.60	$-NCH_3$ (1)		3
		d	7.31	H (3)	J 3,4 = 9.0	1
		mlt	7.45 - 8.05	H (3',4',5',6',5)		5
		mlt { t	8.63	H (4)	J 3,4 ≈ J 4,5 = 9.0	2
		d	8.75	H (6)	J 5,6 = 6.0	

+ Table 2.3.2.1-1a shows the proposed structure of these carbonylic adducts.

Table 2.3.2.2-1c ^{1}H NMR absorptions of carbonylic adducts$^+$ isolated from the thermal dediazoniation of 2,6-dimethylbenzenediazonium salts (XLIX) in 1,1,3,3-tetramethylurea (TMU) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Integration
LIVb	CD_3CN	s	2.26	CH_3 (2',6')	6
		s	3.07	$-N(CH_3)_2$ (1,3)	12
		s	7.33	H (3',4',5')	3
LIVc	CD_3CN	s	2.28	CH_3 (2',6')	6
		s	3.13	$-N(CH_3)_2$ (1,3)	12
		s	7.37	H (3',4',5')	3
LIVe	CD_3CN	s	2.28	CH_3 (2',6')	6
		s	3.15	$-N(CH_3)_2$(1,3)	12
		s	7.35	H(3',4',5')	3

$^+$ Table 2.3.2.1-1b shows the proposed structure of these carbonylic adducts.

Table 2.3.2.2-1d ^{1}H NMR absorptions of carbonylic adducts^{+} isolated from the thermal dediazoniation of 2,6-dimethylbenzenediazonium salts (XLIX) in 1-methyl-2-pyridone (MPY) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LVb	CD_3CN	s	2.20	CH_3 (2',6')		6
		s	4.37	$-NCH_3$ (1)		3
		d	7.02	H (3)	J 3,4 = 8.0	1
		s	7.45	H (3',4',5')		3
		t	7.75	H (5)	J 4,5 ≈ J 5,6 = 7.5	1
		mlt t	7.52	H (4)	J 3,4 ≈ J 4,5 = 8.0	2
		d	8.65	H (6)	J 5,6 = 7.0	
LVc	CD_3CN	s	2.20	CH_3 (2',6')		6
		s	4.36	$-NCH_3$ (1)		3
		d	7.03	H (3)	J 3,4 = 8.0	1
		s	7.47	H (3',4',5')		3
		t	7.72	H (5)	J 4,5≈J 5,6 = 7.5	1
		mlt t	8.50	H (4)	J 3,4≈J 4,5 = 8.0	2
		d	8.63	H (6)	J 5,6 = 7.0	
LVe	CF_3CO_2D	s	2.27	CH_3 (2',6')		6
		s	4.63	$-NCH_3$(1)		3
		d	7.22	H (3)	J 3,4 = 9.0	1
		s	7.52	H (3',4',5')		3
		t	7.90	H (5)	J 4,5≈J 5,6 = 7.0	1
		mlt t	8.67	H (4)	J 3,4≈J 4,5 = 8.0	2
		d	8.83	H (6)	J 5,6 = 7.0	

$^{+}$ Table 2.3.2.1-1b shows the proposed structure of these carbonylic adducts.

Table 2.3.2.2-1e ^{1}H NMR absorptions of carbonylic adducts$^+$ isolated from the thermal dediazoniation of 2,4,6-trimethylbenzenediazonium salts (L) in 1,1,3,3-tetramethylurea (TMU) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Integration
LVIb	CD_3CN	s	2.23	CH_3 (2',6')	6
		s	2.32	CH_3 (4')	3
		s	3.08	$-N(CH_3)_2$ (1,3)	12
		s	7.15	H (3',5')	2
LVIc	CD_3CN	s	2.23	CH_3 (2',6')	6
		s	2.33	CH_3 (4')	3
		s	3.05	$-N(CH_3)_2$ (1,3)	12
		s	7.18	H(3',5')	2
LVIe	CF_3CO_2D	s	2.32	CH_3 (2',6')	6
		s	2.38	CH_3 (4')	3
		s	3.28	$-N(CH_3)_2$ (1,3)	12
		s	7.21	H (3',5')	2

$^+$ Table 2.3.2.1-1c shows the proposed structure of these carbonylic adducts.

Table 2.3.2.2-1f ^{1}H NMR absorptions of carbonylic adducts[+] isolated from the thermal dediazoniation of 2,4,6-trimethylbenzenediazonium salts (L) in 1-methyl-2-pyridone (MPY) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LVIIb	CD_3CN	s	2.17	CH_3 (2',6')		6
		s	3.40	CH_3 (4')		3
		s	4.40	$-NCH_3$(1)		3
		d	7.13	H (3)	J 3,4 = 8.0	1
		s	7.35	H (3',5')		2
		t	7.82	H (5)	J 4,5 ≈ J 5,6 = 7.0	1
		mlt t	8.62	H (4)	J 3,4 ≈ J 4,5 = 8.0	2
		d	8.75	H (6)	J 5,6 = 6.0	
LVIIc	CD_3CN	s	2.12	CH_3 (2',6')		6
		s	2.36	CH_3 (4')		3
		s	4.32	$-NCH_3$(1)		3
		d	7.03	H (3)	J 3,4 = 8.0	1
		s	7.26	H (3',5')		2
		t	7.70	H (5)	J 4,5 ≈ J 5,6 = 7.0	1
		mlt t	8.50	H (4)	J 3,4 ≈ J 4,5 = 8.0	2
		d	8.62	H (6)	J 5,6 = 6.0	
LVIIe	CF_3CO_2D	s	2.23	CH_3 (2',6')		6
		s	2.43	CH_3 (4')		3
		s	4.59	$-NCH_3$(1)		3
		overlap d	~7.22	H (3)	?	3
		s	7.31	H (3',5')		
		t	7.85	H (5)	J 4,5 ≈ J 5,6 = 7.0	1
		mlt t	8.65	H (4)	J 3,4 ≈ J 4,5 = 8.0	2
		d	8.81	H (6)	J 5,6 = 7.0	

[+] Table 2.3.2.1-1c shows the proposed structure of these carbonylic adducts.

Table 2.3.2.2-1g ^{1}H NMR absorptions of carbonylic adducts[+] isolated from the thermal dediazoniation of some aryldiazonium hexafluorophosphates in 1,1,3,3-tetramethylurea (TMU), 1-methyl-2-pyridone (MPY), 1,3-dimethylimidazolidinone (DMI), tropone and their assignments.

Compounds	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LVIIIb	CD_3CN	s	2.36	CH_3(2',4')		6
		s	3.12	$-N(CH_3)_2$(1,3)		12
		mlt	6.83 - 7.55	H (3',5',6')		3
LIXb	CD_3CN	s	2.22	CH_3(2')		3
		s	2.42	CH_3 (4')		3
		s	4.27	$-NCH_3$(1)		3
		d	7.09	H (3)	J 3,4 = 10.0	1
		mlt	7.20 - 7.50	H (3',5',6')		3
		t	7.67	H (5)	J 4,5 ≈ J 5,6 = 8.0	1
		mlt { t	8.45	H (4)	J 3,4 ≈ J 4,5 = 9.0	} 2
		d	8.55	H (6)	J 5,6 = 7.0	
LXb	CD_3CN	s	2.33	CH_3 (2',6')		6
		s	2.83	$-NCH_3$ (1,3)		6
		s	3.90	CH_2 (4,5)		4
		s	7.35	H (3',4',5')		3
LXIb	CD_3CN	s	2.15	CH_3 (2',6')		6
		s	7.45	H (3',4',5')		3
		mlt	8.4 - 9.3 (large abs at 8.95)	H (2,3,4,5,6,7)		6

[+] Table 2.3.2.1-1d shows the proposed structures of these carbonylic adducts.

Table 2.3.2.2-2a The assignments of the major IR absorption bands (cm^{-1}) of carbonylic adducts^{+} isolated from the thermal dediazoniations of 2-methylbenzenediazonium salts (XLVIII) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.

Compound	C-H str (Arom)	CH_3(C-H)str.	C=N str	Aromatic ring modes	P-F str	γ C-H Aromatic ring modes	Sb-F str
LIIb	3070 w-mlt	2955 w-mlt	1662 s	1613 w 1492 m 1465 w	840 vs	752 m 768 m	
LIIc	3070 w-mlt	2958 w-mlt	1670 s	1613 w 1492 m 1468 m		755 m 772 m	660 s
LIIe	3040 w-mlt	2950 w-mlt	1670 s	1613 w 1490 m 1458 m		757 m 770 m	
LIIIb	3120 m-mlt	2950 w-mlt	1638 m	1577 m 1510 s 1492 s 1450 m	837 vs	773 m 748 m	
LIIIc	3110 m-mlt	2950 w-mlt	1642 m	1580 m 1510 s 1495 s 1450 m		780 m 752 m	660 s
LIIIe	3080 m-mlt	2923 w-mlt	1638 m	1580 m 1510 s 1494 s 1445 m		777 m 748 m	

$^{+}$ Table 2.3.2.1-1a shows the proposed structures of these carbonylio adducts.

Table 2.3.2.2-2b The assignments of the major IR absorption bands (cm^{-1}) of carbonylic adducts[+] isolated from the thermal dediazoniations of 2,6-dimethylbenzenediazonium salts (XLIX) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.

Compound	C-H str (Arom)	CH_3(C-H) str	C=N str	Aromatic ring modes	P-F str	γC-H Aromatic ring modes	Sb-F str
LIVb	3050 w-mlt	2950 w-mlt	1657 s	1612 w 1528 m 1470 m	840 vs	787 m 725 w 714 w	
LIVc	3050 w-mlt	2950 w-mlt	1657 s	1612 w 1530 m 1470 m		790 m 728 w 716 w	660 s
LIVe	3040 w-mlt	2950 w-mlt	1655 s	1612 w 1520 m 1465 m		795 m 725 w 712 w	
LVb	3110 m-mlt	2950 w-mlt	1640 m	1592 m 1508 s 1460 m	837 vs	772 m	
LVc	3110 m-mlt	2950 w-mlt	1642 m	1593 m 1510 s 1452 m		775 m	662 s 633 m
LVe	3080 m-mlt	2920 w-mlt	1639 m	1592 m 1508 s 1440 m		775 m	

[+] Table 2.3.2.1-1b shows the proposed structures of these carbonylic adducts.

Table 2.3.2.2-2c The assignments of the major IR absorption bands (cm^{-1}) of carbonylic adducts[+] isolated from the thermal dediazoniations of 2,4,6-trimethylbenzenediazonium salts (L) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.

Compound	C-H str (Arom)	CH_3(C-H) str	C=N str	Aromatic ring modes	P-F str	γC-H Aromatic ring modes	Sb-F str
LVIb	3030 w-mlt	2950 w-mlt	1665 s	1608 w 1528 m 1470 m	840 vs	904 w 803 w	
LVIc	3030 w-mlt	2950 w-mlt	1660 s	1610 w 1530 m 1470 m		902 w 857 w 804 w	655 s
LVIe	3030 w-mlt	2950 w-mlt	1660 s	1607 w 1523 m 1468 m		900 w 857 w 803 w	
LVIIb	3100 m-mlt	2950 w-mlt	1638 m	1585 m 1508 s 1447 m	840 vs	884 m	
LVIIc	3105 m-mlt	2950 w-mlt	1638 m	1585 m 1510 s 1447 m		882 m 858 m	658 s
LVIIe	3060 m-mlt	2920 w-mlt	1635 m	1585 m 1512 s 1442 m		882 m 867 m	

[+] Table 2.3.2.1-1c shows the proposed structures of these carbonylic adducts.

Table 2.3.2.2-2d The assignments of the major IR absorption bands (cm^{-1}) of carbonylic adducts^{+} isolated from the thermal dediazoniations of some aryldiazonium hexafluorophosphates in 1,1,3,3-tetramethylurea (TMU), 1-methyl-2-pyridone (MPY), and tropone solutions.

Compound	C-H str (Arom)	CH_3(C-H) str	C=N str	Aromatic ring modes	P-F str	γ C-H Aromatic ring modes
LVIIIb	3040 w-mlt	2960 w-mlt	1670 s	1612 w 1500 m 1470 m	840 vs	825 m 742 w
LIXb	3110 m-mlt	2930 w-mlt	1642 m	1587 m 1512 s 1455 m	840 vs	742 w
LXb	3040 w-mlt	2940 w-mlt	1638 s	1600 m 1477 m 1455 w	838 vs	787 m 740 w 708 w
LXIb	3040 m-mlt	2950 w-mlt	absent	1613 m 1510 m 1450 w	837 vs	772 m 740 w

$^{+}$ Table 2.3.2.1-1d shows the proposed structures of these carbonylic adducts.

2.3.3 Photodediazoniations in 1,1,3,3-tetramethylurea, and 1-methyl-2-pyridone solutions

2.3.3.1 Introduction

In view of the large number of carbonylic adducts which were isolated from the thermal dediazoniation of a variety of aryl diazonium salts in ch. 2.3.2, it was now decided to return to the question of whether carbonylic adducts could be isolated in the photodediazoniation of aryl diazonium salts. With this in mind the photodediazoniation of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb) in TMU and MPY solutions was investigated along with a number of other photosensitive aryl diazonium salts, containing electron donating methoxy or methylmercapto substituents. Some of these photolytic studies also employed the use of diazonium hexafluoroantimonate and hexachlorostannate salts. Tables 2.3.3.1-1a and 2.3.3.1-1b give the structure, mp, crude yield, yield upon reprecipitation and UV absorption data of all diazonium salts used in the photolytic studies. All photodediazoniations in TMU and MPY solutions were conducted at $\sim 0^{\circ}$ using a high pressure mercury lamp.

Table 2.3.3.1-1a Table of structure, mp, crude yield, reprecipitation recovery, and UV absorption bands of the diazonium salts used in photodediazoniations.

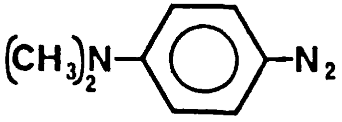
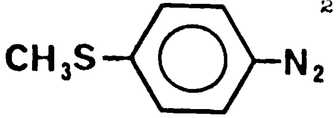
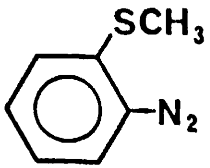
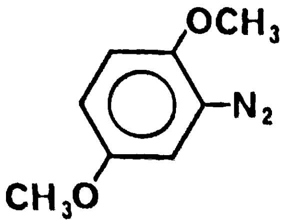
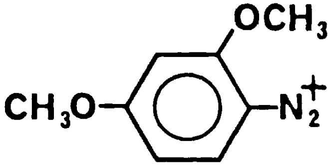
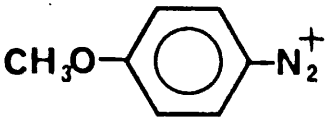
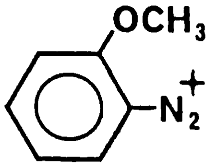
Compound	Structure	mp	Crude yield %	% recovery from purification by reprecipitation	UV Absorbance (nm)
IIb	 PF_6^-	161.5 - 2.0 dec	95	66	378 (375)[37] 244 (250)
IIc	" SbF_6^-	144.0 - 4.5 dec	86	68	
IId	" BF_4^-	150.5 - 1.0 dec	88	75	
IIe	" $\frac{1}{2}SnCl_6^{2-}$	162.5 - 3.5 dec	97		
LXVIb	 PF_6^-	143.0 - 3.5 dec	89	79	373 237
LXVIIb	 PF_6^-	100.0 0.5 dec	94	75	411 245
LXVIIIb	 PF_6^-	127.5 - 8.0 dec	78	82	405 (405)[173] 273 (272) 220 (220)

Table 2.3.3.1-1b

Compound	Structure		mp	Crude yield %	% recovery from purification by reprecipitation	UV Absorbance (nm)
LXIXb		PF_6^-	139.5 - 40.5	76	83	350 (350)[173] 300 (300) 233 (232)
LXXb		PF_6^-	146.5 - 7.0 dec.	87	79	314 (313)[173] 230 (231)
LXXIb		PF_6^-	117.5 - 8.5	84	72	354 (356)[173] 265 (264)

2.3.3.2 Isolation of products

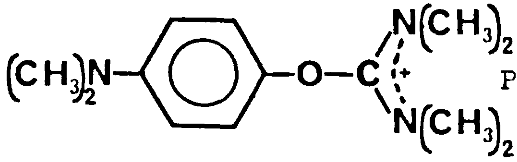
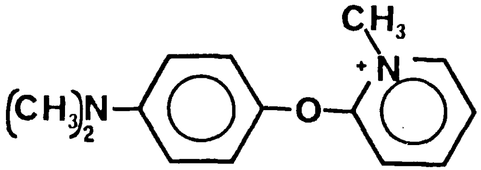
There was no rapid spontaneous thermal dediazoniation observed for any of the diazonium salts listed in tables 2.3.3.1-1a and 2.3.3.1-1b however, by use of ^{1}H NMR spectroscopy, a slow thermal dediazoniation of those diazonium salts having substituents ortho to the diazonium group could be observed. The thermolysis of 2-methoxybenzenediazonium hexafluorophosphate (LXXIb) was judged to be the most rapid, showing ~10% decomposition after 24 hr storage in the dark at room temperature. The thermolyses of 2-methylmercapto-(LXVIIb), 2,5-dimethoxy-(LXVIIIb), and 2,4-dimethoxybenzenediazonium hexafluorophosphate (LXIXb) were judged to be $<5\%$ under the same conditions.

The photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb), hexafluoroantimonate (IIc), and hexachlorostannate (IIe) in TMU and MPY solutions all yielded products which were isolated by the method described in ch. 4.5.4. The photolysis of 4-methylmercapto-(LXVIb), 2-methylmercapto-(LXVIIb), and 2,5-dimethoxybenzenediazonium hexafluorophosphate (LXVIIIb) in TMU solution was also undertaken and the products isolated by the same method. All of the products isolated from the above photolyses were recrystallized. Tables 2.3.3.2-1a and 2.3.3.2-1b, give the structure of these products together with their mp, yields (crude and recrystallized), and also the elemental analysis for one of the products.

Unlike the diazonium salts listed in table 2.3.3.1-1a, which are orange or yellow in colour, those in table 2.3.3.1-1b absorb at lower wavelengths and are colourless. Further, unlike the diazonium salts in table 2.3.3.1-1a no crystalline products were isolated from their photolyses in TMU solutions, although LXIXb and LXXIb were both observed by ^{1}H NMR spectroscopy to be photolysed by the lamp.

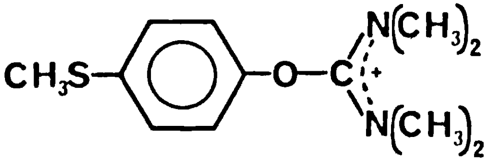
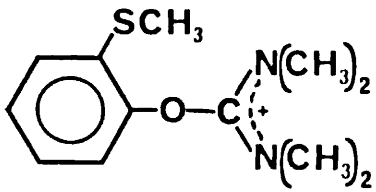
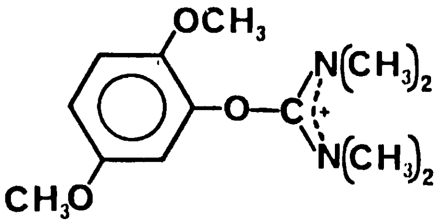
The ^{1}H NMR spectrum of 4-methoxybenzenediazonium hexafluorophsophate (LXXb) in TMU solution was unchanged by irradiation with the high pressure mercury lamp, but inspection of the lamp's spectral distribution (fig. 4.2.1-1) shows very little emission < 350 nm in the UV absorption region of LXXb (table 2.3.3.1-1b).

Table 2.3.3.2-1a The structure, mp, crude yield, yield after recrystallization, and elemental analysis of the carbonylic adducts isolated from photochemical dediazoniations of p-N,N-dimethylaminobenzenediazonium salts (II). in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.+

Compound	Structure	mp	Crude yield	After recrystallization (yield, solvent)	Elemental analysis%
LXXIIb	 PF_6^-	159 - 61	0.73 g	0.56 g (21%, EtOH)	Calc. C 40.95 H 5.82 N 11.02 PF_6^- 38.02 Found C 40.80 H 5.64 N 10.89 PF_6^- 38.92 38.73
LXXIIc	" SbF_6^-	122 - 3.5	0.61 g	0.44 g (18%, EtOH)	
LXXIIe	" $\frac{1}{2}SnCl_6^{2-}$	228 - 9.5	0.83 g	0.62 g (24%, MeOH)	
LXXIIIb	 PF_6^-	180 - 1.5	0.62 g	0.49 g (19%, EtOH)	
LXXIIIc	" SbF_6^-	148 - 50	0.51 g	0.36 g (15%, EtOH)	
LXXIIIe	" $\frac{1}{2}SnCl_6^{2-}$	242 - 5	0.69 g	0.54 g (22%, MeOH)	

+ 2.0 g of diazonium salt in 12.0 g of either TMU or MPY solution.

Table 2.3.3.2-1b The structure, mp, crude yield, and yield after recrystallization of miscellaneous carbonylic adducts+ isolated from photochemical dediazoniations in 1,1,3,3-tetramethylurea (TMU) solutions.

Compound	Structure	mp	Crude yield	After recrystallization (yield, solvent)
LXXIVb		129-30	0.94 g	0.65 g (25%, EtOH)
LXXVb		124.5 - 5.5	0.88 g	0.60 g (23%, EtOH)
LXXVIb		112 - 3	1.04 g	0.74 g (29%, EtOH)

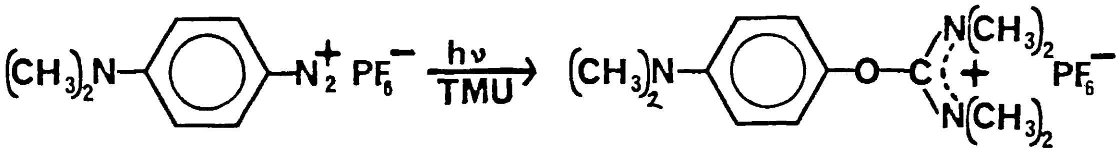
+ 2.0 g of diazonium salt in 8.0 g of TMU.

2.3.3.3 Identification of products

The products isolated from photodediazoniations in TMU, and MPY solutions were assigned structures on the basis of their ^{1}H NMR spectra, and IR spectra which were all consistent with the assigned carbonylic adduct structures shown in tables 2.3.3.2–1a and 2.3.3.2–1b. The assignments of the ^{1}H NMR absorption bands for all these photodediazoniation products are given in tables 2.3.3.3–1a — 2.3.3.3–1c, while the assignments of their major IR absorption bands are given in tables 2.3.3.3–2a and 2.3.3.3–2b.

Three products were chosen as being representative of all the products obtained in these photodediazoniation studies, viz. those obtained from the photolysis of IIb in TMU, IIb in MPY and LXVIb in TMU solution.

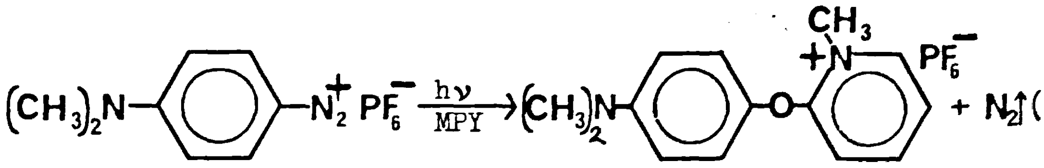
The product isolated from the photolysis of IIb in TMU was assigned the structure 2-(p-N,N-dimethylaminophenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (LXXIIb). Fig. 2.3.3.3–1 shows the ^{1}H NMR spectrum of this product which is consistent with the structure LXXIIb, and whose assignment of absorptions is given in table 2.3.3.3–1a. The ^{1}H NMR spectrum of LXXIIb has a singlet absorption at δ = 3.02 ppm, assigned as



IIb LXXIIb + $N_2\uparrow$ (86)

the six hydrogens of the aromatic dimethylamino substituent, a large singlet at δ = 3.28 ppm, assigned as the twelve equivalent hydrogens of the two amidinium dimethylamino groups, and two pairs of doublets, centred at δ = 6.95 ppm (J = 9.5 Hz) and δ = 7.28 ppm (J = 9.5 Hz) characteristic of para-substituted benzenes. The position of the amidinium dimethylamino hydrogens at 3.28 ppm is typical of those encountered for the amidinium carbonylic adducts in ch. 2.3.2.2, being in the range 3.05 — 3.32 ppm. The most important features in the IR spectrum of LXXIIb (table 2.3.3.3-2a) are the strong absorption bands at 1677 cm^{-1} and 843 cm^{-1} corresponding to C $=$ N and P-F stretching vibrations respectively, in accord with an amidinium hexafluorophosphate structure. The elemental analysis of LXXIIb (table 2.3.3.2-1a) is also fully consistent with its molecular formula.

The product isolated from the photolysis of IIb in MPY was 2-(p-N,N-dimethylaminophenoxy)-1-methylpyridinium hexafluorophosphate (LXXIIIb). Fig. 2.3.3.3-2 shows the ^{1}H NMR spectrum of this product,



(87)

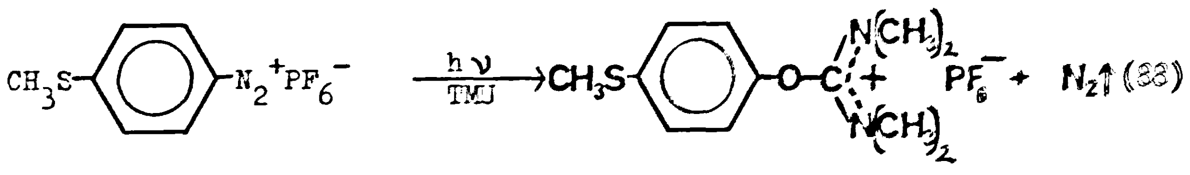
IIb LXIIIb

and the assignment of the absorptions are given in table 2.3.3.3-1b. The singlet absorption at δ = 3.03 ppm arises from the six hydrogens of the aryl ring's dimethylamino substituent, and a singlet at δ = 4.23 ppm from the three hydrogens of the pyridinium N-methyl substituent. The aromatic region of fig. 2.3.3.3-2 appears to be quite complex but is fully consistent with that already observed for thermalitically produced pyridinium carbonylic adducts. Two pairs of doublets centred at δ = 6.98 and 7.31 ppm (J = 10 Hz), being characteristic of para-substituted benzenes, were assigned to be the aryl ring aromatic hydrogens. The numbering system shown in fig. 2.3.2.2-1 was also used here and in other assignments of pyridinium ring hydrogens (table 2.3.3.3-1b).

As in the interpretation of LVIIc H(5) in fig. 2.3.3.3-2 appears similarly as a triplet at $\delta = 7.63$ ppm ($J = 7.0$ Hz), while the multiplet at $\delta = 8.5$ ppm is proposed to be composed of H(4) appearing as a triplet at 8.45 ppm ($J = 7.0$ Hz) and H(6) as a doublet at 8.54 ppm ($J = 7.5$ Hz). The H(3) doublet is predicted to be obscured by the much larger aryl hydrogen absorptions, and the integrated spectrum supports this prediction.

The most important features in the IR spectrum of LXXIIIb (table 2.3.3.3-2a) are again the absorption band at 1642 cm^{-1}, assigned as the C = N str., and the strongest band at 840 cm^{-1} (P-F str) indicative of the hexafluorophosphate anion. The absorption band at 1642 cm^{-1} accords with the observation of a similar band in the region 1642—33 cm^{-1} for all other pyridinium type carbonylic adducts.

The product isolated from the photolysis of LXVIb in TMU was 2-(4'-methylmercaptophenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (LXXIVb).



LXVIb LXXIVb

Fig. 2.3.3.3-3 shows the ^1H NMR spectrum of this product and the analysis of the spectrum is given in table 2.3.3.3-1c. The singlet absorption at $\delta = 2.55$ ppm relates to the three hydrogens of the methylmercapto substituent, the large singlet at $\delta = 3.12$ ppm to the twelve equivalent hydrogens of the two amidinium dimethylamino groups, and the two pairs of doublets, centred at $\delta = 7.25$ and 7.60 ppm ($J = 9.5$ Hz) characteristic of para-substituted benzenes. The position of the amidinium dimethylamino hydrogens at 3.12 ppm is again in the range 3.05 — 3.32 ppm encountered for other amidinium type carbonylic adducts.

The IR spectrum of LXXIVb (table 2.3.3.3-2b) shows the C$=$N and P-F stretching vibrations at 1673 cm^{-1} and 842cm^{-1} respectively.

Fig. 2.3.3.3-1 60 MHz ^1H NMR spectrum of LXXIIb, assigned the structure 2(p-N',N'-dimethylaminophenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate.

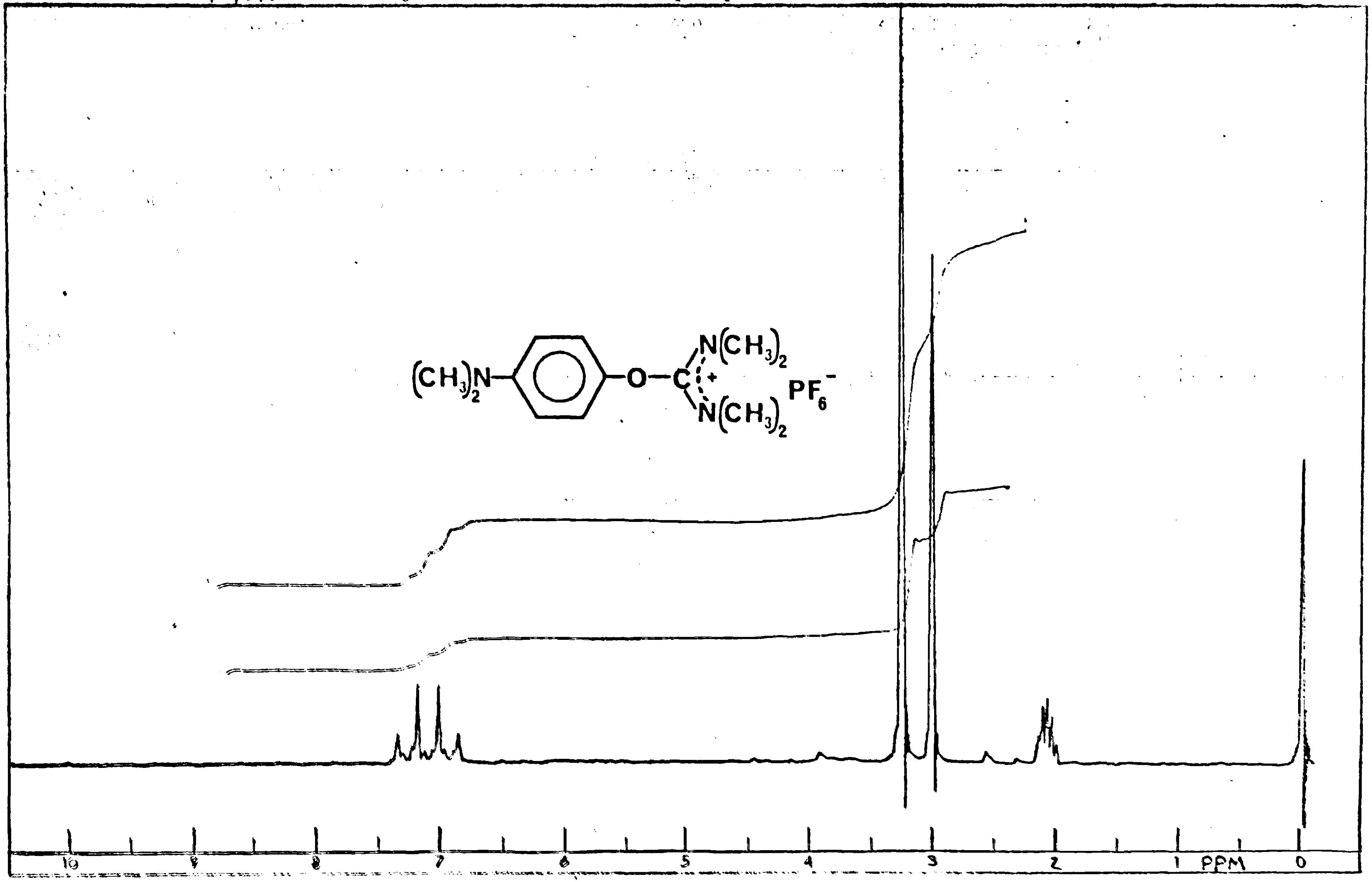


Fig. 2.3.3.3-2 60 MHz ^{1}H NMR spectrum of LXXIIIb, assigned the structure 2-(p-N',N'-dimethylaminophenoxy)-1-methylpyridinium hexafluorophosphate.

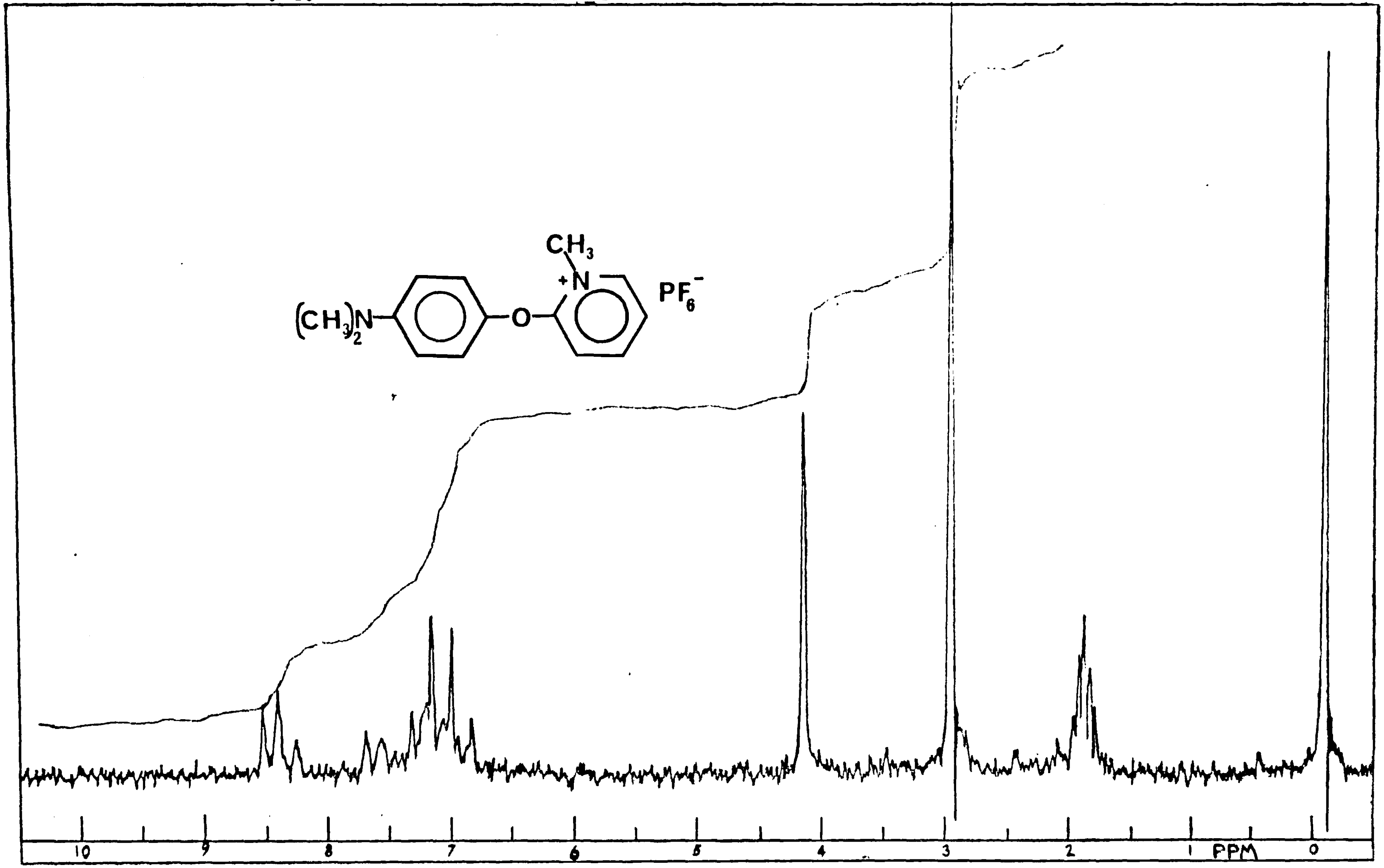


Fig. 2.3.3.3-3 60 MHz ^{1}H NMR spectrum of LXXIVb, assigned the structure 2-(p-methylmercaptophenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate.

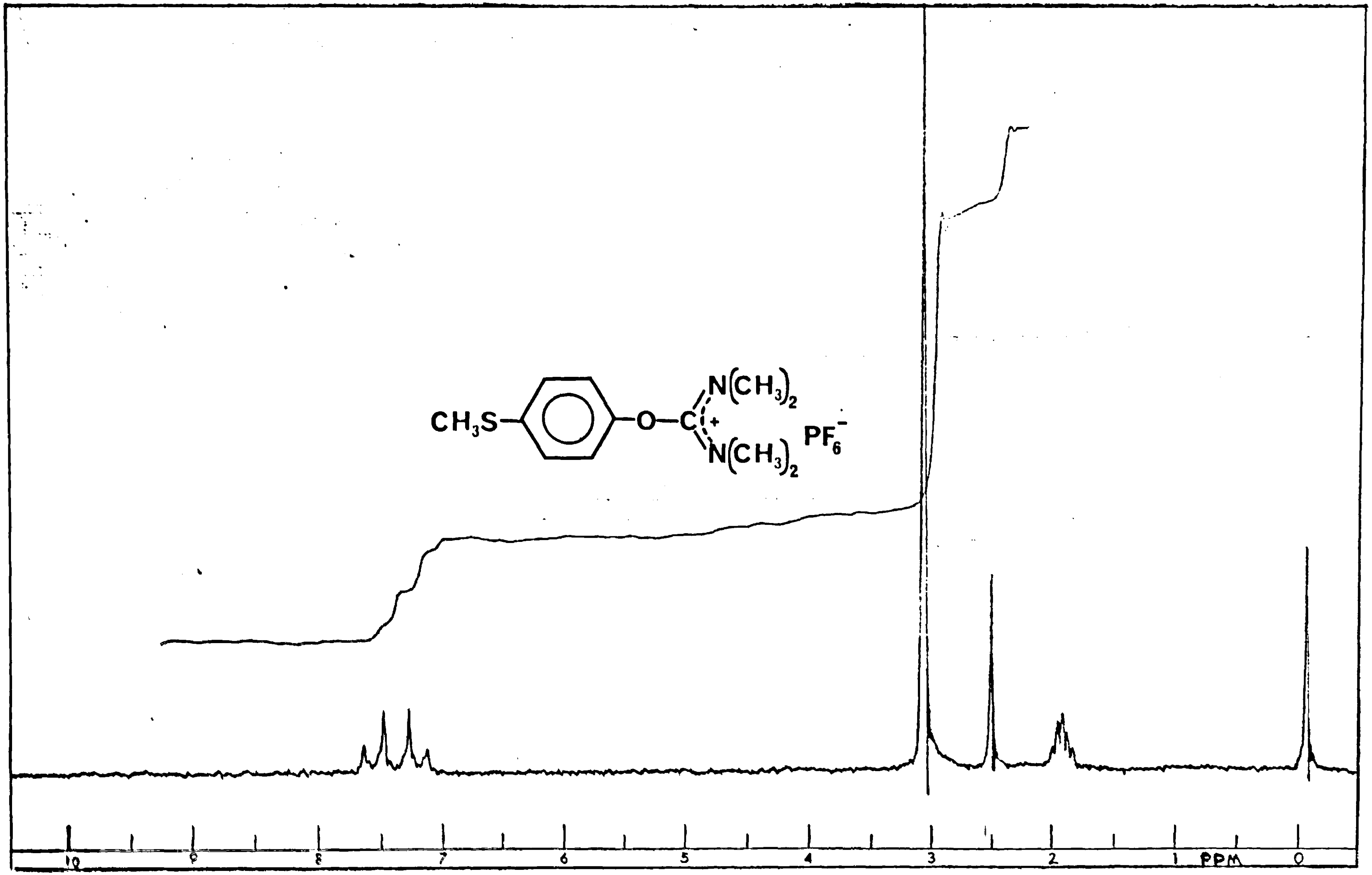


Table 2.3.3.3-1a ^{1}H NMR absorptions of carbonylic adducts[+] isolated from the photochemical dediazoniation of p-N,N-dimethylaminobenzenediazonium salts (II) in 1,1,3,3-tetramethylurea (TMU) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LXXIIb	$(CD_3)_2CO$	s	3.02	$-N(CH_3)_2$ (4')		3
		s	3.28	$-N(CH_3)_2$(1,3)		6
		d	6.95	H (3',5')	J 2',3' = J 6', 5' = 9.5	1
		d	7.28	H (2',6')		1
LXXIIc	CD_3CN	s	3.00	$-N(CH_3)_2$ (4')		3
		s	3.12	$-N(CH_3)_2$ (1,3)		6
		d	6.93	H (3', 5')	J 2',3' = J 6',5' = 10.0	1
		d	7.18	H (2', 6')		1
LXXIIe	CF_3CO_2D	s	3.36	$-N(CH_3)_2$ (1,3)		6
		s	3.58	$-N(CH_3)_2$ (4')		3
		d	7.65	H (3',5')	J 2',3' = J 6',5' = 10.0	1
		d	8.18	H (2',6')		1

[+] Table 2.3.3.2-1a shows the proposed structure of these carbonylic adducts.

Table 2.3.3.3-1b ^{1}H NMR absorptions of carbonylic adducts$^+$ isolated from the photochemical dediazoniation of p-N,N-dimethylaminobenzenediazonium salts (II) in 1-methyl-2-pyridone(MPY) and their assignments.

Compound	Solvent		Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LXXIIIb	CD_3CN		s	3.03	$-N(CH_3)_2$ (4')		6
			s	4.23	$-NCH_3$ (1)		3
		mlt	d	6.98	H (3',5')	J 2',3' = J 6',5' = 10.0	5
			d	7.31	H (2',6')		
			d	obscured	H (3)		
			t	7.63	H (5)	J 4,5 ≈ J 5,6 = 7.0	1
		mlt	t	8.45	H (4)	J 3,4 ≈ J 4,5 = 7.0	2
			d	8.54	H (6)	J 5,6 = 7.5	
LXXIIIc	CD_3CN		s	3.07	$-N(CH_3)_2$ (4')		6
			s	4.26	$-NCH_3$ (1)		3
		mlt	d	7.03	H (3',5')	J 2',3' = J 6',5' = 10.0	5
			d	7.37	H (2',6')		
			d	obscured	H (3)		
			t	7.70	H (5)	J 4,5 ≈ J 5,6 = 7.0	1
		mlt	t	8.51	H (4)	J 3,4 ≈ J 4,5 = 7.0	2
			d	8.60	H (6)	J 5,6 = 7.5	
LXXIIIe	CF_3CO_2D		s	3.60	$-N(CH_3)_2$ (4')		6
			s	4.61	$-NCH_3$(1)		3
			d	7.25	H (3)	J 3,4 = 8.0	1
		mlt	d	7.66	H (3',5')	J 2',3' = J 6',5' = 10.0	3
			t	7.84	H (5)	J 4,5 ≈ J 5,6 = 7.0	
			d	8.20	H (2',6')	J 2',3' = J 6',5' = 10.0	2
		mlt	t	8.66	H (4)	J 3,4 ≈ J 4,5 = 8.0	2
			d	8.80	H (6)	J 5,6 = 7.0	

$^+$ Table 2.3.3.2-1a shows the proposed structure of these carbonylic adducts.

Table 2.3.3.3-1c ^{1}H NMR absorptions of carbonylic adducts$^+$ isolated from the photochemical dediazoniation of p-methylmercapto-, o-methylmercapto-, and 2,5-dimethoxybenzenediazonium hexafluorophosphate in 1,1,3,3-tetramethylurea (TMU) and their assignments.

Compound	Solvent	Signal	Chemical shift (δ) in ppm	Assignment	Coupling constant in Hz	Integration
LXXIVb	CD_3CN	s	2.55	$-SCH_3$ (4')		3
		s	3.12	$-N(CH_3)_2$ (1,3)		12
		d	7.25	H (3',5')	J 2',3' = J 6',5' = 9.5	2
		d	7.60	H (2',6')		2
LXXVb	CD_3CN	s	2.56	$-SCH_3$ (2')		3
		s	3.10	$-N(CH_3)_2$ (1,3)		12
		mlt	7.0 - 7.7	H (3',4',5',6')		4
LXXVIb	CD_3CN	s	3.09	$-N(CH_3)_2$(1,3)		12
		s	3.83	$-OCH_3$ (5')		3
		s	3.90	$-OCH_3$ (2')		3
		mlt	6.8 - 7.4	H (3',4',6')		3

$^+$ Table 2.3.3.2-1b shows the proposed structures of these carbonylic adducts.

Table 2.3.3.3-2a The assignments of the major IR absorption bands (cm^{-1}) of carbonylic adducts[+] isolated from the photochemical dediazoniations of p-N,N-dimethylaminobenzenediazonium salts (II) in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions.

Compound	C-H str (Arom)	CH_3 (C-H) str	C=N str	Aromatic ring modes	P-F str	γC-H Aromatic ring modes	Sb-F str
LXXIIb	3050 w-mlt	2960 w-mlt	1677 s	1615 w 1516 s	843 vs	822 m	
LXXIIc	3050 w-mlt	2950 w-mlt	1670 s	1608 w 1510 s		827 m	665 s 635 s
LXXIIe	3030 w-mlt	2920 w-mlt	1665 s	1608 w 1510 s		825 m	
LXXIIIb	3110 w-mlt	2890 w-mlt	1642 m	1612 m 1590 m 1503 s	840 vs	813 m	
LXXIIIc	3110 w-mlt	2890 w-mlt	1642 m	1611 m 1590 m 1505 s		814 m	658 s 637 m
LXXIIIe	3075 m-mlt	2930 w-mlt	1633 m	1603 w 1570 m 1500 s		810 w	

[+] Table 2.3.3.2-1a shows the proposed structures of these carbonylic adducts.

Table 2.3.3.3-2b The assignments of the major IR absorption bands (cm^{-1}) of carbonylic adducts^{+} isolated from the photochemical dediazoniation of p-methylmercapto-, o-methylmercapto-, and 2,5-dimethoxybenzenediazonium hexafluorophosphate in 1,1,3,3-tetramethylurea (TMU) solution.

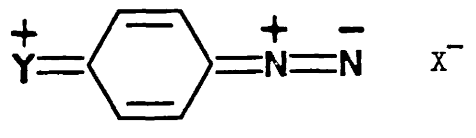
Compound	C-H str (Arom)	CH_3(C-H) str	C = N str	Aromatic ring modes	P-F str
LXXIVb	3075 w-mlt	2940 w-mlt	1673 s	1526 s 1490 s 1470 m	842 vs
LXXVb	3100 w-mlt	2950 w-mlt	1675 s	1595 w 1475 s 1450 m	840 vs
LXXVIb	3100 w-mlt	2940 w-mlt	1675 s	1596 w 1476 m 1460 m	840 vs

[+] Table 2.3.3.2-1b shows the proposed structures of these carbonylic adducts.

2.3.4 Mechanistic interpretation

Rutherford[67] after investigating the spontaneous thermal dediazoniation of aryl diazonium hexafluorophosphates in TMU solution, favoured a heterolytic mechanism, via aryl cations, for the formation of amidinium carbonylic adducts. In accord with the work of Rutherford, a heterolytic mechanism (scheme 2.3.4-1) is proposed for the formation of all the carbonylic adducts isolated from both thermal and photochemical dediazoniations in TMU, DMI, MPY, and tropone solutions. Scheme 2.3.4-1 shows the initial formation of an aryl cation by either a thermal, eqn. (89), or a photochemical path, eqn. (90), followed by the subsequent reaction of the aryl cation with the carbonylic solvents, eqns. (91) - (94), to form the respective carbonylic adducts.

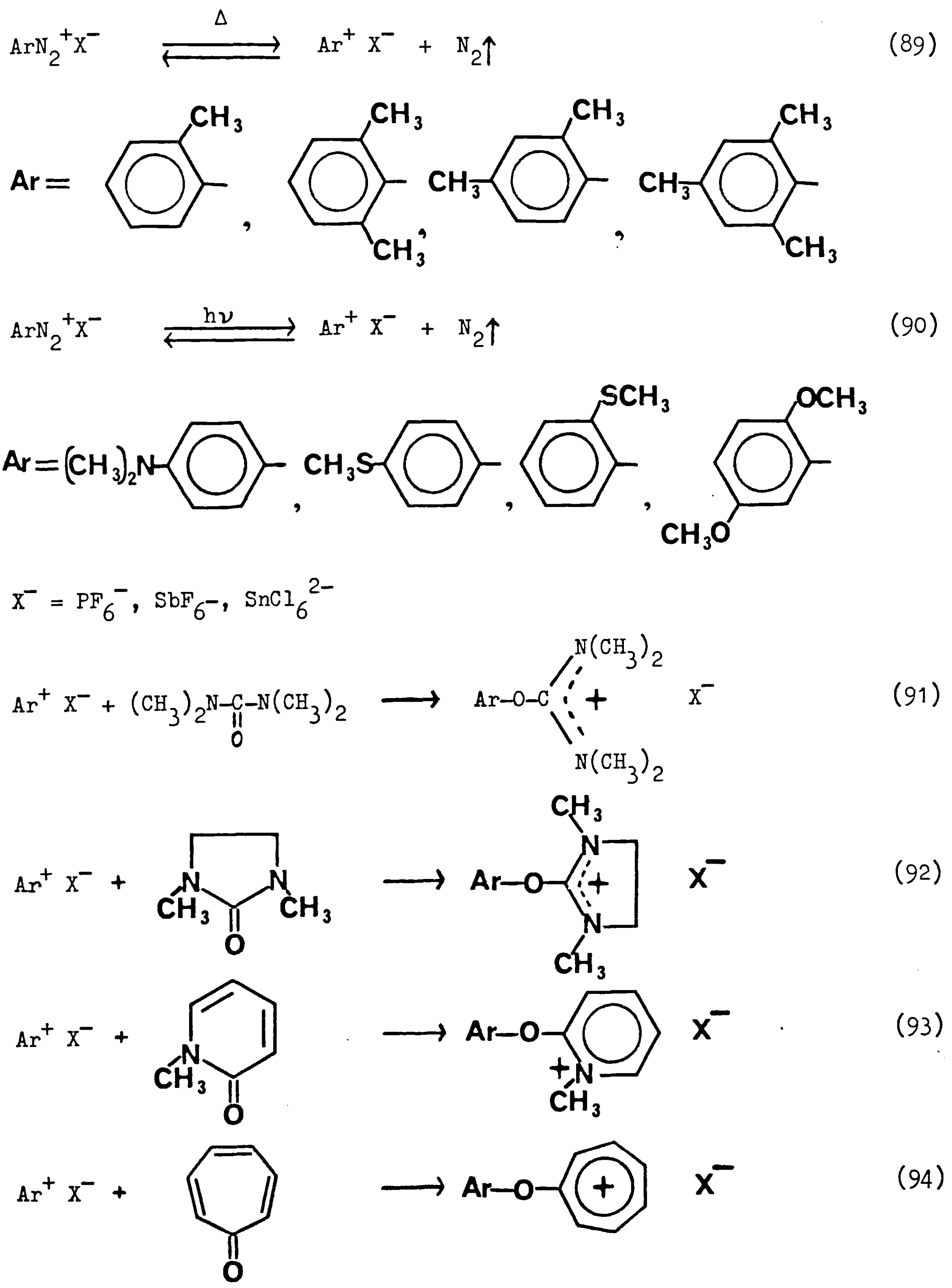
The photosensitive diazonium salts with powerfully electron donating substituents (4-dimethylamino, 4-methylmercapto, 2-methylmercapto, and 2,5-dimethoxy) were all of sufficient thermal stability to prevent spontaneous thermal dediazoniations. This is presumably due to the contribution of resonance structures such as LXXVII to the ground state of the diazonium ion, as discussed in ch. 1.2, which increases the C-Nα bond order. The photolysis of these photosensitive diazonium salts in TMU, and MPY solutions is in agreement with that observed by Becker[160] (ch. 1.7.2) for the photolysis of p-N,N-dimethylaminobenzenediazonium tetrafluoroborate (IId) in alcoholic solutions, and with the present



(b) $X^- = PF_6^-$
(c) SbF_6^-
(e) $\frac{1}{2}SnCl_6^{2-}$

LXXVII

Scheme 2.3.4-1 Heterolytic mechanism proposed for the formation of carbonylic adducts in TMU, DMI, MPY and tropone solutions



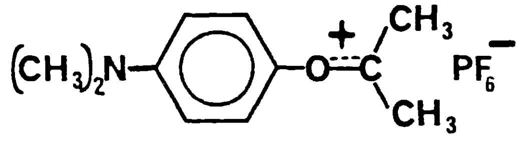
$$ArN_2^+X^- \overset{\Delta}{\rightleftarrows} Ar^+\ X^- + N_2\uparrow \qquad (89)$$

$$ArN_2^+X^- \overset{h\nu}{\rightleftarrows} Ar^+\ X^- + N_2\uparrow \qquad (90)$$

$X^- = PF_6^-,\ SbF_6^-,\ SnCl_6^{2-}$

$$Ar^+\ X^- + (CH_3)_2N\text{-}\underset{\substack{\|\\ O}}{C}\text{-}N(CH_3)_2 \longrightarrow Ar\text{-}O\text{-}C^+(N(CH_3)_2)_2\ X^- \qquad (91)$$

photolytic studies of IIb in the solid state (ch. 2.1), acetone (ch 2.2.2), acetonitrile (ch. 2.2.3), and TFE (ch. 2.2.4) solutions. Following the work of Becker[160–162] electron donation from the carbonylic solvents to the diazonium ions after the initial absorption of light, is unlikely to be a major reaction path for these photosensitive diazonium salts. Also, formation of an amidinium carbonylic adduct was judged by ^{1}H NMR spectroscopy of the reacting mixture to constitute at least 90% of the product distribution from the photolysis of IIb in TMU and d_4-MPY solutions, and 4-methylmercaptobenzenediazonium hexafluorophosphate (LXVIb) in TMU solution. The isolation of carbonylic adducts from the photolysis of IIb in TMU and MPY solutions, supports the previous proposal that a carbonylic adduct intermediate (XLI) is formed in the photolysis of IIb in acetone solution (scheme 2.2.2.2-1). The ease of hydrolysis of the tropylium carbonylic adduct (fig. 2.3.2.2-6) also indicates that XLI should be highly susceptible to hydrolysis.



XLI

The failure to isolate carbonylic adducts from the photolysis of 2-methoxy-(LXXIb), or 2,4-dimethoxybenzenediazonium hexafluorophosphate (LXIXb) in TMU solutions, is attributed to insufficient electron donation from the substituents in the photo-excited states of these diazonium ions to prevent transfer of an electron from the solvent (TMU), and it is therefore anticipated that large amounts of the respective arenes were formed in these photolysis reactions.

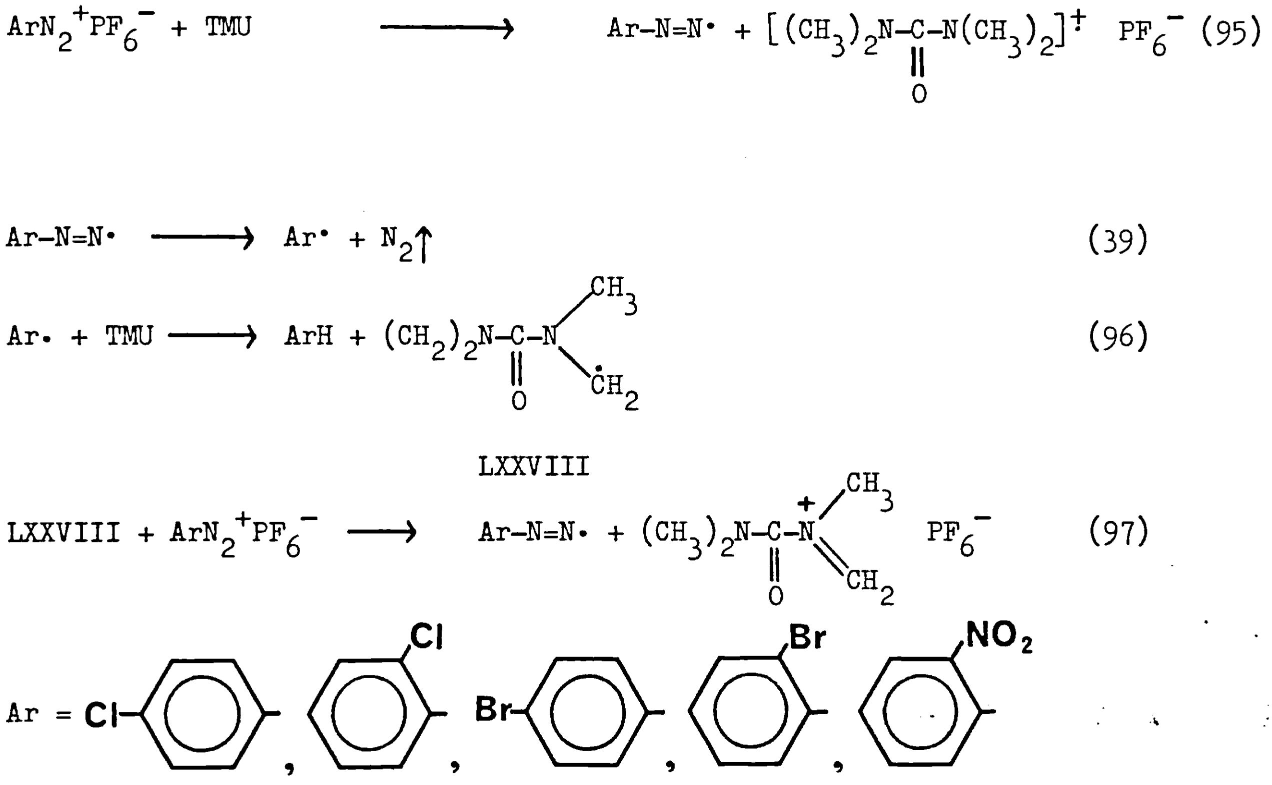
The finding that 2,5-dimethoxybenzenediazonium hexafluorophosphate (LXVIIIb), unlike LXIXb, has an electronic absorption band in the visible region of the spectrum and yielded an isolatable carbonylic adduct (LXXVIb) from its photolysis in TMU solution, reflects the peculiar and complex relationship for alkoxy substituted aryl diazonium ions between position of substitution, the energies of their excited states, and the stability of triplet aryl cations derived from them as Kemp[174-177] observed by ESR spectroscopy (ch. 1.7.4). Although Kemp did not observe a triplet spectrum on irradiation of LXVIIIb, he found that 4-alkylmercapto and 4-alkoxy substituted aryl diazonium salts required additional alkoxy substituents in both the 2 and 5-positions to stabilize their photochemically generated triplet state aryl cations with respect to their singlet aryl cations.

The heterolytic thermal dediazoniations indicated in scheme 2.3.4-1, occur with diazonium salts which have no contribution to their ground states from resonance structures like LXXVII. The inductive effect of the methyl substituents is however expected to stabilize both the ground state of the diazonium ion and the ground state singlet aryl cations. A discussion of whether ortho methyl substituents destabilize these diazonium salts by steric interaction with the diazo group, or the complex anion is given later (ch. 2.5.2) in the light of molecular orbital calculations.

Rutherford[67] isolated high yields of arenes from the spontaneous thermal dediazoniation of aryl diazonium salts having electron withdrawing substituents. He proposed a mechanism for this involving the formation of an aryl cation, followed by hydride transfer from TMU to the aryl cation in analogy with De Tar's[87] mechanism for arene formation in alcoholic solutions. However, as discussed in ch. 1.6.1 such a mechanism lost favour after the much more recent work of Bunnett.[122,123]

A mechanism is therefore proposed for the homolytic thermal dediazoniation of these aryldiazonium salts in TMU solution (scheme 2.3.4-2), in accord with the work of Bunnett.[122,123]

Scheme 2.3.4-2 Homolytic chain reaction proposed for arene formation from thermal dediazoniations in TMU solution



$$ArN_2^+PF_6^- + TMU \longrightarrow Ar\text{-}N{=}N\cdot + [(CH_3)_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}N(CH_3)_2]^{\ddagger}\ PF_6^- \quad (95)$$

$$Ar\text{-}N{=}N\cdot \longrightarrow Ar^\cdot + N_2\uparrow \quad (39)$$

$$Ar\cdot + TMU \longrightarrow ArH + (CH_2)_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}N\begin{matrix} CH_3 \\ \dot{C}H_2 \end{matrix} \quad (96)$$

LXXVIII

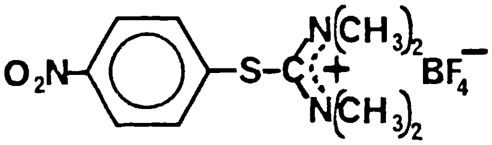
$$LXXVIII + ArN_2^+PF_6^- \longrightarrow Ar\text{-}N{=}N\cdot + (CH_3)_2N\text{-}\underset{\underset{O}{\|}}{C}\text{-}\overset{+}{N}\begin{matrix} CH_3 \\ CH_2 \end{matrix}\ PF_6^- \quad (97)$$

Ar =

Scheme 2.3.4-2 shows that the homolytic chain reaction is initiated by electron transfer from TMU to the diazonium ion, forming an arylazo radical, eqn. (95). The propagation steps of the chain reaction are the loss of nitrogen from the arylazo radical to form an aryl radical, eqn. (39), the abstraction of hydrogen by the aryl radical from TMU forming the arene and the radical LXXVIII, eqn. (96), and the regeneration of the arylazo radical by the reaction of LXXVIII with the diazonium ion, eqn. (97).

A mixture of arene and carbonylic adduct products, claimed by Rutherford [67] to be obtained from the thermolysis of 4-methylbenzenediazonium and benzenediazonium hexafluorophosphate in TMU solutions, must indicate competition between schemes 2.3.4-1 and 2.3.4-2. Such competition between these thermal heterolytic, and homolytic paths is consistent with the behaviour of these diazonium salts in alcoholic solutions.[122,123]

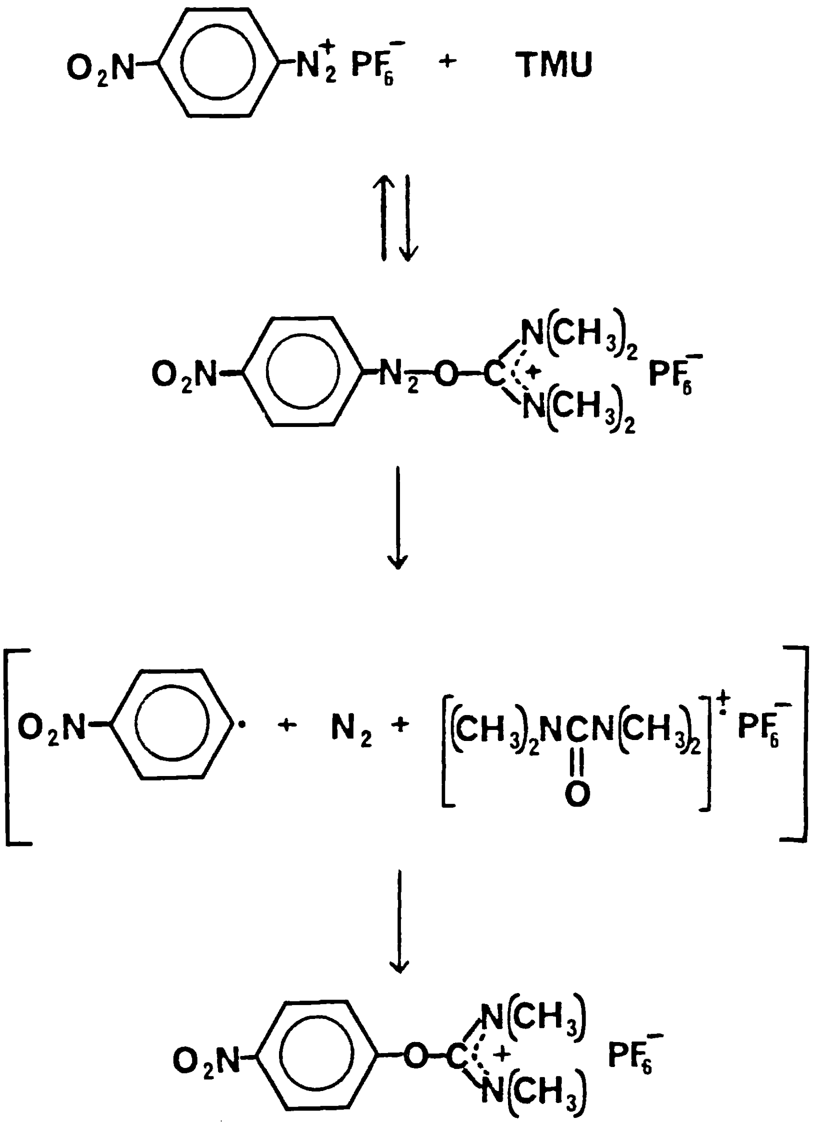
A curious observation made by Rutherford[67] was that 4-nitrobenzenediazonium hexafluorophosphate (LXXIXb) yielded both arene and carbonylic adduct products from its thermal dediazoniation in TMU solution. It was however pointed out that Meerwein[187] obtained an almost quantitative yield (90%) of the adduct LXXXd from the thermal dediazoniation of 4-nitrobenzenediazonium tetrafluoroborate (LXXIXd) in an acetonitrile solution of 1,1,3,3-tetramethylthiourea (TMTU).



LXXXd

It can hardly be expected that a heterolytic mechanism such as scheme 2.3.4-1 could be responsible for the formation of an almost quantitative yield of LXXXd from the thermal dediazoniation of LXXIXd in an acetonitrile/TMTU solution since, as discussed in ch. 2.2.3, a high yield of arylamide would also be expected assuming the presence of adventitious water. This behaviour seems however to be more consistent with a mechanism involving charge-transfer complex formation, as proposed by Zollinger[140] (ch. 1.6.2.2) for the thermal dediazoniation of LXXIXd in dimethylsulphoxide solution. It is therefore proposed that as in dimethylsulphoxide solution LXXIXb forms a charge-transfer complex with TMU, primarily due to its powerfully electron withdrawing nitro substituent, from which the carbonylic adduct is formed, and that it is this process (scheme 2.3.4-3) that is in competition with scheme 2.3.4-2 and not the heterolytic scheme 2.3.4-1.

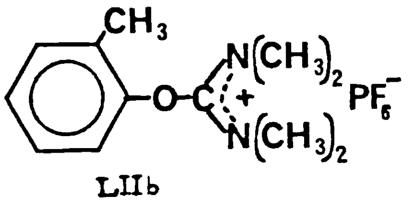
Scheme 2.3.4-3 Homolytic mechanism proposed for the thermal dediazoniation of 4-nitrobenzenediazonium hexafluorophosphate (LXXIXb) in TMU solution



2.4 THE REACTION OF 2-(2',6'-DIMETHYLPHENOXY)-1,1,3,3-TETRAMETHYLAMIDINIUM HEXAFLUOROPHOSPHATE WITH AQUEOUS AMMONIA

2.4.1 Introduction

The relevance to industrial diazocopying of aryl diazonium salt photodediazoniations in carbonylic solvents, was initially demonstrated by the high yield of phenolic product isolated from the photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb) in acetone solutions (ch. 2.2.2). Scheme 2.2.2.2-1 showed a mechanism for the formation of the phenolic product via a carbonylic adduct intermediate (XLI), but for the existence of which no direct evidence was presented. The thermal and photodediazoniations in TMU, DMI, MPY, and tropone solutions (ch. 2.3.2) established the existence of a wide range of carbonylic adducts which were able to be isolated from these solutions. The ease of hydrolysis of the carbonylic adduct (2',6'-dimethylphenoxy) tropylium hexafluorophosphate (ch. 2.3.2.2) was also consistent with the susceptibility to hydrolysis predicted for XLI in scheme 2.2.2.2-1. Rutherford[67] has already shown that the hydrolysis of the amidinium carbonylic adduct 2-(2'-methylphenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (LIIb) with aqueous sodium hydroxide yields 2-methylphenol. However, since the development of the dye image for diazotypes following exposure is usually carried out by ammonia vapour in commercial diazo processes, the reaction of a carbonylic adduct with aqueous ammonia was investigated. The amidinium type carbonylic adduct 2-(2',6'-dimethylphenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (LIVb) was used in this study.



LIIb

2.4.2 Determination of products

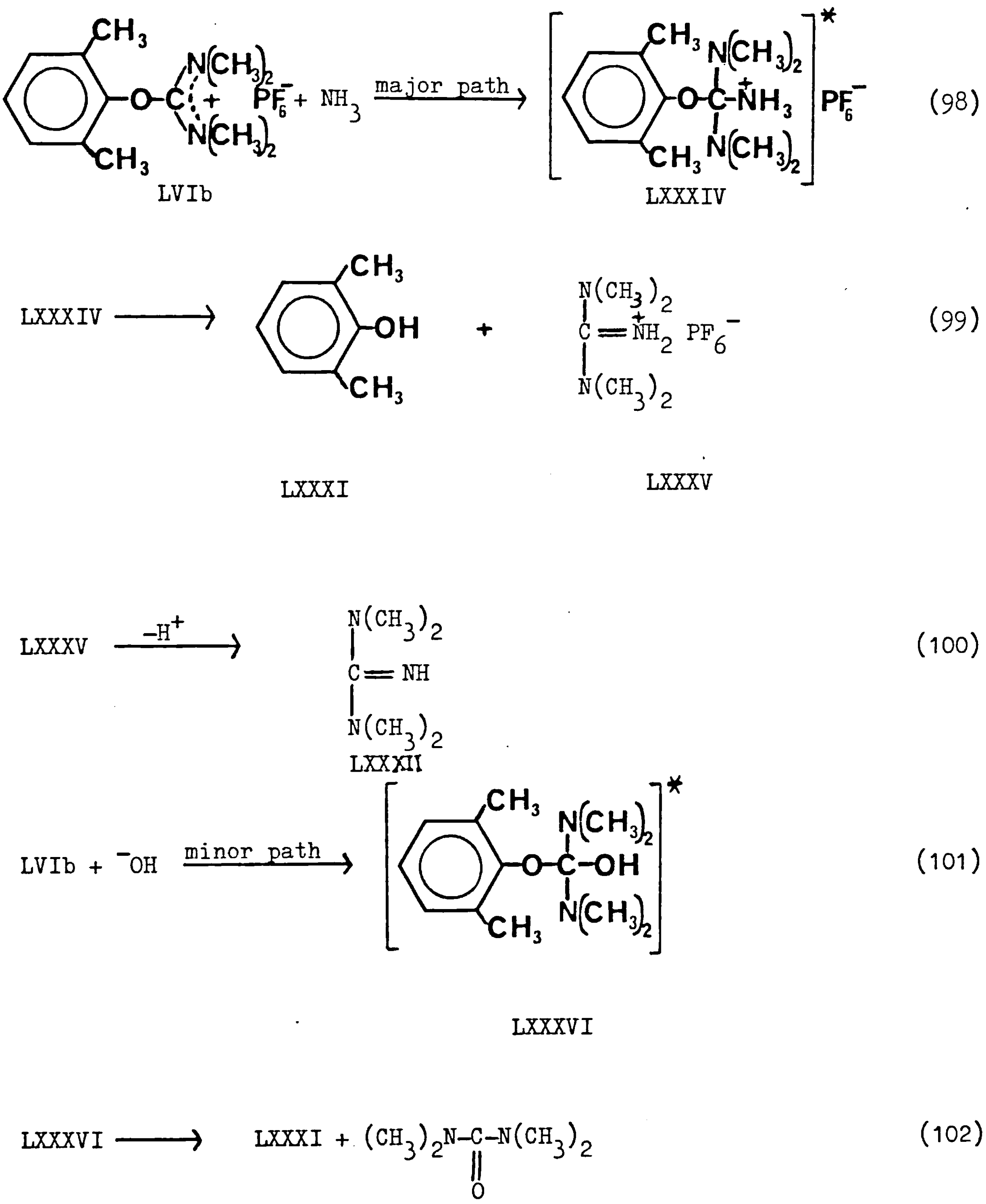
The ^{1}H NMR spectrum of LIVb was recorded in d_3-acetonitrile solution. Excess aqueous ammonia was added and the spectrum recorded periodically. After 2 hr the reaction was complete. On comparison of the ^{1}H NMR spectrum with that of an authentic sample of 2,6-dimethylphenol (LXXXI), this was judged to be the only aromatic reaction product. Two singlet absorptions at $\delta = 2.98$ ppm and 2.87 ppm were assigned to two non-aromatic reaction products LXXXII and LXXXIII respectively. Addition of a sample of TMU to the reaction mixture indicated that TMU, could be assigned to LXXXIII, but corresponded to only ~20% of the non-aromatic reaction products. After leaving the reaction mixture to stand for a further 2 hr, the conversion of the added TMU to the major non-aromatic product LXXXII was not observed. A fresh NMR sample of LIVb was prepared and the reaction with ammonia repeated. The peak at $\delta = 2.98$ ppm was again observed as the major reaction product LXXXII (~80%). A drop of 1,1,3,3-tetramethylguanidine was added to the fresh NMR sample and the absorption at $\delta = 2.98$ ppm was observed to have increased in intensity.

A sample of LIVb was reacted with aqueous ammonia in acetonitrile solution and the products LXXXII and LXXXIII were separately extracted from the mixture (ch. 4.7.1). The IR spectra of LXXXII and LXXXIII were identical with authentic samples of 1,1,3,3-tetramethylguanidine and TMU respectively.

2.4.3 Mechanistic interpretation

A mechanistic scheme for the reaction of LIVb with aqueous ammonia is proposed (scheme 2.4.3-1). This shows that the reaction of ammonia with LIVb via the tetrahedral intermediate LXXXIV, eqn. (98), and subsequent formation of LXXXII, eqns. (99) and (100), to be the major path. The minor path is shown to be the reaction of LVIb with

Scheme 2.4.3-1 Mechanism proposed for the reaction of LVIb with aqueous ammonia



the hydroxide ion, eqn. (101), leading to the formation of TMU, eqn. (102). Both reaction paths lead to the formation of 2,6-dimethylphenol (LXXXI).

2.5 AB INITIO QUANTUM MOLECULAR CALCULATIONS

2.5.1 Gaussian 70 calculations on the p-N,N-dimethylaminophenyl cation

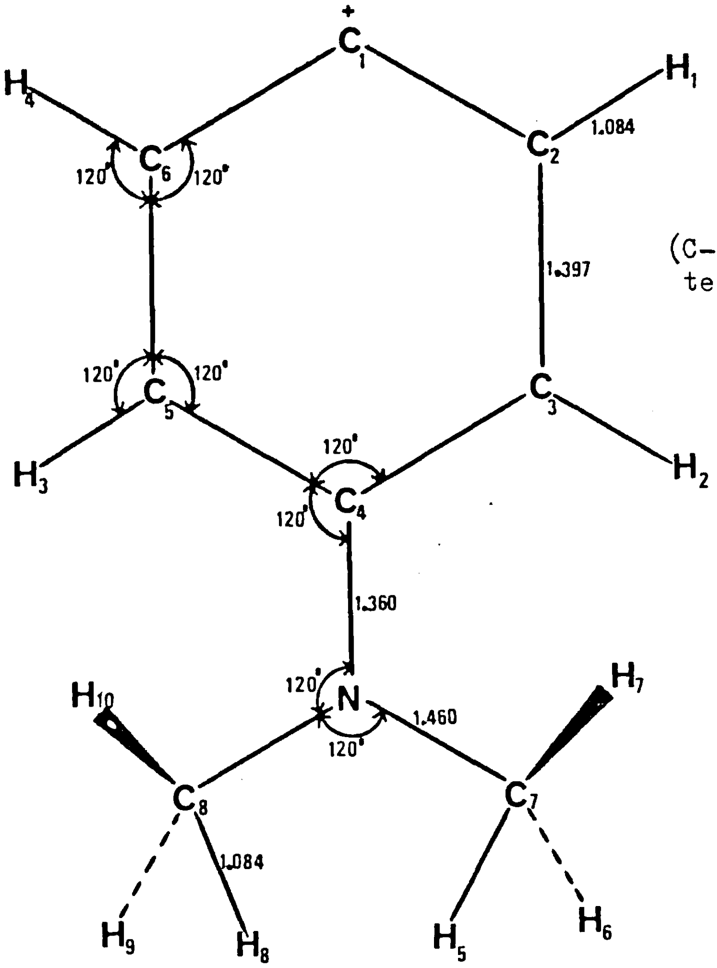
2.5.1.1 Introduction

Following the studies with IIb for which a heterolytic mechanism via the p-N,N-dimethylaminophenyl cation (DAPC) was proposed for its photolysis in the solid state (scheme 2.1.4-1), acetone (scheme 2.2.2.2-1), acetonitrile (scheme 2.2.3.3-1), TFE (scheme 2.2.4.3-1), TMU and MPY solutions (scheme 2.3.4-1), the question was posed as to the possible electronic structure of DAPC in the ground state.

Both Evleth[172] and Pople[136] (ch. 1.7.3) in performing calculations to determine the electronic structure of the p-aminophenylcation (APC), predicted the triplet state to be more stable than the singlet. These theoretical expectations were substantiated by the ESR spectroscopic experiments of Kemp[174-177] (ch. 1.7.4), in which he observed triplet ground state spectra for many aryl cations including DAPC and APC.[177]

Pople[136] performed his ab initio calculations of aryl cations using standard geometries (i.e. not optimized), and a Gaussian 70 computer package[188] with a minimal STO-3G basis set. Since this same Gaussian 70 (STO-3G) package was available this was used to perform both singlet (closed shell) and triplet (open shell) calculations of the DAPC. The standard geometry used for the DAPC is shown in fig. 2.5.1.1-1.

Fig. 2.5.1.1-1 Geometry used in the molecular orbital calculations of the p-N,N-dimethylaminophenyl cation, with distances in Å.



(C-7 and C-8 are regular tetrahedral centres)

DAPC (C_{2v})

2.5.1.2 Discussion

The difference between the singlet and triplet energies for DAPC together with Pople's[136] value for APC are given in table 2.5.1.2-1.

Table 2.5.1.2-1 Calculated singlet-triplet energy separations for DAPC and APC [E (singlet) -E (triplet)], kJ mol^{-1}

	calc.	corr[a]
DAPC	409	165
APC[136]	348	104

[a] Corrected for geometrical and theoretical errors[136] based on calculated vs. experimental values for CH_2: (ie -244 kJ mol^{-1})

The calculations clearly show that for DAPC, as with APC, the triplet is more favoured than the singlet. This is even true when the calculations are corrected for geometrical and theoretical errors.

It is well known that Hartree-Fock theory gives artificially low energies for triplet states.[189] Pople[136] showed this error to be compounded for the phenyl cation by the fact that the standard-geometry singlet is farther from its equilibrium geometry than is the triplet.

(i) The E (singlet) -E (triplet) separation for the standard-geometry phenyl cation (160 kJ mol^{-1})was reduced to 31 kJ mol^{-1} upon geometry optimization. Pople[136] took this energy difference (ie. -129 kJ mol^{-1}) as an estimate for the geometrical component of standard-geometry aryl cation singlet minus standard-geometry triplet.

(ii) The theoretical component of the total error (-115 kJ mol^{-1}) was taken to be the difference between the geometry optimized singlet-triplet separation energy for carbene, CH_2: (156 kJ mol^{-1})[190] and a reliable experimental estimate (41 kJ mol^{-1})[191]. Pople[136] therefore combined these values to arrive at a correction for geometrical and theoretical errors for standard-geometry aryl cation singlet-triplet energy separation of -244 kJ mol^{-1}.

Even though the corrected value of 165 kJ mol^{-1} for the singlet-triplet separation of DAPC is expected to be unreliable as a quantitative result, the qualitative result viz. that the triplet state is energetically more favoured than the singlet is believed to be reliable in view of the ESR experiments on DAPC by Kemp.[177]

A discussion of electronic effects based on calculated electron populations of aryl cation singlets or triplets is expected to be reliable, since these are less sensitive to geometrical changes than energies. The electron populations calculated for the singlet and triplet DAPC are given in fig. 2.5.1.2-1.

The atomic orbital electron populations of (C-1) in the singlet-DAPC show that the $SP^2\sigma$ orbital in the z direction is essentially vacant, since the electron population of 2Pz (0.16) is very small. The importance of inductive effects in the stabilization of the singlet-DAPC is seen from the low electron populations of the ring hydrogens, and in particular the very low value for the ortho hydrogens, (H-1) and (H-4) (0.85), is indicative of hyperconjugation. From ring hydrogen isotope experiments of Swain[73] (ch. 1.5.2.4) and the theoretical calculations on singlet-aryl cations by Swain[73] and others[136] (ch. 1.7.3), hyperconjugation has been proposed to be an important process for the delocalization of the positive charge in these cations. An inspection of the π-electron populations for the singlet-DAPC reveals a slight excess of π-electrons in the aryl ring (6.25), which coincides with a loss of π-electrons from (N-1) (1.71) of a similar magnitude. The π-electron population of (C-1) (1.36) is very high, and results from the major donation of electrons from the nitrogen to this electron deficient carbon. The loss of π-electrons from (N-1) seems to have been largely compensated by the inductive donation of electrons from the methyl groups (8.80). The various mechanisms of delocalization described above, leave a charge of + 0.24 on (C-1) of the singlet-DAPC.

In contrast to the singlet-DAPC, the delocalization of electrons in the triplet-DAPC is much more effective, leaving only a slight charge of +0.08 on (C-1). The electron population of 0.87 for the 2Pz orbital on (C-1) of the triplet-DAPC, shows that its sp^2 σ orbital in the z direction essentially contains an unpaired electron. Since this orbital is occupied then hyperconjugation of the ring hydrogens (H-1) and (H-4) would not be expected, and the relatively high (H-1) and (H-4) (0.89) electron populations are indeed consistent with a lack of hyperconjugation. An inspection of the π-electron populations for the triplet-DAPC reveals only a slight deficiency of π-electrons in the aryl ring (5.81), which is presumably due to a large π-donation from (N-1) (1.21). This implies that, in accord with the results of other calculations[136] π-donation is relatively more important for the stabilization of triplet-aryl cations than for singlets. The large loss of π-electrons from (N-1) is however compensated by a large inductive donation of electrons from the methyl groups (8.69), which demonstrates an even larger inductive effect than occurs in the singlet-DAPC.

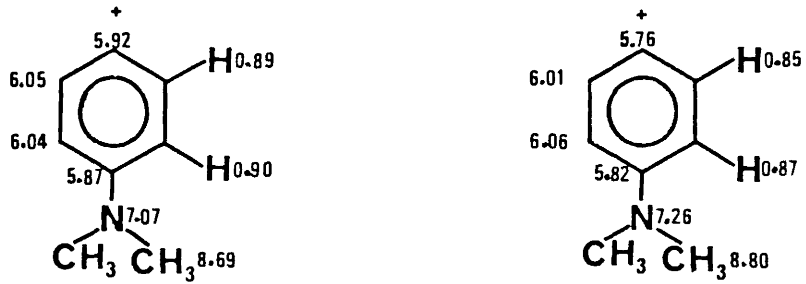
In consideration of the greater stability of the triplet-DAPC with respect to the singlet-DAPC, and the electronic structure calculated for the triplet-DAPC, the following suggestions are now proposed. The photodediazonation of IIb in the solid state (ch. 2.1) and in acetone (ch. 2.2.2), acetonitrile (ch. 2.2.3), 2,2,2-trifluoroethanol (ch. 2.2.4), 1,1,3,3-tetramethylurea and 1-methyl-2-pyridone (ch. 2.3.3) solutions is now proposed to proceed via the triplet-DAPC. The formation of the p-N,N-dimethylfluoroaniline phosphorus pentafluoride adduct (XXXIII) is now believed to occur within an ion-pair by a concerted reaction between the triplet-DAPC and the hexafluorophosphate anion (eqn. (58) suggested in ch. 2.1.4). This proposal is concluded from the extensive delocalization of the positive charge calculated for the triplet-DAPC, which implies that the hexafluorophosphate anion of the ion-pair will be positioned above the π-layer of the triplet-DAPC between (C-1) and (N-1).

Fig. 2.5.1.2-1 The calculated electron populations for the triplet and singlet p-N,N-dimethylaminophenyl cation

a) π-electron populations

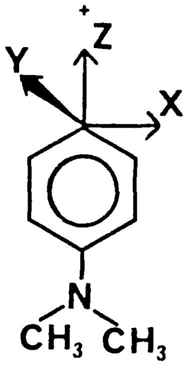
Triplet-DAPC Singlet-DAPC

b) Ring hydrogen, and the net carbon, nitrogen, and methyl group electron populations



Triplet-DAPC Singlet-DAPC

c) Atomic orbital electron populations for C-1



	Triplet	Singlet
1S	1.99	1.99
2S	1.20	1.22
2PX	0.92	1.03
2PY	0.93	1.36
2PZ	0.87	0.16

2.5.2 Gaussian 76 calculations on the Nα, Nβ rearrangement of the 2,6-dimethylbenzenediazonium ion

2.5.2.1 Introduction

In view of the thermal dediazoniation studies of aryl diazonium salts (ch. 2.3.2), it was decided to investigate whether ortho methyl substituents destabilize diazonium ions with respect to their aryl cations by steric interaction between the methyl and diazo groups. Fortunately Vincent and Radom[137] have investigated the Nα, Nβ rearrangement in the benzenediazonium ion (BDI) by performing Gaussian 70 (STO-3G) calculations on BDI, its symmetrically bridged intermediate (INT), the transition state (TS), and the singlet-phenyl cation (PC). It was therefore proposed to carry out a similar investigation on the 2,6-dimethylbenzenediazonium ion (DBDI), its symmetrically bridged intermediate (DINT), the transition state (DTS), and the singlet-2,6-dimethylphenyl cation (DPC).

Unfortunately of the above species, the Gaussian 70 calculations for the DINT and DTS did not converge to a minimum energy, and to overcome this all the calculations were repeated using the Gaussian 76 (STO-3G) computer package.[192] The Gaussian 76 calculations were shown to be compatible with Gaussian 70 calculations, by comparison of the DBDI results from both computer packages. All of the structures for which Gaussian 76 calculations were made are shown in fig. 2.5.2.1-1.
In an effort to investigate the interaction of the methyl hydrogens with the diazo group two conformations of the methyl substituents were employed, as shown in fig. 2.5.2.1-1, and the geometries used for all of these species is indicated in fig. 2.5.2.1-2.

The aryl ring geometries used in the calculations (fig. 2.5.2.1-2) were standard (ie not optimized) and, with the exception of the methyl substituents, was the same as that used by Vincent and Radom[137] for the

BDI system. The Nα, Nβ geometry used in the DBDI, DINT, and DTS calculations is also given in fig. 2.5.2.1-2 and corresponds to the optimized Nα, Nβ geometries obtained for the BDI system.

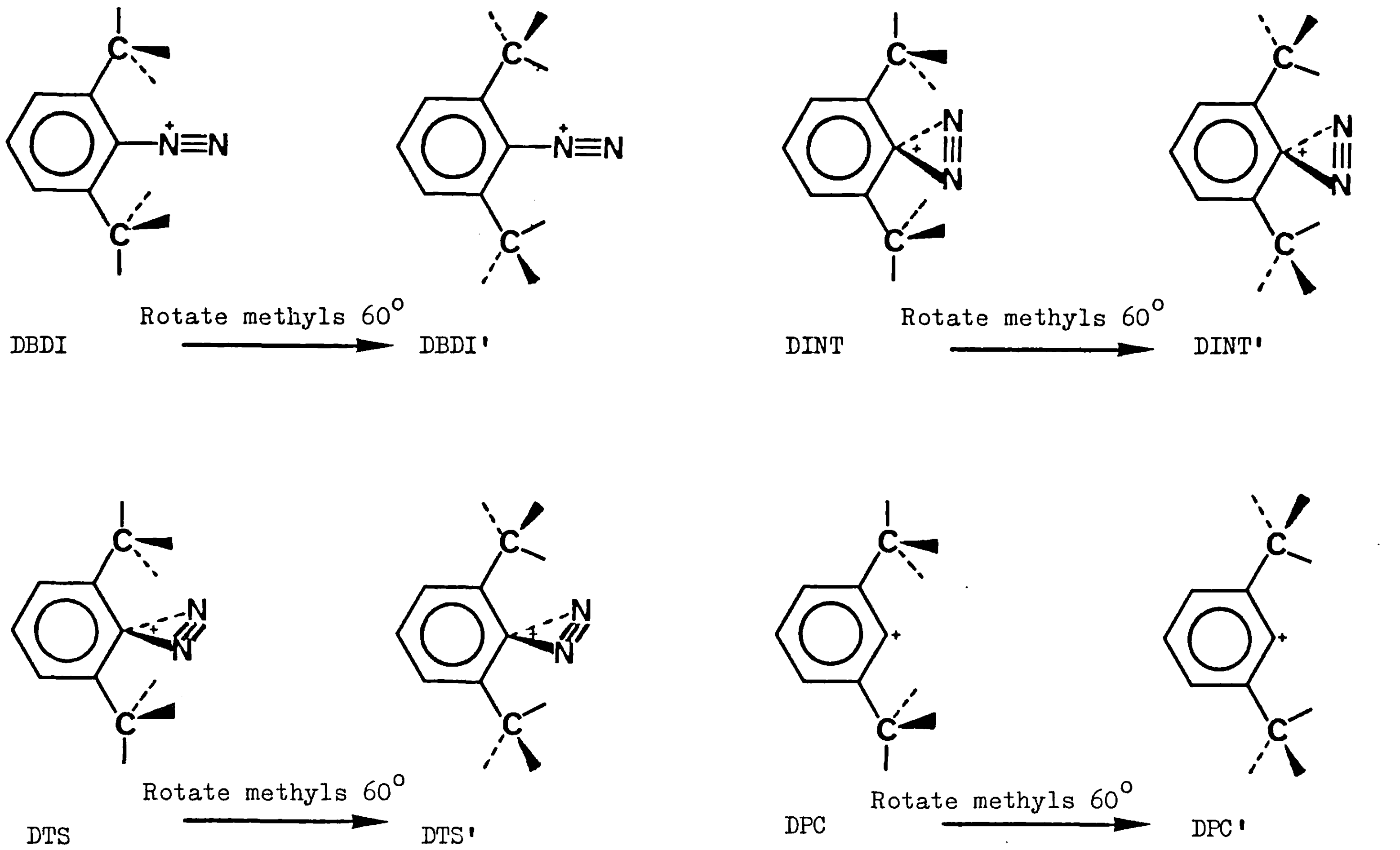
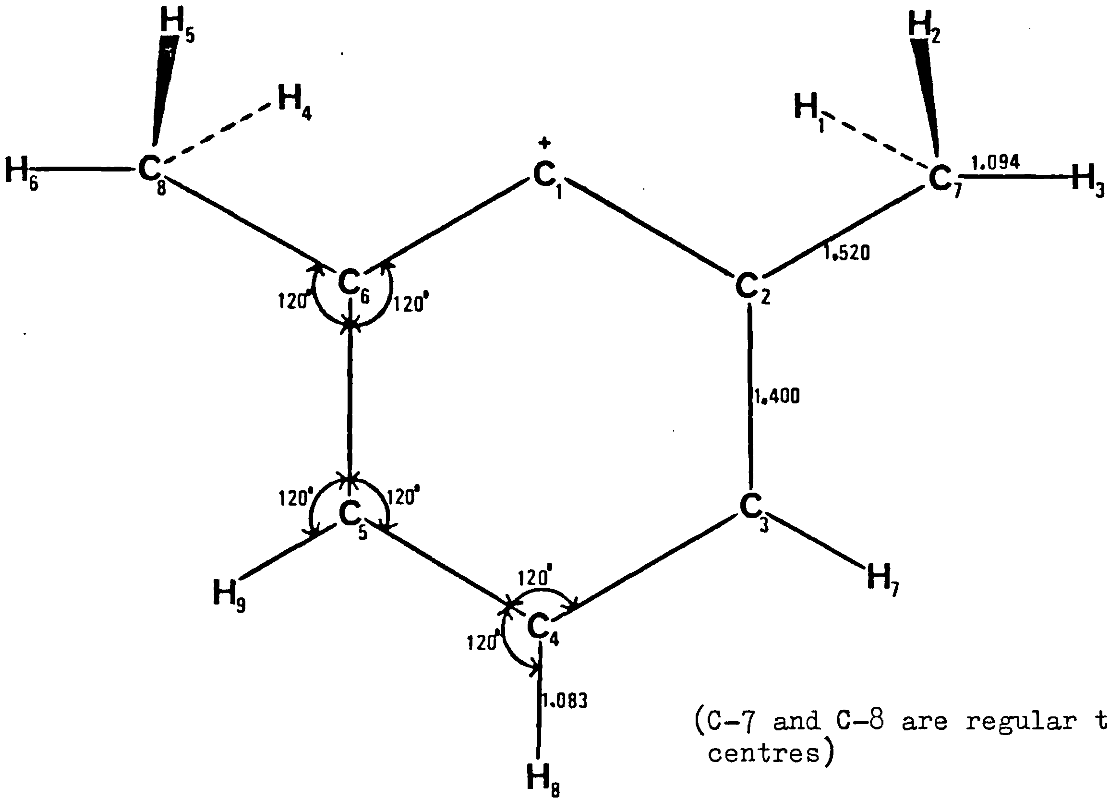


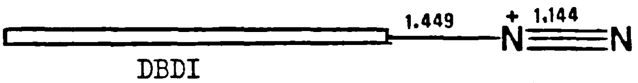
Fig. 2.5.2.1-1 The 2,6-dimethylbenzenediazonium ion series of structures for which Gaussian 76 calculations were performed.

Fig. 2.5.2.1-2 Geometry used in the molecular orbital calculations of the 2,6-dimethylbenzenediazonium ion series of structures, with distances in Å.



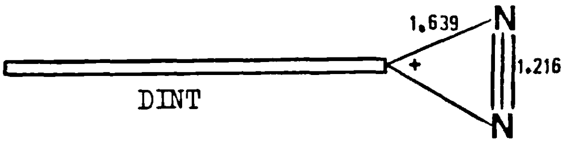
(C-7 and C-8 are regular tetrahedral centres)

DPC (C_{2v})

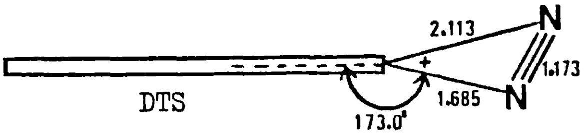


DBDI

(DBDI, DINT, and DTS all have the aryl ring geometry of DPC)



DINT



DTS

2.5.2.2 Discussion

The calculated total energies (AU) for all the structures of the DBDI system are listed in table 2.5.2.2-1 together with those calculated by Vincent and Radom[137] for the BDI system. Table 2.5.2.2-1 also includes the conversion of these energies to a new scale, which lists them with respect to the most stable species of their system, while the energies of the aryl cations are combined with that for molecular nitrogen to yield the respective binding energies.

Table 2.5.2.2-1 Calculated total energies (AU) and energies with respect to the most stable species (kJ mol^{-1}) for the 2,6-dimethylbenzenediazonium ion (a), and benzenediazonium ion[137] (b) systems.

	AU	kJ mol^{-1}		AU	kJ mol^{-1}
DBDI[a]	-411.73172	0	BDI[b]	-334.55623	0
DBDI'	-411.72870	7.91	TS	-334.48313	192.0
DTS	-411.65879	191.5	INT	-334.50009	147.4
DTS'	-411.65512	201.1	PC+N_2	-334.44480	292.6
DINT	-411.68264	128.9			
DINT'	-411.67757	142.2			
DPC + N_2	-411.62399	282.9			
DPC' + N_2	-411.62275	286.2			

The most unreliable energies quoted in table 2.5.2.2-1 are expected to be the aryl cation binding energies, since energies are very sensitive to changes in geometry[136] and these standard geometry aryl cations are expected to be further from their optimized geometry than the other species. Vincent and Radom[137] demonstrated this by obtaining an optimized geometry binding energy of 184 kJ mol^{-1} for PC, as opposed to 292.6 kJ mol^{-1} with standard geometry. Despite this, the standard geometry binding energy for DPC (282.9 kJ mol^{-1}) is not significantly different from that for PC. These calculations therefore provide no evidence to suggest that the methyl substituents destablize the DBDI with respect to the DPC. This conclusion is substantiated by the relatively small changes in energy obtained in rotation of the methyl substituents, going from the DBDI to the DBDI' system.

Vincent and Radom[137] showed that, in contrast to the PC calculations, there was relatively little change in energy between the fully optimized geometry calculations of BDI, or INT and their standard geometry calculations. The calculations for the DBDI, DBDI', DINT and DINT' are therefore expected to be fairly reliable and a schematic energy profile for the Nα, Nβ rearrangement in the DBDI and DBDI' systems is given in fig. 2.5.2.2-1, together with that for BDI.[137] From this the DBDI and BDI Nα, Nβ rearrangement profiles are shown to be very similar. DTS lies 191.5 kJ mol^{-1} above DBDI, while TS lies 192.0 kJ mol^{-1} above BDI. A slight difference however occurs in the energies of the symmetrical intermediates. INT is 147.4 kJ mol^{-1} above BDI, while DINT lies in a deeper well, being only 128.9 kJ mol^{-1} above DBDI.

Fig. 2.5.2.2-2, showing electron populations, was constructed in order to further investigate the stability of the species in the DBDI system relative to those of the BDI system. Fig. 2.5.2.2-2 gives π-electron populations as well as the total electron populations of atoms for each structure, with the exception of the TS structure for which the data was not available. All the electron populations shown for the BDI system were obtained from full geometry-optimized structures, while those for the DBDI system were obtained from standard geometry calculations. Fig. 2.5.2.2-2 shows very little difference in either the π-electron or total electron populations for analogous structures of both systems. This similarity is demonstrated by an identical electron population for Nα, Nβ in DINT and INT, and an almost identical π-electron and total electron population of Nα and Nβ in DBDI and BDI.

Swain[72] using the kinetic data of Crossley[76] (see ch. 1.5.2.5) showed that log (k/k_H) values for a range of meta and para monosubstituted aryl diazonium chlorides in 0.1 mol dm^{-3} HCl solvolysis, obeyed the linear free energy relationship using $\mathcal{F}$ and $\mathfrak{R}$ ("field" and "resonance") substituent constants.[86] Crossley[76] also provided data for some ortho substituted aryl diazonium salts, showing that o-methyl and o-methoxybenzenediazonium chloride are both less stable towards solvolysis than benzenediazonium chloride. In ch. 2.3.3 it was observed that o-methoxy and o-methylmercaptobenzenediazonium hexafluorophosphate are less stable towards thermal dediazoniation in 1,1,3,3-tetramethylurea (TMU) solution than the p-methoxy and p-methylmercapto derivatives. However, the theoretical calculations for the DBDI system show a close similarity to the BDI system, and as such provide no evidence for destabilization of DBDI with respect to DPC by a steric interaction between the methyl and diazo substituents.

It has generally been believed that the effect on a reaction or equilibrium constant of an ortho substituent, called the "ortho effect", is not amenable to a simple Hammett treatment because of the importance of steric effects. Work on the "ortho effect" has therefore been centred on attempts to separate steric from electronic effects. In this way Charton[193-197] reached the unexpected conclusion that the effect of ortho substituents is independent of steric effects except for bulky substituents such as I, Ph, or t-Bu. Charton[198] also reports that for ortho substituents, unlike meta or para substituents, the relative contribution of inductive and resonance effects change with the solvent. The absence of a steric interaction between the methyl and diazo substituents of the DBDI, as concluded from the theoretical calculations, is therefore in accord with the findings of Charton.[193-198] It should also be noted that the effect of solvation on the solvolytic stability of ortho substituted diazonium salts, via molecular orbital calculations of ion-pairs, solvated ions, or solvent-separated ion-pairs, is at present beyond the scope of computer packages. It appears that one or more of these would be necessary to predict the relative instability observed for the ortho-substituted diazonium salts.

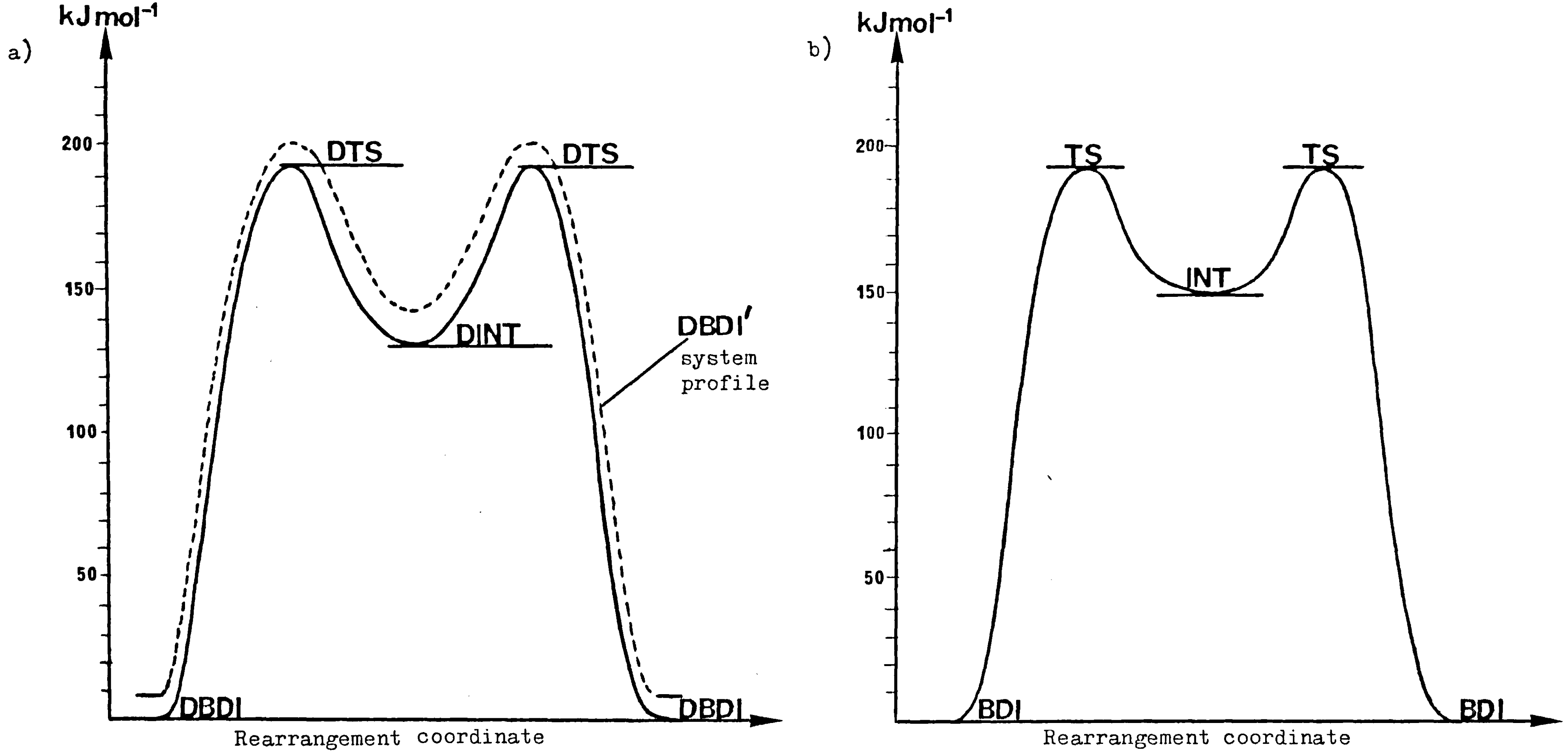


Fig. 2.5.2.2-1 Schematic energy profiles (STO-3G) for N_α, N_β rearrangement of a) the 2,6-dimethylbenzenediazonium ion (DBDI), and b) the benzenediazonium ion (BDI).

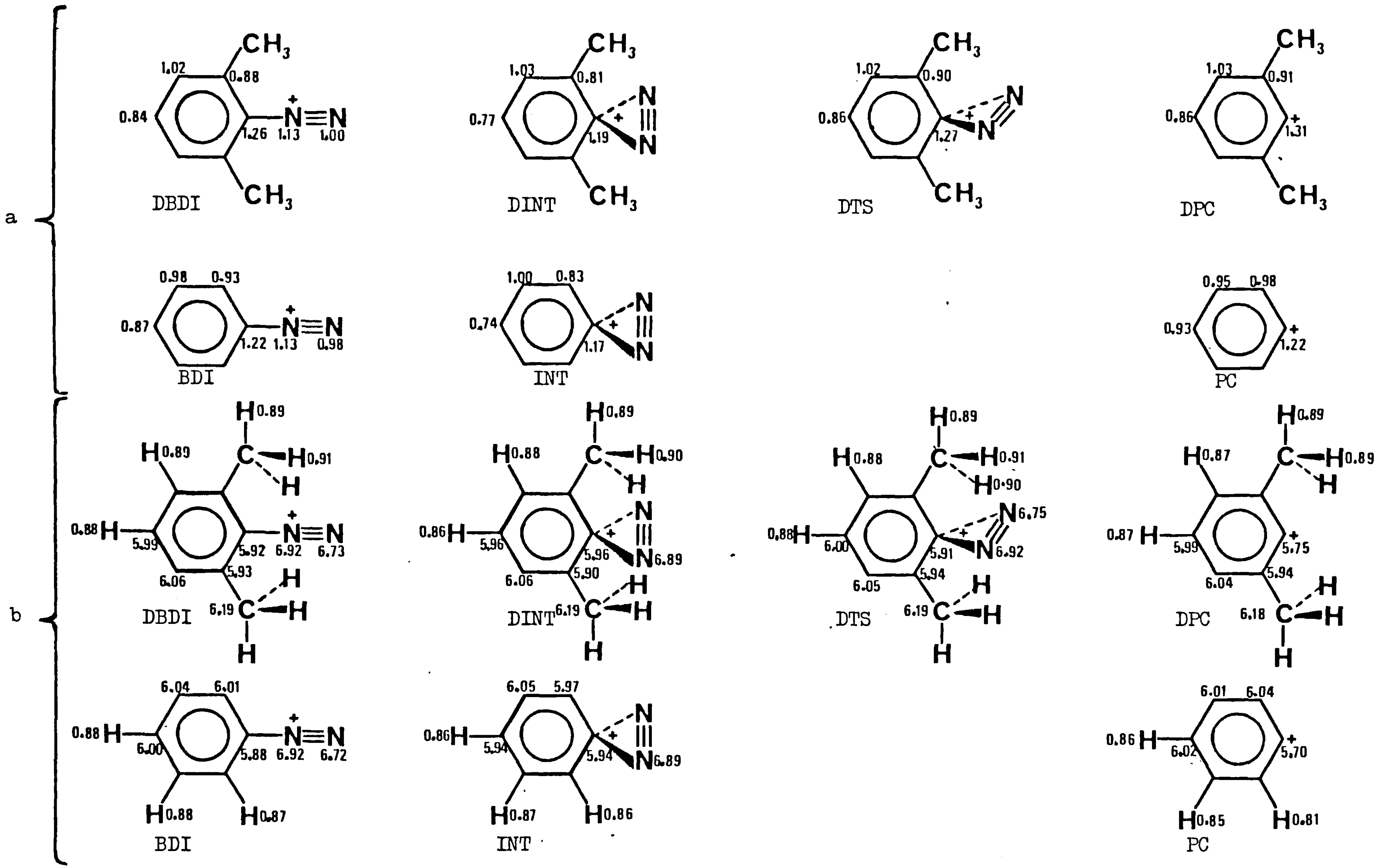


Fig. 2.5.2.2-2 The π-electron populations (a), and total electron populations (b) for the structures of the DBDI and BDI systems.

2.6 ESR SPECTROSCOPIC STUDY OF p-N,N-DIMETHYLAMINOBENZENEDIAZONIUM HEXAFLUOROPHOSPHATE PHOTOLYSES

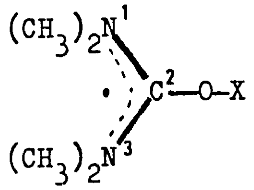
2.6.1 Introduction

In view of the ESR spectroscopic studies of Kemp[174-177] (ch. 1.7.4), in which he observed triplet ground state spectra for many aryl cations including the p-N,N-dimethylaminophenyl cation[177] (DAPC), an ESR spectroscopic study of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb) photolysis was conducted. It was proposed to undertake the recording of ESR spectra during the photolysis of IIb in the solid state and in acetone and 1,1,3,3-tetramethylurea (TMU) solutions.

2.6.2 Discussion

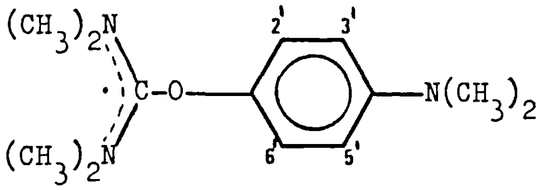
No radicals were observed by ESR spectroscopy during the photolysis of IIb in the solid state or acetone solution, even at -70°. Kemp however observed the ESR spectrum of the triplet DAPC at a much lower temperature (77 K) in a LiCl glass.

A large ESR signal was however observed for the photolysis of IIb in TMU solution at ambient temperature. Fig. 2.6.2-1 shows that this ESR signal is split firstly into thirteen lines, secondly into a quintuplet, and thirdly into an incompletely resolved triplet. This spectrum has been interpreted as that of a TMU spin-adduct of general structure LXXXVII; the thirteen lines arising from the twelve equivalent hydrogen nuclei $CH_3(1,1,3,3)$ the quintuplet arising from the two equivalent nitrogen nuclei N (1,3), and the triplet arising from the trapped radical X. Two possibilities for the identity of X are

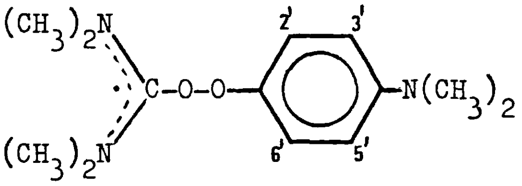


LXXXVII

the p-N,N-dimethylaminophenyl and p-N,N-dimethylaminophenoxy radicals whose TMU spin-adduct structures, LXXXVIII and LXXXIX respectively, are shown below. For either spin-adduct the weak



LXXXVIII



LXXXIX

hyperfine triplet splitting may be attributed to the two equivalent aromatic hydrogens H(2',6'). The hyperfine splittings and the spin densities of all the nuclei are given in table 2.6.2-1.

Table 2.6.2-1 Hyperfine splittings and spin densities of the ESR signal observed during the photolysis of IIb in TMU solution

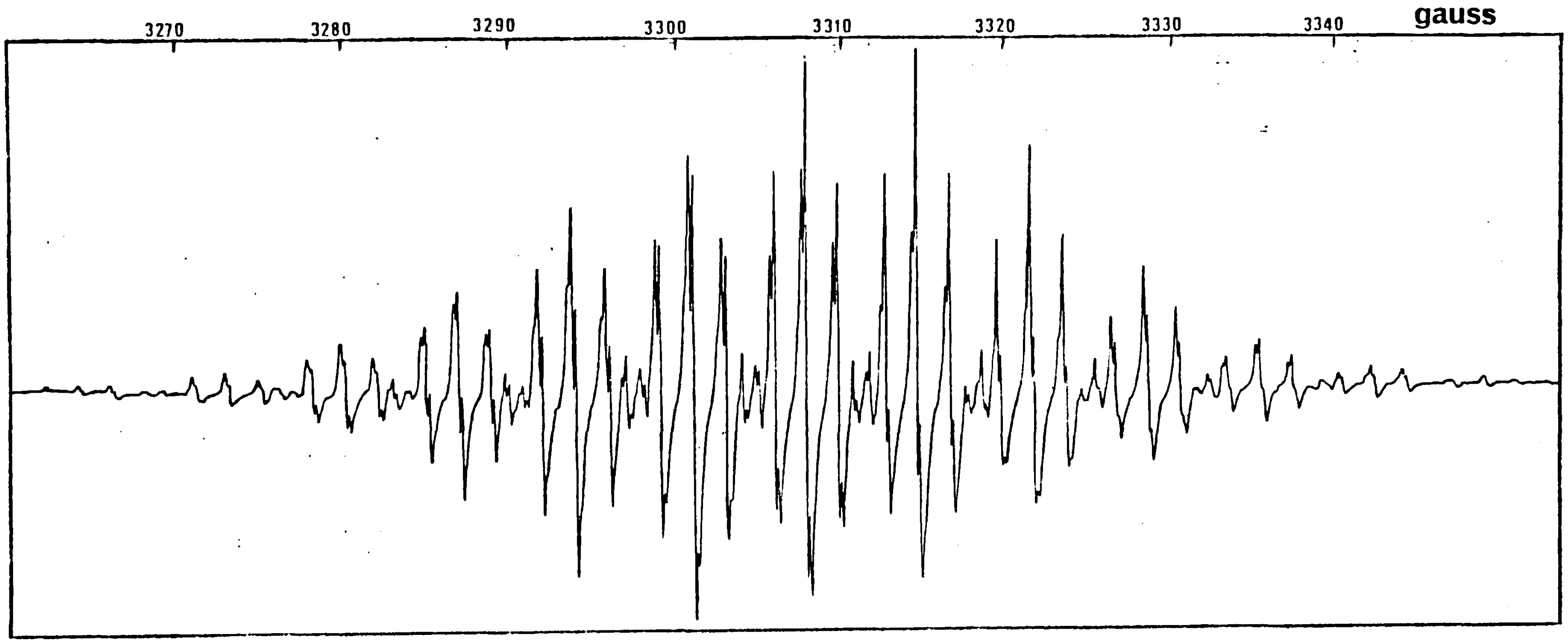
Nuclei	Hyperfine splittings (gauss)	Spin densities (e^- per $10^{-24}cm^3$)
^1H (1,3)	6.97	0.059
^{14}N (1,3)	1.92	0.22
^1H (2',6')	0.23	0.0019

Although the ESR experiments are inconclusive in determining the full structure of LXXXVII, the following observations were made. The sample of IIb in TMU solution did not give rise to the ESR signal prior to irradiation. On commencement of irradiation there was observed a rapid increase in the amplitude of the ESR signal which was maintained at a constant amplitude for 4 hr, after which time it decreased rapidly. Irradiation of TMU in the absence of IIb did not give rise to the signal.

The above evidence tends to suggest that the observed ESR signal is due to the trapping of a radical produced along a dediazoniation reaction path, or a radical generated from the destruction of a dediazoniation product. In view of the wavelength dependence observed for the photolysis of diazonium salts by Becker[160–162] (ch. 1.7.2), the use of a low pressure mercury lamp in these studies rather than a high pressure lamp (used in all other present photolytic studies) may be responsible for the introduction of a competing homolytic dediazonation along with the heterolytic mechanism (scheme 2.3.4-1) proposed previously. A generation of the p-N,N-dimethylaminophenyl radical by the homolytic photodediazonation of IIb at wavelengths < 365 nm, and the subsequent trapping of this radical with TMU, may therefore explain the observed ESR signal as that of the spin-adduct LXXXVIII.

Another possible explanation for the observed ESR signal is through the decomposition of the dediazonation product 2-(p,N,N-dimethylaminophenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (LXXIIb). This could lead directly to LXXXVIII or via the formation of the p-N,N-dimethylaminophenoxy radical to LXXXIX. It is of interest to note that Boudreaux and Boulet[155] searched for radicals accompanying the photolysis of p-N,N-dimethylaminobenzenediazonium chloride, and suggested that the observed magnetism was due to the chlorine radical and an aryl radical. These results were however strongly disputed by Zandstra and Evleth,[156] who deduced from their ESR studies that these results could be explained by the presence of the p-N,N-dimethylaminophenoxy radical.

Fig. 2.6.2-1 The ESR signal observed during the photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (IIb) in 1,1,3,3-tetramethylurea (TMU) solution.



3. CONCLUSIONS AND RECOMMENDATIONS

3.1 PHOTODEDIAZONIATIONS

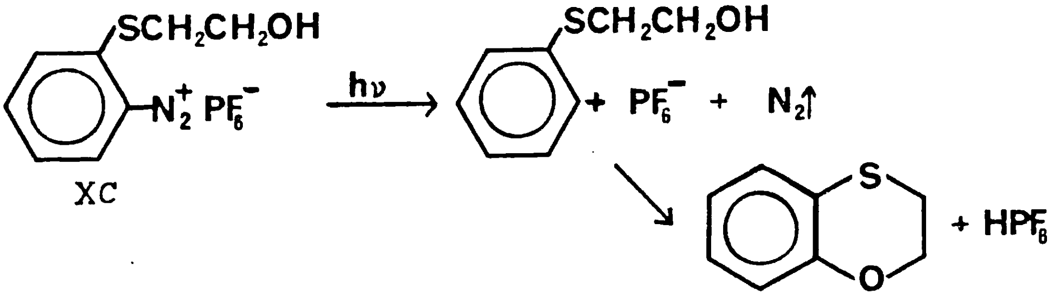
All the photodediazoniation studies of p-N,N-dimethylaminobenzenediazonium salts (II) undertaken with a high pressure mercury lamp are proposed to proceed by a heterolytic mechanism via the formation of a triplet p-N,N-dimethylaminophenyl cation (DAPC). The DAPC is suggested to be a triplet cation in view of the ESR experiments of Kemp[174-177] and the present theoretical calculations (ch. 2.5.1), which show that the triplet-DAPC is more stable than the singlet-DAPC. These photodediazonation studies include the photolysis of IIb in the solid state (ch. 2.1), in acetone solution (ch. 2.2.2), in acetonitrile solution (ch. 2.2.3), in 2,2,2-trifluoroethanol (TFE) solution (ch. 2.2.4), and in 1,1,3,3-tetramethylurea (TMU) and 1-methyl-2-pyridone (MPY) solutions (ch. 2.3.3).

The solid state photolysis product of IIb was proposed to be a 1:1 p-N,N-dimethylfluoroaniline phosphorus pentafluoride adduct (XXXIII). Consideration of the calculated electronic structure of the triplet-DAPC implies that the structure of the ion-pair, from which fluorodediazoniation is believed to proceed,[56] includes the hexafluorophosphate anion positioned above the π-layer of the triplet-DAPC. In view of this structure for the ion-pair, formation of XXXIII was proposed to be a concerted reaction.

The photodediazoniation of IIb in acetonitrile and TFE solutions yielded products consistent with heterolytic mechanisms already established for the thermal dediazoniation of aryldiazonium salts. Photolyses in TFE solutions showed no significant change in the product distribution on varying the anion (PF_6^-, BF_4^-, SbF_6^-), or the temperature from 0° to 60°. Since only a small change in the product distribution was obtained on varying the anion, a common dediazonation mechanism was implied. The temperature independence of these photolysis product distributions, together with the finding that slightly more product was formed with acetonitrile rather than water in 1:1 aqueous acetonitrile, is consistent with the thermolysis behaviour of the benzenediazonium ion.[56] Since solvation is believed to play an important part in the aryl cation/anion ion-pair formation during benzenediazonium ion thermolysis, it is suggested that this is also the case for the photolysis of IIb.

A heterolytic mechanism via the formation of a carbonylic adduct (scheme 2.2.2.2-1) was proposed for the photolysis of IIb in acetone solution, while the isolation of carbonylic adducts was achieved from the photolysis of IIb in TMU and MPY solutions. Photolysis of other diazonium salts having UV-VIS absorption bands close to that of IIb (373 - 411 nm) also yielded analogous carbonylic adducts in TMU and MPY solutions, while the scope of these reactions was expanded to include hexafluoroantimonate and hexachlorostannate diazonium salts.

The industrial importance of photolysis in carbonylic solvents was demonstrated by the high yield of phenolic product, which is associated with the "yellowing" of diazotypes.[18] The recommendation of a change in coating solvent from MEK to a non-carbonylic solvent may not be industrially acceptable on purely economic considerations. The industrial use of diazonium salts which can undergo photodediazoniation to yield intramolecular cyclisation products may be one possible solution, provided that this cyclisation is favoured over the formation of phenolic products. A model compound for such a study would be 2-(2'-hydroxyethylmercapto)benzenediazonium hexafluorophosphate (XC)



XC

(103)

which, like 2-methylmercaptobenzenediazonium hexafluorophosphate, should have a UV-VIS absorption band close to 400 nm.

A test of the mechanistic scheme 2.2.2.2-1, proposed for the photodediazonation of IIb in acetone solution, would be to use acetone made wet with $H_2{}^{18}O$. According to scheme 2.2.2.2-1, mass spectroscopic analysis of the products should show incorporation of the majority of the ^{18}O label into the acetone and not the phenolic product. (It would of course be necessary to determine first the case of incorporation of the ^{18}O into acetone in the absence of the diazonium salt).

Further indirect evidence for the existence of the DAPC may be obtained by conducting the photodediazonation of IIb in TFE solutions containing various aromatic substrates. GLC analysis of the biphenyl isomer distribution, as with similar studies of benzenediazonium ion thermolyses,[40,107,108] should reveal the nature of the arylating agent. A comparison of arylations using IIb with heterolytic thermal dediazoniations and photodediazoniations of other diazonium ions, may even provide some distinction between triplet-aryl cation and singlet-arylcation arylations.

3.2 THERMAL DEDIAZONIATIONS

The thermal dediazoniation of ortho-methyl substituted benzenediazonium salts in the carbonylic solvents TMU, MPY, 1,3-dimethyl-2-imidazolidinone (DMI), and cyclohepta-2,4,6-triene-1-one (tropone) were shown to yield carbonylic adducts in a parallel fashion to the photodediazoniation of other diazonium salts in TMU and MPY solution. The scope of these thermal dediazoniation reactions was expanded to include hexafluorophosphate, hexafluoroantimonate, and hexachlorostannate diazonium salts.

The ease of hydrolysis of the carbonylic adduct isolated from the dediazoniation of 2,6-dimethylbenzenediazonium hexafluorophosphate (XLIXb) in tropone solution (ch. 2.3.2.2) indicated that as predicted the carbonylic adduct formed with acetone (scheme 2.2.2.2-1) should be highly susceptible to hydrolysis. The carbonylic adduct isolated from the dediazoniation of XLIXb in TMU solution was however much less susceptible to hydrolysis. 2,6-Dimethylphenol was formed on reaction of this adduct with aqueous ammonia, but ammonia rather than the hydroxide ion was shown to be the preferred nucleophile for this reaction.

The industrial implications of the above studies are that even if a relatively stable carbonylic adduct is formed in the diazotype by the initial photolysis step, then phenol formation would nevertheless ensue from the development step with ammonia vapour.

From the theoretical calculations (ch. 2.5.2) the schematic energy profile for the Nα, Nβ rearrangement of the 2,6-dimethylbenzenediazonium ion (DBDI) was shown to be very similar to the profile calculated for the benzenediazonium ion,[137] and provides no evidence for destabilization of the DBDI with respect to its aryl cation by a steric interaction between the methyl and diazo substituents.

4 EXPERIMENTAL

4.1 MATERIALS

4.1.1 Preparation of diazonium salts

In the preparation of aryl diazonium hexafluorophosphates, or hexachlorostannates, the amine (2.0 g) was treated slowly with concentrated hydrochloric acid (15 cm^3). Depending on the solubility of the hydrochloride, either ethanol (15 cm^3) or distilled water (15 cm^3) was then added and the solution cooled in an ice bath to 0^o. Diazotization was effected in the usual manner by the dropwise addition ($0-5^o$) of an aqueous solution containing a slight molar excess of sodium nitrite until an excess of nitrous acid was indicated by starch-iodide paper.

While the solution was still cold, either hexafluorophosphoric acid or hexachlorostannic acid was added (c.a. 20% excess) rapidly while the flask was stirred. The diazonium salt precipitated from the solution and the cold mixture was filtered under vacuum. The precipitate was then washed with cold water (2 x 15 cm^3) followed by cold ethanol (2 x 15 cm^3) and finally diethyl ether (2 x 15 cm^3).

Diazonium hexafluoroantimonates were prepared as above excepting that a slight molar excess of sodium hexafluoroantimonate was added to the solution prior to diazotization and the diazonium salt precipitate was washed with 10 cm^3 of cold water.

For purification of the hexafluorophosphate and hexafluoroantimonate diazonium salts they were reprecipitated from their saturated acetone solutions by adding an equal volume of diethyl ether. In the preparation of the diazonium salts used in photochemical dediazoniations, charcoal was added prior to this reprecipitation. The reprecipitated diazonium salt was collected by vacuum filtration and washed with diethyl ether (2 x 15 cm^3). Hexachlorostannates, and the reprecipitated hexafluorophosphates and hexafluoroantimonates were finally dried in a vacuum desiccator for 30 min.

The diazonium salts prepared for thermal dediazoniation reactions were used immediately after their preparation. The other diazonium salts were generally used soon after their preparation or stored in a vacuum desiccator in the dark. If stored for longer than two weeks these diazonium salts were reprecipitated again prior to use.

The diazotization yield, reprecipitation recovery, and decomposition temperature of all diazonium salts prepared are given in tables 2.3.1-1, 2.3.3.1-1a, and 2.3.3.1-1b.

4.1.2 Preparation of p-N,N-dimethylaminobenzenediazonium salts

p-N,N-Dimethylaminobenzenediazonium hexafluorophosphate, hexafluoroantimonate, hexachlorostannate, and tetrafluoroborate were prepared via the zinc chloride double salt.

In the preparation of the hexafluorophosphate diazonium salt the zinc chloride double salt (100 g, 0.397 mol) was dissolved in 3 dm^3 of water. Charcoal (ca. 2.0 g) was added and the solution stirred for 30 min. The charcoal was removed and 70 cm^3 (0.409 mol) of aqueous hexafluorophosphoric acid (65% w/w) was added with stirring. The orange diazonium hexafluorophosphate which precipitated from the solution was collected by vacuum filtration. The product was washed with distilled water (2 x 100 cm^3) followed by cold methanol (3 x 50 cm^3). After air drying, the stock material was stored in a dark bottle and kept below 5°. The yield was 110 g (95%).

Prior to its use, a small sample of the stock was removed and reprecipitated as follows. The diazonium salt was dissolved in acetone at room temperature to give a saturated solution (8 g in 100 cm^3). Charcoal was added and after filtration an equal volume of methanol added to the filtrate. When the solutions were well mixed crystallization commenced and the flask was cooled in ice to complete the process. The recovery of crystals was ca. 66% (5.28 g). The bright orange crystals after drying in a vacuum desiccator decomposed at 161.5-2.0°. The IR spectrum (KBr disc) showed ν = 2140 (N-N str), 1600 (aromatic skeletal str), 1130 (C-N str of dimethylamino), and 845 cm^{-1} (P-F str) which were in good agreement with those found by R.H. Nuttall et al[33].

Hexachlorostannic acid and saturated aqueous solutions of sodium hexafluoroantimonate, and ammonium tetrafluoroborate were used to prepare the other diazonium salts by the same method. The hexafluoroantimonate and tetrafluoroborate diazonium salts were reprecipitated from their saturated acetone solutions by the addition of an equal volume of diethyl ether, while the hexachlorostannate diazonium salt was used without reprecipitation.

4.1.3 Chemicals used in the preparation of diazonium salts

All aromatic amines were commercially available and were used as supplied. Hexafluorophosphoric acid(65% w/w) was supplied by Alpha, while sodium hexafluoroantimonate (99%) and ammonium tetrafluoroborate (97%) were supplied by Fluorochem. Stannic chloride (98%), from which the hexachlorostannic acid was prepared, and sodium nitrite (96%) were supplied by BDH. The p-N,N-dimethylaminobenzenediazonium zinc chloride double salt was supplied by GAF Gt. Britain Ltd.

4.1.4 Organic solvents used in dediazoniation studies

Tetramethylurea (99%, Aldrich), 1,3-dimethyl-2-imidazolidinone (98%, Aldrich), 2,2,2-trifluoroethanol (Fluorochem), d_6-acetone (99.5% d, Nuclear Magnetic Resonance), 1-methyl-2-pyridone (prepared by the method of Prill and McElvain[199]), and cycloheptatrieneone (prepared by the method of Radlick[200]) were dried over 4A molecular sieves before use. Acetone (Analytical grade, May and Baker) was dried first over calcium sulphate (Drierite) and secondly over 4A molecular sieves. The d_3-acetonitrile (99.6% d, CEA. France) was dried over 3A molecular sieves.

4.1.5 Materials used in quantitative analyses

The ammonium molybdate (98-102%, oxidimetric assay), used in the preparation of the reagent by the method of Vogel,[201] anhydrous disodium hydrogen phosphate (99.5%, analytical grade), ammonium nitrate (98%), and sodium fluoride (97%) were all supplied by BDH. The 0.1 mol dm^{-3} hydrochloric acid and sodium hydroxide (analytical grade volumetric solutions) were also supplied by BDH.

In the gravimetric determinations of the hexafluorophosphate ion a size 4 glass sinter crucible was used. The tetraphenylarsonium chloride, used to prepare the 0.015 mol dm^{-3} reagent, was supplied by Aldrich while the 8 mol dm^{-3} ammonium hydroxide stock was prepared from an ammonia solution (s.g. 0.88) supplied by May and Baker.

GLC analysis was carried out with a 1.0 m column, packed with 15% Apiezon L on Chromosorb W, using a Pye 104 chromatograph. Bromobenzene (97%), p-dibromobenzene, and p-ethoxyacetanilide were used as marker compounds as supplied by BDH. The p-N,N-dimethylaminoacetanilide hydrohexafluorophosphate was synthesized via the addition of a two-fold excess of acetyl chloride to p-amino-N,N-dimethylaniline (5.0 g) in diethyl ether (ca. 100 cm^3) at 0°. The p-N,N-dimethylaminoacetanilide was collected by vacuum filtration as the hydrochloride (7.50 g, 95%). Acetonitrile (50 cm^3) was added to the hydrochloride followed by the dropwise addition of saturated aqueous sodium carbonate. After neutralization, the solution was dried with sodium sulphate, filtered, an equimolar portion of hexafluorophosphoric acid added, and the solution dried again with sodium sulphate. After rotary evaporation, the residue was a crude pink solid which was recrystallized from ethanol to yield white crystals mp 203-205° (7.59 g, 67%).

The p-N,N-dimethylaminophenol[202] hydrofluoride was prepared from p-N,N-dimethylaminophenol and hydrofluoric acid. The white crystals were recrystallized from water and had mp 211.5-3.5° dec.

The p-N,N-dimethylamino-(2',2',2'-trifluoroethoxy)benzene was isolated from the photolysed solution of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate in 2,2,2-trifluoroethanol solution, and purified by recrystallization (described in ch 4.5.3)

The p-N,N-dimethylfluoroaniline was supplied by GAF Gt. Britain Ltd.

4.2 APPARATUS

4.2.1 The high pressure mercury lamp photochemical reactor

The spectral distribution of the 700W high pressure mercury lamp (Kolorlux MBFR, supplied by Thorn Lighting Ltd.) is shown in fig 4.2.1-1. The mercury lamp was housed in a photochemical reactor, the construction of which is shown in diagram 4.2.1-1. The photochemical reactor consisted of a metal box, open at the top and bottom, which housed the downward directing mercury lamp and was fitted with a cooling air extraction fan at the top. The mercury lamp and extraction fan were powered from the mains via the same control box, which also stepped down the mains voltage from 200/250 V to 125/155 V. Photolysis samples, immersed in a water-bath, were positioned under the lamp by means of a lab-jack.

Fig 4.2.1-1 Spectral distribution of the 700W high pressure mercury lamp

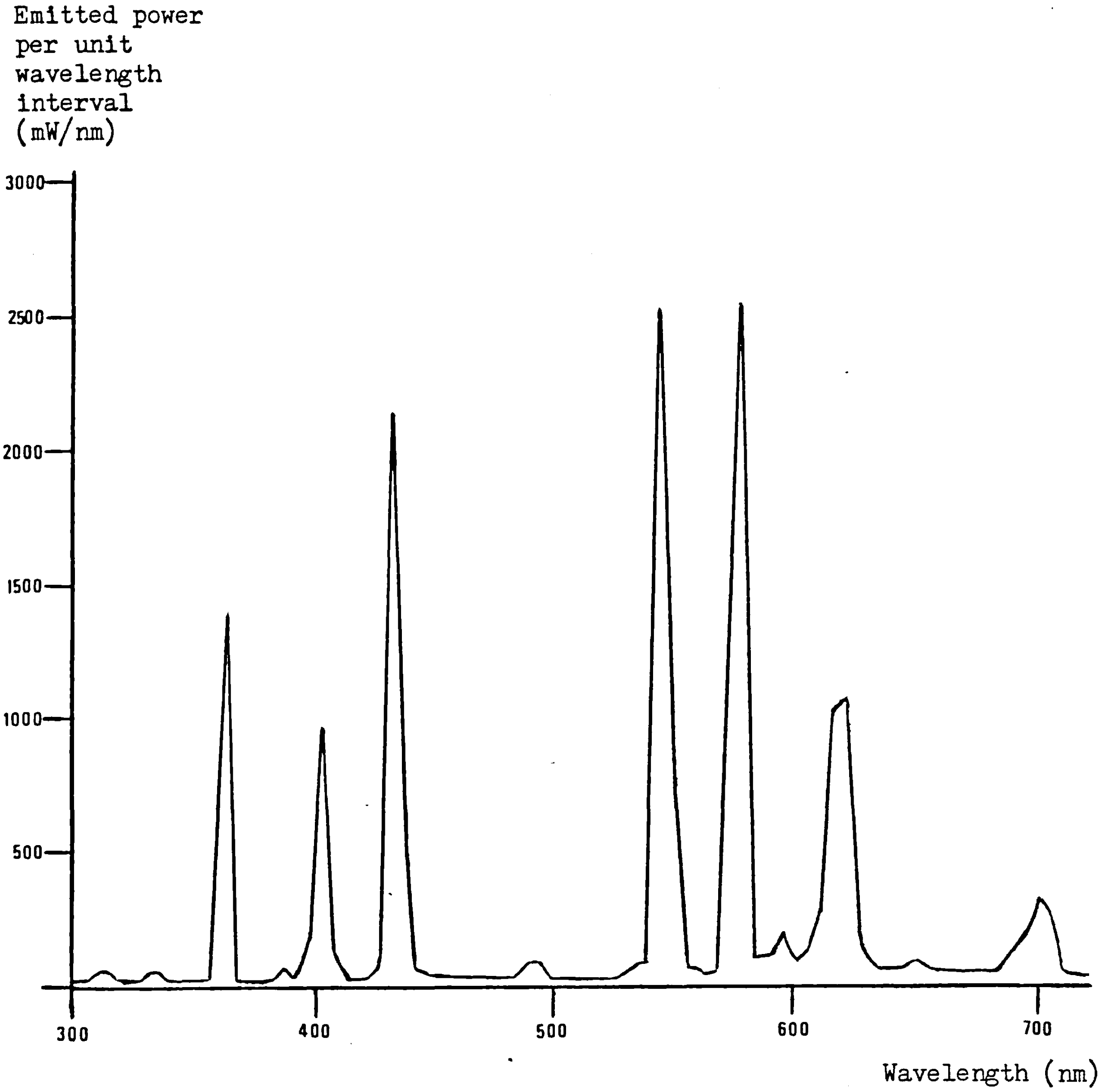
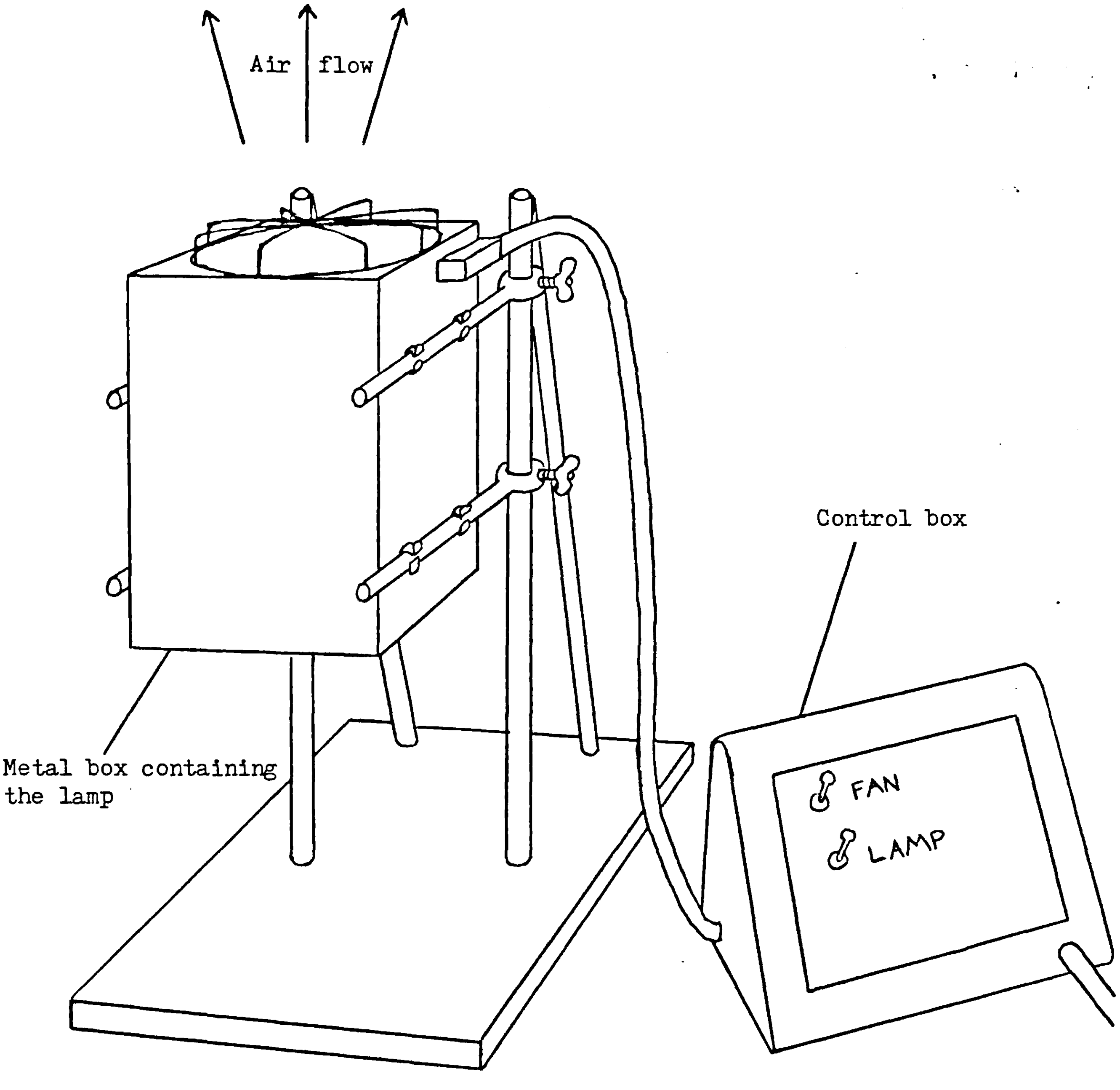


Diagram 4.2.1-1 Diagram of the high pressure mercury lamp photochemical reactor



4.3 SPECTROSCOPY

4.3.1 ^{31}P NMR spectroscopy of the solid state photolysis product of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate

After photolysis the flask was removed from the desiccator and immediately stoppered. The flask was sealed with sealing tissue prior to transportation to the Bruker HFX-90 NMR spectrometer housed at King's College, London. On arrival the photolysis product (ca. 0.2 g) was dissolved in 20% CD_3CN/CH_3CN (ca. 5 cm^3), the instrument having a deuterium lock. The sample was transferred to a 1.0 cm diameter NMR tube and the ^{31}P spectrum recorded, using phosphoric acid as an external standard at 36.43 MHz with a fourier transform pulse width of 9.0×10^{-6} s taking 8.0×10^3 points. The sweep width was 1.0×10^4 Hz.

4.3.2 ESR spectroscopy

A Decca X3 ESR spectrometer was used with a Newport Instrument M4X eleven-inch magnet, which were housed at Queen Mary College, London. The concentration of the diazonium salt solutions was ca. 0.2 mol dm^{-3}, and the samples were irradiated with a low pressure mercury lamp.

4.3.3 ^1H NMR, IR and UV spectroscopy

The ^1H NMR spectra were recorded using a 60 MHz Varian EM360 NMR Spectrometer, while the IR and UV spectra were recorded using a Perkin-Elmer 177 Grating Infrared Spectrophotometer and a Perkin-Elmer 550s UV-VIS Spectrophotometer respectively.

4.4 ANALYSIS

4.4.1 Quantitative elemental analysis

The elemental analysis of carbon, hydrogen,and nitrogen were determined commercially (Elemental Micro-Analysis Ltd.).

4.4.2 Quantitative phosphorus determination of the solid state photolysis product of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate

The method of Vogel[201] was adopted for the formation of an ammonium molybdophosphate complex. Removal of fluoride ions was carried out as suggested by Hillebrand and Lundell[203] and their method used for dissolving the complex prior to volumetric analysis. Since organic compounds may sometimes interfere with the formation of the complex[201] these were removed first by an ether extraction.

About 0.2 g of the diazonium salt was accurately weighed, added to a 50 cm^3 conical flask, and photolysed in the manner described in ch 4.5.1. The photolysis period was 2 days. On completion of the photolysis the flask was removed, and 4 mol dm^{-3} sodium hydroxide (25 cm^3) added. The flask was stoppered and shaken for several minutes. A condenser was fitted and the solution refluxed for 1 hr to ensure the complete conversion of phosphorus to phosphate. When cool the organic component was removed by extracting (3 x) with an equal volume of diethyl ether and discarding the ether. Any remaining ether was removed under reduced pressure. The resultant aqueous solution was diluted to 250 cm^3 with distilled water in a volumetric flask to make a stock solution. A 25 cm^3 aliquot of the stock solution was added to a 250 cm^3 conical flask together with approximately 1.0 g of boric acid and the solution boiled for several minutes. When cool 25 cm^3 of nitric acid (s.g. 1.42) was added and the solution heated to 60° on a water bath. The ammonium molybdate reagent, also at 60°, was added (ca. 50 cm^3) and the yellow molybdate complex $(NH_4)_3[PMo_{12}O_{40}]2HNO_3.H_2O$ precipitated from the solution. The solution was maintained at 60° for 1 hr to complete the precipitation. The solid precipitate was filtered using several layers of fluted filter paper and washed with a 2% ammonium nitrate solution until neutral. When the filtrate indicated neutral washings the complex was then in the form: $(NH_4)_3[PMo_{12}O_{40}]$. The top filter paper was transferred to a 250 cm^3 conical flask (the same used for precipitation and washing) along with a 50 cm^3 aliquot of 0.1 mol dm^{-3} sodium hydroxide. This provided an excess of alkali to decompose the precipitate according to eqn. (104) .

$$(NH_4)_3[PMo_{12}O_{40}] + 23NaOH = 11Na_2MoO_4 + (NH_4)_2MoO_4 + NaNH_4HPO_4 + 11H_2O \quad (104)$$

The excess of alkali was back-titrated against 0.1 mol dm^{-3} hydrochloric acid using phenol phthalein indicator.

To check the accuracy of the analysis a solution containing disodium hydrogen phosphate and sodium fluoride was prepared, having phosphorus and fluoride concentrations as close as possible to those anticipated in the photolysis stock solution. This solution was analysed for phosphorus as above. The results of the phosphorus determinations are given in table 2.1.3-1b.

4.4.3 Gravimetric determination of hexafluorophosphate as tetraphenylarsonium hexafluorophosphate

The method used for the analysis was an adaptation of that suggested by H.E. Affspring and V.S. Archer.[204] About 0.1 g of the carbonylic adduct was accurately weighed and transferred to a 100 cm^3 conical flask together with 8 mol dm^{-3} ammonium hydroxide (40 cm^3). The flask was fitted with a condenser and the solution boiled until the adduct had dissolved. When cool the solution was transferred to a 250 cm^3 beaker and heated to 50°. Two equivalents of 0.015 mol dm^{-3}

tetraphenylarsonium chloride reagent (also at 50°) were added with stirring. The tetraphenylarsonium hexafluorophosphate commenced precipitation and the solution was maintained at 50° for 30 min, at which time the process was complete. When cool the precipitate was collected under vacuum on an accurately weighed sintered glass crucible. (Prior to weighing, the crucible had been dried at 105-115° and allowed to cool in a desiccator.) The beaker was washed with 50 cm^3 of dilute ammonium hydroxide in 5 cm^3 portions and particles of precipitate removed from the sides using a glass rod fitted with a "rubber policeman". The crucible was dried at 105-115° for 30 min, allowed to cool in a desiccator, and reweighed. The results of the gravimetric determinations are given in tables 2.3.3.2-1a and 2.3.2.1-1a - 2.3.2.1-1d.

4.4.4 Weight loss in the solid state photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate

A 50 cm^3 conical flask and glass stopper were dried in an oven at 180° for 4 hr and were then allowed to cool in a desiccator for 1 hr. The flask and stopper were removed and the stopper was fitted with a teflon sleeve prior to stoppering. The flask was weighed on a four figure balance to constant weight. The finely powdered diazonium salt was added to the flask (ca. 1.25 g) so as to evenly cover the bottom. The flask was stoppered and reweighed. The unstoppered flask was returned with the stopper to the desiccator, the flask being positioned over aluminium foil to improve the photolysis efficiency. The desiccator was evacuated and the photolysis conducted as described in ch 4.5.1 excepting that the photolysis period was 5 days. After this time the flask was removed, immediately stoppered, and reweighed. The ^1H NMR spectrum of the sample was recorded to ensure completion of the reaction. The results of the weight loss experiment are given in table 2.1.3-1a.

4.4.5 GLC product analysis of p-N,N-dimethylaminobenzenediazonium salt photolyses in organic solvents

4.4.5.1 Acetone and acetonitrile solutions

On removal of photolysis samples from the photochemical reactor, samples were processed in the following manner. To the acetone solutions an accurately weighed amount of p-dibromobenzene (ca. 0.0300 g) was added as an internal standard. To the acetonitrile solutions p-dibromobenzene (ca. 0.0300 g) and p-ethoxyacetanilide (ca. 0.0800 g) were both added as internal standards. The p-dibromobenzene was used to quantify p-N,N-dimethylfluoroaniline and p-N,N-dimethylaminophenol, while p-ethoxyacetanilide was used to quantify p-N,N-dimethylaminoacetanilide. The acetone and acetonitrile solutions were then neutralized by the dropwise addition of saturated aqueous sodium carbonate solution, and the water subsequently removed with sodium sulphate. The solutions were made to 25 cm^3 in volumetric flasks with the respective solvents. Standard solutions were prepared with p-N,N-dimethylaminophenol hydrofluoride, p-N,N-dimethylfluoroaniline, and p-N,N-dimethylaminoacetanilide hydrochloride as above. The GLC conditions were set with a nitrogen flow rate of 40 ml min^{-1} and the column temperature of 245^o for the p-N,N-dimethylaminoacetanilide determinations and 199^o for the others.

4.4.5.2 2,2,2-Trifluoroethanol solutions

After photolysis the total volume of the 2,2,2-trifluoroethanol solutions was increased to 25 cm^3 with saturated aqueous sodium carbonate. The solution was extracted with diethylether (2 x 25 cm^3) and the first portion included bromobenzene (ca. 0.0500 g) as the internal standard. The ether layers were combined, dried over sodium sulphate, evaporated to approximately 15 cm^3, and made up to 25 cm^3 in a volumetric flask. Standard solutions were prepared with p-N,N-dimethylamino(2',2',2'-trifluoroethoxy)benzene, and p-N,N-dimethylfluoroaniline. The nitrogen flow rate was 40 ml min^{-1} and the column temperature 176°.

The product distributions determined by GLC analysis are given in table 2.2.2.2-3.

4.5 PHOTOCHEMICAL DEDIAZONIATION STUDIES

4.5.1 Photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate in the solid state

A sample of the finely powdered diazonium salt (0.3 g) was added carefully to a 6 cm diameter watch glass so as to evenly cover the surface with the solid. The watch glass was placed inside a desiccator and evacuated to 4 mm Hg. The greased seals of the desiccator were protected from the strong photolysing light by aluminium foil, since without protection the grease was found to become mobile resulting in a loss of the vacuum.

The photolysis procedure was carried out in a cold-room ca. 0° with the desiccator positioned as close as possible under the lamp, by means of a lab-jack, but without physical contact. The sample was irradiated for 24 hr and then removed from the desiccator. The product was a viscous red liquid. The ^{1}H NMR spectrum of the red liquid was recorded in d_3-acetonitrile (see fig 2.1.2-1) and its IR spectrum recorded between KBr plates (see table 2.1.3.3).

4.5.2 Photolysis of p-N,N-dimethylaminobenzenediazonium hexafluorophosphate in acetone and acetonitrile solutions

The p-N,N-dimethylaminobenzenediazonium hexafluorophosphate (ca. 4.0 g) was added to a 150 cm^3 round bottom flask together with 100 cm^3 of acetone or acetonitrile. When dissolved, water (ca. 0.75 g) was added and the flask stoppered and sealed with sealing tissue. The photolysis was carried out in a cold-room (ca. 4°). The flask was immersed in a water-bath to the level of the reaction mixture, and positioned 10 cm from the lamp. The underside of the flask was covered with aluminium foil and the water-bath contained some ice throughout the photolysis period (ca. 3 hr). After photolysis the solvents were removed by rotary evaporation.

The residue from the acetonitrile reaction was a crude pink solid (4.07 g), which was recrystallized from ethanol to give white crystals (2.65 g) mp 203.5-5.0°. The ^{1}H NMR and IR spectra of this white solid (XLIII) were recorded and the assignments are given in table 2.2.2.2-1 and table 2.2.2.2-2b respectively.

The residue from the acetone reaction was refluxed in methanol (ca. 100 cm^3) for 1 hr and after rotary evaporation a white solid was obtained (1.78 g), which was recrystallized from water (1.10 g) and had a mp 211.5-3.5° dec. The ^{1}H NMR and IR spectra were recorded and the assignments are given in table 2.2.2.2-1 and table 2.2.2.2-2a respectively.

In separate experiments the products of photolyses in acetone and acetonitrile solutions were analysed by GLC. A sample of the diazonium salt, $\sim$0.127 g (4.33 10^{-4} mol), was added to a 20 cm^3 screw top vial followed by 0.10 g of water which was made up to 10.00 g with the organic solvent. The sample was flushed with nitrogen prior to the sealing of the vial, fitted inside a blue filtered glass bottle, and photolysed for 2 hr.

4.5.3 Photolysis of p-N,N-dimethylaminobenzenediazonium salts in 2,2,2-trifluoroethanol solutions

A sample of p-N,N-dimethylaminobenzenediazonium tetrafluoroborate (ca. 4.0 g) was dissolved in 2,2,2-trifluoroethanol (ca. 20 g) and photolysed for 5 hr. The total volume of the solution was then increased to 50 cm^3 by the addition of saturated aqueous sodium carbonate. The solution was extracted with diethyl ether (2 x 50 cm^3), the ether layers combined, dried over calcium sulphate, and rotary evaporated to a volume of 10 cm^3. The crude solid, p-N,N-dimethylamino-(2',2',2'-trifluoroethoxy)benzene, began to precipitate from the solution and, after cooling to 0°, was collected by vacuum filtration to yield 2.76 g (74%). The crude product was recrystallized from diethylether to yield 2.15 g (78%) of the aryl ether mp 74.5-5.0°, whose ^1H NMR and IR spectra were recorded and the assignments are given in table 2.2.2.2-1 and table 2.2.2.2-2c respectively.

The 2,2,2-trifluoroethanol solutions prepared for GLC analysis contained ca. 4.33 10^{-4} mol of diazonium salt in 10.00 g of 2,2,2-trifluoroethanol.

4.5.4 Photolyses in 1,1,3,3-tetramethylurea and 1-methyl-2-pyridone solutions

Into a 50 cm^3 round bottom flask was placed the diazonium salt (2.0 g) followed by 8.0 g of either 1,1,3,3-tetramethylurea or 1-methyl-2-pyridone (except the case of p-N,N-dimethylaminobenzenediazonium salts where 12.0 g of solvent was required). After the diazonium salt had dissolved, the solution was flushed with dry nitrogen, the flask stoppered and sealed with sealing tissue, and then photolysed (ca. 5 hr) in the manner described in ch 4.5.2 (except the case of p-N,N-dimethylaminobenzenediazonium hexachlorostannate where, due to its poor solubility, a magnetic follower was added and the solution stirred throughout the photolysis).

After each photolysis diethyl ether (30 cm^3) was added to the reaction mixture. The solution formed two layers, the upper being the ether layer and the lower containing the carbonylic solvent together with most of the dediazoniation products. The lower layer was stirred for several minutes, after which time most of the carbonylic solvent had dissolved in the upper layer. The upper layer was decanted off and another 30 cm^3 of ether was added to the lower layer. The solution was again stirred and the process repeated until the lower layer became very viscous. Finally with the upper layer removed n-butanol (30 cm^3) was added to the lower layer. With the exception of the p-N,N-dimethylaminobenzenediazonium hexafluorophosphate and hexafluoroantimonate salts, a white precipitate appeared and the mixture was stirred until the precipitate was well formed. It was collected by vacuum filtration and washed with n-butanol (3 x 20 cm^3) followed by diethyl ether (3 x 10 cm^3). Recrystallization was from ethanol unless otherwise stated in tables 2.3.3.2-1a— 2.3.3.2-1b . The crude oily products from p-N,N-dimethylaminobenzenediazonium hexafluorophosphate and hexafluoroantimonate salts were dissolved in ethanol (25 cm^3), three drops of N,N-dimethylaniline and some charcoal added. After refluxing for 5 min the charcoal was removed and the solution concentrated until crystallization commenced. When cool the crystals were collected and washed as described above. The addition of N,N-dimethylaniline removed traces of acid which prevented crystallization. The ^1H NMR and IR assignments of all the photochemically produced products are given in tables 2.3.3.3-1a—2.3.3.3-1c and tables 2.3.3.3 -2a—2.3.3.3-2b respectively. The recrystallization recovery, mp, and elemental analysis data is given in tables 2.3.3.2-1a— 2.3.3.2-1b.

4.6 THERMAL DEDIAZONIATION STUDIES

4.6.1 Dediazoniations in 1,1,3,3-tetramethylurea, 1-methyl-2-pyridone, and 1,3-dimethyl-2-imidazolidinone solutions

The method of Rutherford and Redmond[67] was employed for the thermal dediazoniation reactions in the solvents 1,1,3,3-tetramethylurea, 1-methyl-2-pyridone, and 1,3-dimethyl-2-imidazolidinone, excepting that a 2.0 g sample of each diazonium salt was decomposed in 5.0 g of the solvent. With the exception of the hexachlorostannates, all diazonium salts decomposed spontaneously at room temperature. After the evolution of bubbles was no longer observed (1-2 hr), the solution was maintained at 50° for 10 min (except in the case of the poorly soluble hexachlorostannate diazonium salts, where the solution was maintained at 50° throughout the reaction).

The method of Rutherford and Redmond[67] was also employed for the isolation of the hexafluorophosphate carbonylic adducts. The method used for the isolation of carbonylic adducts with different anions was the same as for the photochemical dediazoniations. The ^1H NMR and IR assignments of all the carbonylic adducts isolated from thermal reactions are given in tables 2.3.2.2-1a—2.3.2.2-1g and 2.3.2.2-2a—2.3.2.2-2d respectively. The recrystallization recovery, mp, and elemental analysis data is given in tables 2.3.2.1-1a—2.3.2.1-1d.

4.6.2 Dediazoniation of 2,6-dimethylbenzenediazonium hexafluorophosphate in cyclohepta-2,4,6-triene-1-one solutions

A 50 cm^3 conical flask containing 2,6-dimethylbenzenediazonium hexafluorophosphate (ca. 2.0 g) was dried in a desiccator under vacuum. After removal from the desiccator cyclohepta-2,4,6-triene-1-one (ca. 6.0 g) was added to the flask and the reaction carried out in an atmosphere of dry nitrogen. After 1 hr, the flask was heated to 50° and maintained at that temperature until nitrogen was no longer evolved from the solution. When the reaction was complete, the flask was allowed to cool, removed, and stoppered. A 25 cm^3 portion of dry diethyl ether was added to the reaction mixture whereupon an oil separated. The ether solution was decanted from the top of the oil. A further 25 cm^3 portion of ether was added and this initiated the separation of a crude solid onto the walls of the flask. The ether was decanted from the solid and the washing procedure continued until the ether remained clear. The crude product was then dissolved in dry dichloromethane (ca. 20 cm^3). Dry ether was added to initiate precipitation. The solid was collected by filtration and was washed with ether until the washings again became clear. This reprecipitation process was continued with first 15 cm^3 and secondly 10 cm^3 of dichloromethane. The remaining solid was finally washed with n-butanol (3 x 10 cm^3), to remove any hydrolysis products, and traces of butanol removed with ether (2 x 10 cm^3). The product was stored in a desiccator under vacuum. The yield of the white carbonylic adduct, together with the spectroscopic data and elemental analysis are listed with the other carbonylic adducts.

4.7 MISCELLANEOUS EXPERIMENTS

4.7.1 The reaction of 2-(2',6'-dimethylphenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate with aqueous ammonia

The carbonylic adduct 2-(2',6'-dimethylphenoxy)-1,1,3,3-tetramethylamidinium hexafluorophosphate (0.25 g) was dissolved in acetonitrile (20 cm^3), followed by the addition of aqueous ammonia (20 cm^3, s.g. 0.88). The solution was stoppered and, after standing (8 hr), the solvent was removed by rotary evaporation. The residue was treated with 0.1 mol dm^{-3} aqueous sodium hydroxide (25 cm^3) and the solution saturated with the addition of sodium chloride. The solution was first extracted with diethylether (2 x 25 cm^3) followed by extraction with chloroform (2 x 25 cm^3). After drying over sodium sulphate, followed by rotary evaporation, the combined ether extracts yielded the minor product LXXXIII ($\sim$20%) while the combined chloroform extracts yielded the major product LXXXII ($\sim$80%).

4.7.2 Ab initio quantum molecular calculations

All of the quantum molecular calculations were performed using a CDC 7600 computer housed at University College, London. The original Gaussian 70 computer package[188] was modified to run on the CDC 7600 by Mallinson and Peters,[205] while the Gaussian 76 package was modified by Altmann.[206] The input of geometry was performed by the Z-matrix method as described by Mallinson[205] and Altmann[206].

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