"STUDIES OF THE CHLORINATION OF NAPHTHALENE AND RELATED COMPOUNDS"

Thesis submitted for the
Degree of Doctor of Philosophy
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by
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ABSTRACT

This thesis describes the studies of chlorination of naphthalene in different solvents, namely acetic acid, chloroform and carbon tetrachloride.

More than 50% of the reacted naphthalene is converted into the substitution product, 1-chloronaphthalene, when the chlorination is made in acetic acid. Two naphthalene tetrachlorides, α and δ, as well as an acetoxytrichloride are also produced. The variation in the proportion of these products when added electrolytes are present in the solution, as well as their properties and structures, have been studied.

A third naphthalene tetrachloride, the previously known γ-isomer, was isolated from a chlorination of naphthalene in liquid chlorine.

The chlorination of naphthalene in carbon tetrachloride under catalysis by sunlight and benzoyl peroxide yields mainly the γ-te-

trachloride and a new isomer, not previously reported, that we designate ϵ-naphthalene tetrachloride.

The chlorination of naphthalene in chloroform yields all the products characterized from the reactions in acetic acid and in carbon tetrachloride.

The chlorinations in acetic acid and in chloroform have also been studied kinetically. In the former solvent, the kinetic follows the usual second-order reaction. The kinetics in chloroform were complicated by the fact that the hydrogen chloride produced in the substitution catalyzed the chlorination. Traces of iodine had also a very important catalytic effect which was determined kinetically.

The p.m.r. spectra of the compounds formed in the chlorination of naphthalene, kindly recorded and examined by Dr. M. D. Johnson, have led to knowledge of their stereochemistry and structure.

To provide better characterisation of the naphthalene tetrachlorides, their infrared spectra have been recorded and their dipole moments determined.

Finally, the mechanisms of chlorination are discussed in order to interpret the formation of the different products, not only for heterolytic reaction in acetic acid but for the homolytic chlorination of naphthalene.

TO MY WIFE

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The work described in this thesis has been done in the Chemistry Department of Bedford College, between September 1963 and September 1965.

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Part I

INTRODUCTION

1. AROMATIC COMPOUNDS.

1.1) Definition[1,2,3]. In Organic Chemistry the term "aromatic" is used rather loosely for the designation of a certain group of characteristic, but not very precisely defined, physical and chemical properties, and also for the description of the particular (always cyclic) compounds which exhibit these properties.

Thus, benzene is said to be aromatic because it combines a high degree of apparent unsaturation with both a high thermochemical stability (i.e. a low internal energy) and a relatively small tendency to enter into addition reactions. Originally the term aromatic was applied only to compounds containing benzene rings; other substances which are likewise said to be aromatic and which have similar properties, include a large number of more complex hydrocarbons with two or

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1. "Resonance in Organic Chemistry", G. W. Wheland. John Willey & Sons, Inc. New York, 1955. Chapter 3.
2. "Organic Chemistry", F. G. Bordwell. The Macmillan Company. New York, 1955. Chapter 14.
3. "The modern structural theory of Organic Chemistry", L. N. Ferguson. Prentice Hall Inc. New Jersey, 1963. Pages 53, 379 and 489 ff.

more isolated, conjugated or condensed benzene rings.

Later it was recognized that other compounds including furan, pyrrole, pyridine and thiophene, with a "free" sextet of electrons, had greater or lesser aromatic character.

Nowadays many compounds, hydrocarbons or heterocyclic, are known to have aromatic properties.

No generally applicable justification for the concept of the aromatic sextet can be derived from the theory of resonance.

On the other hand, molecular orbital calculations showed that the aromatic sextet could be given a quantum mechanical foundation. In the pictorial representation of these molecules, the six parallel p-orbitals are grouped together to form a composite molecular orbital containing six π-electrons.

The calculations not only accounted for the stabilizing influence of the aromatic sextet, but also predicted that stabilizing effects would be possesed by composite molecular orbitals containing $(4n + 2)$ π-electrons, where n may be 0,1,2,3... Hydrocarbons with these numbers of π-electrons are known to be more or less aromatic. For example: n=0, cyclopropenium cation; n=1, benzene, cyclopentadienylanion and tropylium cation. Cyclodecapentaene, (10-annulene), with n=2, and 14-annulene with n=3, cannot be planar because of transannular interferences of the internal hydrogens in the planar molecule; this prevents the compounds from being aromatic. 18-Annulene, n=4, can be planar and it has been found to be aromatic. Although Hückel's rule is not strictly applicable to di- or poly-cyclic compounds, however, molecular orbital calculations indicate that is generally applicable to such compounds. For example: n=2, naphthalene, azulene and cyclooctatetraenyl dianion (which is planar and shows aromatic character); n=3, anthracene and phenanthrene, etc.

It is noteworthy that aromatic carbon atoms and therefore aromatic rings, have large negative structural parameter constants, λ, in Pascal's expression of the magnetic susceptibilities $X_m = \sum n_i x_i + \lambda$, where n_i is the number of atoms of susceptibility x_i in the molecule and λ is a structural parameter (sometimes called exaltation) which depends upon the nature of the bonding between the atoms. This provides evidence that the π-electrons circulate around the ring and thereby execute large orbital motions to produce relatively large diamagnetic moments (X_m and x_i are always negative quantities; λ is positive in non-aromatic bonds).

Another characteristic of the aromatic rings is found in their p.m.r. spectra. The magnetic anisotropy of an aromatic ring produces an unshielding of the ring protons. The magnetic field induces the electrons to flow around the ring in a closed circuit which sets up a magnetic field at the center opposed to the applied field at the edges of the ring and thereby produce an unshielding effect there, which leads to a low τ value for aromatic protons.

1.2) Stability[1,2].

The aromatic compounds can conveniently be described as resonance hybrids of several structures. Resonance always has the effect of increasing the stability, or in other words, of decreasing the energy of any molecule in which it is an important feature.

The resonance energy has in the past been defined as the quantity obtained by subtracting the actual energy of the molecule from that of the most stable contributing structure; it is therefore always positive, and has sometimes been replaced by the equivalent term "delocali-

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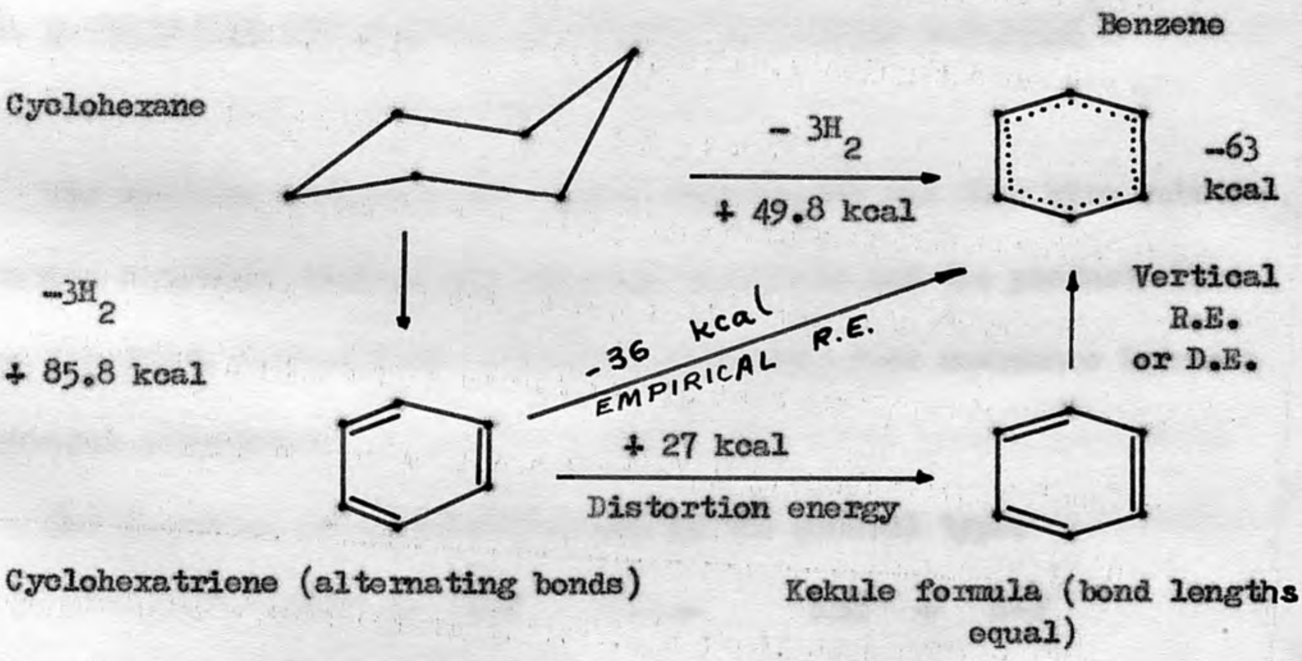
1. "Resonance in Organic Chemistry", G. H. Wheland. John Willey & Sons, Inc. New York, 1955. Chapter 3.
2. "Molecular orbital theory for Organic Chemistry", A. Streitwieser Jr. John Willey & Sons, Inc. New York, London, 1961. Chapter 9.

zation energy" (in the M.O. theory).

With the aromatic compounds the resonance energies are relatively large; this result is to be expected since, for any such compound, it is always posible to write two or more stable structures, which are at least approximately equivalent to each other.

It has been suggested that a better term for the experimentally observed quantities is "stabilization energy", since this quantity is often a composite involving contributions of several kinds, of which one is strictly energy of delocalization. For example the following cycle shows the various resonance energies of benzene:



The vertical resonance energy corresponds more exactly to the delocalization energy but in different treatments it is attributed values from 13 to 112 kcal. All the empirical resonance energies may contain σ-bond energy terms (for example, in the hydrogenation of ethylene, a double bond is converted to a single bond and two C-H bonds, but, in addition, four C_{sp^2}-H bonds are converted to C_{sp^3}-H bonds); to emphasize this point the derived energies are called stabilization energies. As it has been shown, estimation of the factors which contribute to the stabilization energies is subject to uncertainty.

2. SUBSTITUTION AND ADDITION REACTIONS IN AROMATIC COMPOUNDS[1].

The aromatic compounds are highly unsaturated but they give substitution reactions because the starting materials and the products have an important thermodynamic stability resulting from resonance between several structures.

The reactions of substitution are of the general type:

$$ArH + X{-}Y \longrightarrow ArX + H{-}Y$$

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[1] "Aromatic Substitution", P. B. D. de la Mare and J. H. Ridd. Butterworths Scientific Publications. London, 1959. Chapter 13.

In many, but not in all cases it is satisfactory to regard them as following the course:

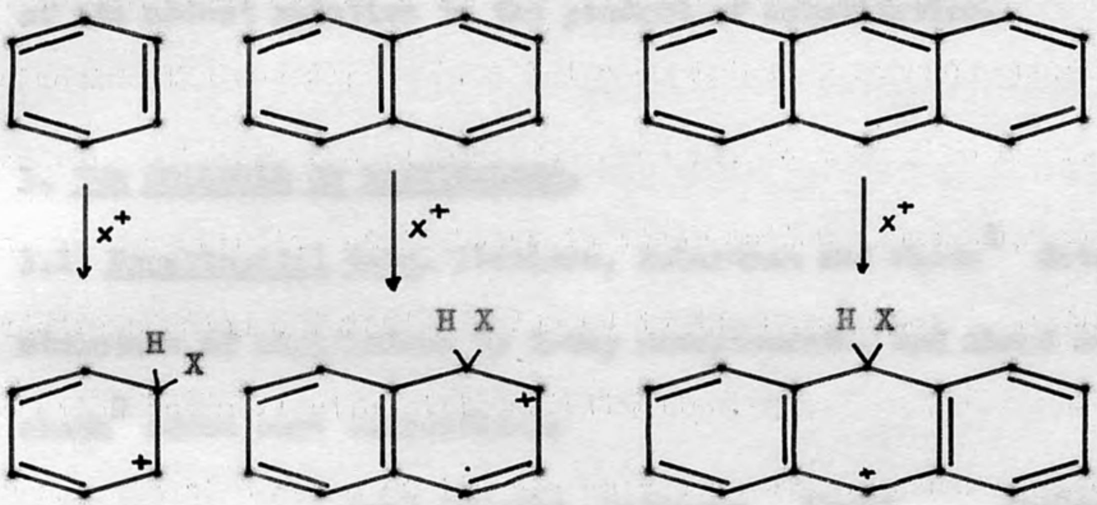
$$ArH + X^{+} \longrightarrow ArX + H^{+}$$

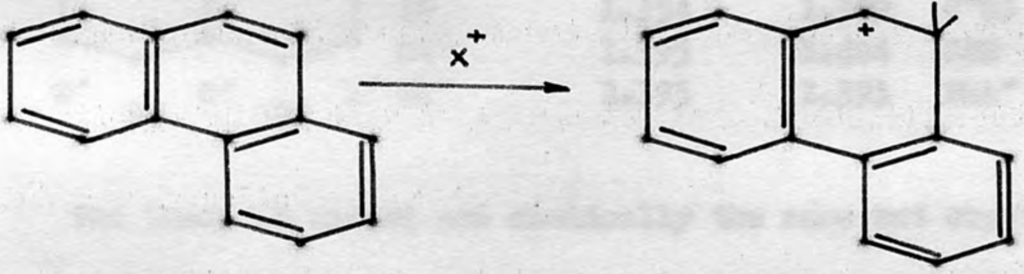
The new substituent is bound in the reaction product by a pair of electrons which originally belonged to the substrate; therefore this reaction is an electrophilic substitution.

Substitution and addition products can be produced from the same intermediate state in different proportions, according to the nature of the aromatic system.

Benzene does not usually react giving addition products but the formation of the latter is thermodynamically less unfavourable for the higher polycyclic hydrocarbons.

The relative ease of addition can be correlated with the amount of stabilization energy "lost" in forming the adduct with an electrophilic reagent X^{+} or X-Y ; all the aromatic systems built up by fusing two or more rings through ortho-carbon atoms have considerable aromatic stability, which in greater or lesser part is lost according to the system as can be seen:





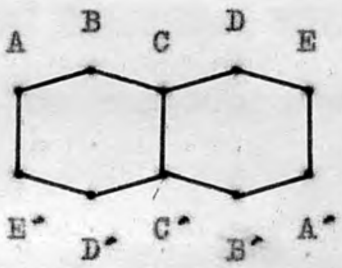
"Lost" energy in forming the adduct, in kcal/mole :

Benzene	(36)	-	Cyclohexa-1,3-diene	(2)	=	34
Naphthalene	(61)	-	Styrene	(38)	=	23
Phenanthrene	(92)	-	Two benzenes	(72)	=	20
Anthracene	(84)	-	Two benzenes	(72)	=	12

The higher the hydrocarbon, the greater the thermodynamic stability of its adduct relative to the product of substitution.

3. THE MOLECULE OF NAPHTHALENE.

3.1) Experimental data. Abrahams, Robertson and White[1] determined the structure of naphthalene by X-ray measurements, and Ahmed and Cruickshank[2] added some corrections:



Bond lengths	Robinson	Ahmed	Angles	
AB	1.363 A	1.369	BAE'	121° 5'
BC	1.421	1.426	ABC	119° 35'
CD	1.420	1.424	BCC'	118° 55'
DE	1.354	1.362	C'CD	120° 10'
AE'	1.395	1.404	CDE	119° 30'
CC'	1.395	1.393	DEA'	120° 50'

The bonds AB and DE are chemically the same but crystallographically different. For chemical reasons it would seem most likely that this difference is due to error, just as the deviations from a strictly coplanar structure, (also about 0.01 A), may be due to error.

On the other hand, it might be argued that structural distortions of about this order of magnitude could arise from the manner in which the molecules are packed together to form the crystal lattice even

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1. S. C. Abrahams, J. Monteath and J. G. White. Acta Cryst. 1949 2 238

2. F. R. Ahmed and D. W. J. Cruickshank, ibid 1952 5 582

although such distortions may not be present in free molecules, e.g. in the vapour phase. There is some evidence to support this view, derived from the analysis of other structures, but not very definite conclusions can yet be drawn.

The chemically reactive bond, AB or DE, is the shortest.

3.2) Theoretical predictions[1,2].

The resonance energy of naphthalene is greater than that of benzene, but it is definitely less than twice as great. Both rings in the naphthalene molecule have two atoms in common and so are not independent of each other, the possibilities for resonance being less than in, say, diphenylmethane.

It may be shown by quantum mechanics that the number of independent or canonical structures amongst which resonance can occur is given by

$$\frac{n!}{n/2\,!\,(n/2+1)\,!}$$ where n is the number of non-localized electrons.

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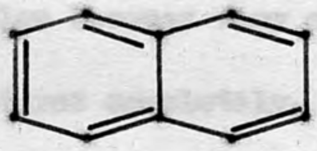
1. "Resonance in Organic Chemistry", G. H. Wheland. John Willey & Sons, Inc. New York, 1955. Chapter 3.
2. "Structure of molecules and the chemical bond", Y. K. Syrkin and M.E. Dyatkina. Butterworths, London, 1950. Chapter 5.

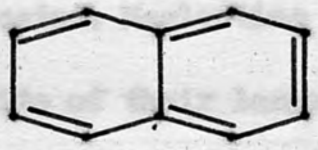
Naphthalene contains 10 π-electrons, and therefore the number of independent structures which contribute to the final state of the molecule is $10! / 5!6! = 42$.

The Erlenmeyer structure, I, which is symmetrical and the two Erdmann structures, II and III, will contribute more to the final state of the molecule than other forms because of the greater number of π-bonds:

I



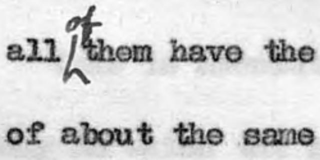
II

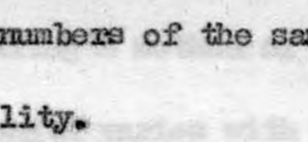


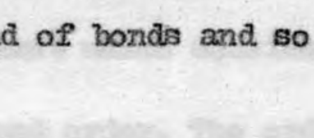
III

Although these latter structures are not equivalent to the former, it is customary to assign them approximately the same weight, since all of them have the same numbers of the same kind of bonds and so are of about the same stability.

The Erlenmeyer and Erdmann structures are Kekule-like formulae; the other 39 are Dewar-like of which 16 have one formal bond:



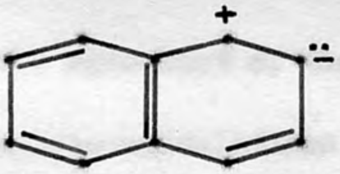


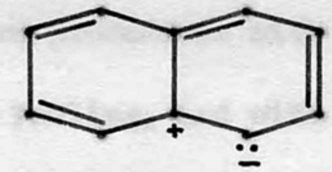


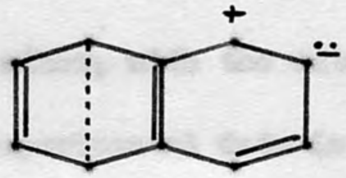
etc

19 have two and 4 have three.

There are also 903 noncanonical structures with dipolar formulae which are not independent because can be deduced from the canonical structures:





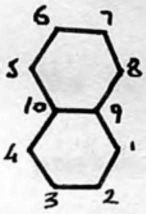


etc

The π-electron problem becomes very complicated. Neglecting the bridged and polar structures completely, in spite of their large numbers, the bond 1-2 possesses two-thirds double bond character, and hence a predicted length of 1.37 A, whereas all the other carbon-carbon bonds have only one-third double bond character and hence a predicted length of 1.42 A .

This is according Pauling's method of treatment which considers the way in which the bond length varies with the bond order. The orders of the carbon-carbon bonds in ethane, graphite, benzene, ethylene and acetylene are, by definition or by calculation, 1.000 , 1.45 , 1.623 , 2.000 and 3.000 A respectively, whereas the corresponding distances are 1.54 , 1.42 , 1.39 , 1.35 and 1.20 A respectively.

Similar treatments, more detailed and better grounded, have been carried through by Penney, using the valence-bond method, and by Coulson who employed instead the molecular-orbital approach. These methods for treating molecular structure differ in the quantum-mechanical approximations introduced into the theoretical calculations of the bond orders. The agreement of the two procedures with each other, with the extremely simple calculations by Pauling, and with the experimental data is far from perfect, but it is probably about as satisfactory as could have been anticipated:



	Bond order			Bond length		
	Penney	Coulson	Pauling	Penney	Coulson	Pauling
1-2	1.690	1.725	1.666	1.38	1.37	1.37
2-3	1.530	1.603	1.333	1.40	1.40	1.42
9-1	1.516	1.555	1.333	1.40	1.40	1.42
9-10	1.433	1.518	1.333	1.42	1.42	1.42

In any event, it is gratifying that all three methods of treatment are consistent with the observation that the 1-2 bonds are considerably shorter than any of the others.

3.3) Properties and reactions[1,2,3].

Naphthalene has a greater unsaturation than benzene ($C_{10}H_8$ instead of C_6H_6). It is more easily oxidised and reduced, and substitution reactions occur much more readily, particulary in the 1-position, than in benzene.

Just as 1,3-butadiene gives 1,2- and 1,4-additions, in some reactions naphthalene behaves similarly. Thus the hydrogenation of naphthalene with sodium and ethanol takes place readily to give 1,4-dihydronaphthalene; further hydrogenation gives tetralin easily and rapidly. The hydrogenation with sodium in liquid ammonia produces 1,2-dihydronaphthalene.

Substitution reactions occur more quickly than in benzene because the intermediate cation is more stabilized by resonance, having the positive charge delocalized over two rings, instead of only over one.

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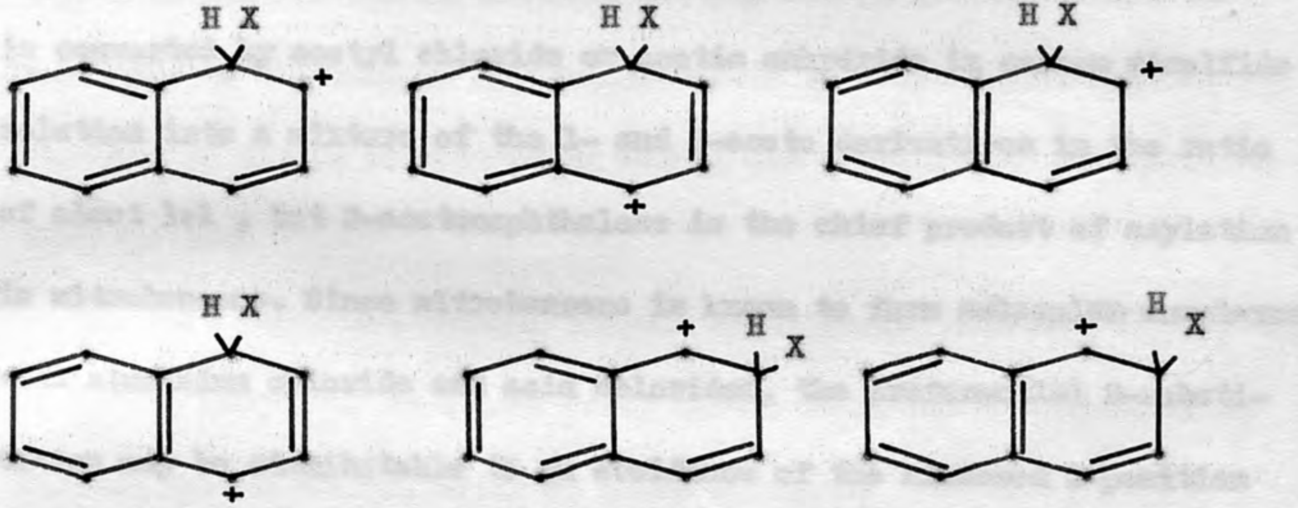
1. "Aromatic Substitution", P. B. D. de la Mare and J. H. Ridd. Butterworths, London 1959. Chapter 13.
2. "Structure of molecules and the chemical bond", Y. K. Syrkin and M. E. Dyatkina. Butterworths, London 1950. Chapter 5.
3. "Advanced Organic Chemistry", L. F. Fieser and M. Fieser. Reinhold Publishing Corporation, New York 1961. Chapter 27 .

The substitution occurs mainly in the 1-position because the resulting cation is more stabilized by resonance than is that formed by attack at the 2-position. Thus it is possible to draw four resonance structures for the cation $1\text{-}XC_{10}H_8^+$ maintaining the benzenoid nature of the other ring, but only two such structures for the $2\text{-}XC_{10}H_8^+$:



Nitration and bromination follow this type of reaction:

$C_{10}H_8 + HNO_3 \longrightarrow 1\text{-}C_{10}H_7NO_2$ $C_{10}H_8 + Br_2 \longrightarrow 1\text{-}C_{10}H_7Br$

Reversible reactions subject to steric hindrance may ultimately result in substitution in the less hindered 2-position, to an extent that increases with increasing reaction temperature but varies with the reagent and perhaps with the bulkiness of specific group complexes.

Sulfonation, notably subject to both steric and temperature effects, can be controlled to yield either the 1- or 2-sulfonic derivative:

$$C_{10}H_8 + H_2SO_4 \text{ (100\%; 0 to 60º) } \longrightarrow 96\% \text{ 1-}C_{10}H_7SO_3H$$

$$C_{10}H_8 + H_2SO_4 \text{ (95\%; 165º) } \longrightarrow 85\% \text{ 2-}C_{10}H_7SO_3H$$

The course of Friedel-Crafts acylations varies more with the nature of the reagent and solvent than with the temperature. The hydrocarbon is converted by acetyl chloride or acetic anhydride in carbon disulfide solution into a mixture of the 1- and 2-aceto derivatives in the ratio of about 3:1 , but 2-acetonaphthalene is the chief product of acylation in nitrobenzene. Since nitrobenzene is known to form molecular complexes with aluminium chloride and acid chlorides, the preferential 2-substitution may be attributable to an avoidance of the hindered 1-position in the formation of a bulky intermediate complex.

4. CHLORINATIONS [1].

Halogenations are some of the electrophilic substitutions which occur with aromatic compounds. Among them, chlorination has probably been

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[1] "Aromatic Substitution", P. B. D. de la Mare and J. H. Ridd. Butterworths, London 1959. Chapter 9 .

the most exhaustively investigated.

The reagents which have been employed in chlorination can be divided into two clases: positively charged and neutral. Among the former, the most important are the chlorinium and hypochlorous acidium ions (Cl^+ and $ClOH_2^+$) formed in aqueous solutions of hypochlorous acid. Also ions, formed by protonation of chlorine acetate and of N-chloroamines in solutions of chlorine or hypochlorous acid in a hydroxylic solvent in presence of acetic acid or of an amine, can probably act as chlorinating species.

The most important neutral reagent is molecular chlorine in anhydrous or nearly anhydrous solutions using acetic acid, nitrobenzene, chloroform, carbon tetrachloride or other solvents.

Orton and Bradfield[1] were the first to determine the rate of chlorination of some aromatic compounds, using chlorine in acetic acid with 0.14 to 1.00% of water. They found that the molecular chlorine was the effective electrophilic reagent and the rate was shown to have the kinetic form

$$-d\,[Cl_2]/dt = k_2\,[ArH][Cl_2]$$

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[1] K. J. P. Orton and A. E. Bradfield, J. Chem. Soc. 1927, 926.

In itself, this kinetic form could be consistent with electrophilic attack by Cl^+, ClOAc or $ClOAcH^+$ formed in a pre-equilibrium according to the following sequences:

$Cl_2 \longrightarrow Cl^+ + Cl^-$ $\quad$ $ArH + Cl^+ \longrightarrow \text{products}$

$Cl_2 + H^+ \longrightarrow Cl^+ + HCl$ $\quad$ $ArH + Cl^+ \longrightarrow \text{products}$

$Cl_2 + AcOH \longrightarrow ClOAc + HCl$ $\quad$ $ArH + ClOAc \longrightarrow \text{products}$

$Cl_2 + AcO^- \longrightarrow ClOAc + Cl^-$ $\quad$ $ArH + ClOAc \longrightarrow \text{products}$

$Cl_2 + AcOH + H^+ \longrightarrow ClOAcH^+ + HCl$ $\quad$ $ArH + ClOAcH^+ \longrightarrow \text{products}$

(HCl is not much dissociated in acetic acid; the dissociation does not affect the following argument).

All these mechanims can be excluded, because they require, if the kinetic form is to be satisfied, either powerful catalysis by acid and anticatalysis by base or anticatalysis by chloride ions[1].

No anticatalysis, either by acetate ions, by chloride ions, or by hydrogen chloride is observed. It is concluded, therefore, that molecular chlorine is the effective electrophilic reagent.

All electrolytes which have been studied accelerate the reaction. The small catalysis by electrolytes and the increase in rate on adding water to the solvent presumably results from the fact that the transition

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[1] P. W. Robertson, J. Chem. Soc. 1954, 1267.

state for the reaction involves polarization of both the chlorine molecule and the aromatic compound. The transition state is therefore more polar than the starting materials, and the reaction is facilitated by increase in the ionizing power of the environment.

5. CYCLOHEXANE DERIVATIVES [1,2,3].

5.1) Isomerism and characteristics of cyclohexane.

Cyclohexane has been examined in the vapour phase by electron diffraction; in contrats to benzene, which has a planar structure (valency angles 120°; carbon-carbon distance 1.40 A; carbon-hydrogen distance 1.04 A), cyclohexane was found to exist in the chair form, in which all the valency angles are 109° 28′; the carbon-carbon distances are 1.54 A, and the carbon-hydrogen distance is 1.10 A.

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1. H. D. Orloff, Chem. Reviews 1954 54 347
2. "Progress in stereochemistry", W. Klyne editor. Vol. I, chapter 2.
3. "The modern structural theory of Organic Chemistry", L. N. Ferguson. Prentice-Hall, Inc. New Jersey, 1963. Chapter 3.

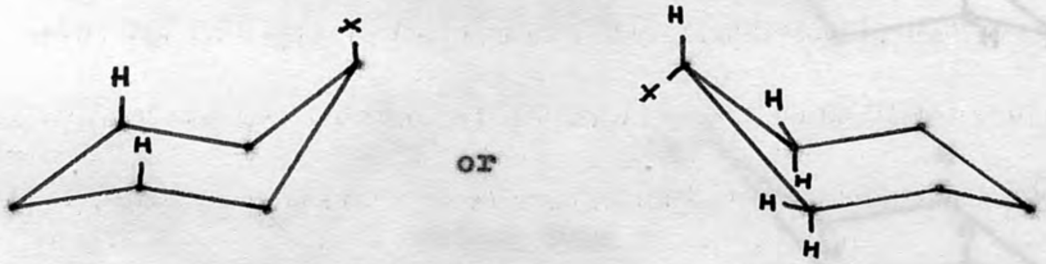
Neither in cyclohexane nor in any of its simple derivatives has the presence of the less symmetrical boat form of the carbon skeleton been detected by this procedure.

The two bonds from each carbon to other susbtituents have directions differing in their geometrical relationship to the trigonal axis of the ring. The vertical bonds, parallel to the trigonal axis have been designated as axial bonds (p, ε and a in different notations); the other bond from each carbon atom, has a direction such that it makes an angle of 109° 28' with the trigonal axis, and is denoted as equatorial (notations e, $\varkappa$ and e).

A ring conversion which changes all the axial bonds into equatorial and vice-versa was suggested and afterwards confirmed (see section 5.3). (The theoretical basis for ring conversion had been sustantiated largely by physical evidence and by the fact that the number of steric isomers of cyclohexane derivatives actually observed may be accounted for adequately by this mechanism). The cyclohexane ring is quite flexible and the chair conformation may invert from one chair into another chair form (page 31).

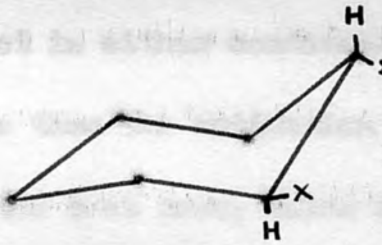
The energy barrier to this transformation is approximately 10 kcal/mole .

Both chairs may or may not be identical with the original configuration depending on the nature of the substituents in the molecule. Whether a compound exists exclusively in one form or the other, or as an equilibrium mixture, will depend on considerations of energy resulting from steric and electrostatic factors. In a monosubstituted cyclohexane, the substituent may occupy an axial or an equatorial position:



A study of scale models shows that the axial substituent is closer to the axial hydrogens on the same side of the ring (1:3 interactions) than the equatorial substituent is to the adjacent equatorial or axial hydrogens (1:2 interactions). Electron diffraction measurements also provide evidence that the equatorial conformation of a monosubstituted cyclohexane is the more stable. However, in most monosubstituted cyclohexanes the energy barrier between the two chair conformations is small, and both forms exist in appreciable proportion.

As a consequence of the stronger 1:3 diaxial repulsive forces, disubstituted cyclohexanes will preferably assume the following conformations:



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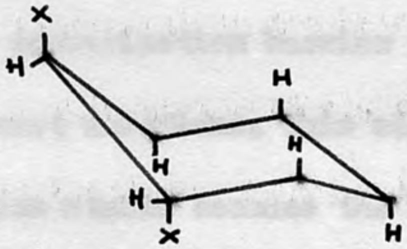

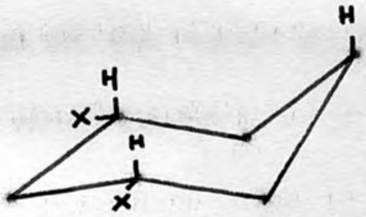

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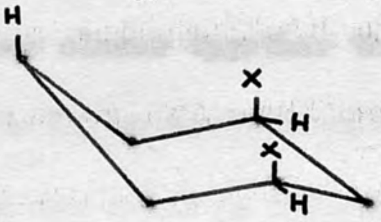

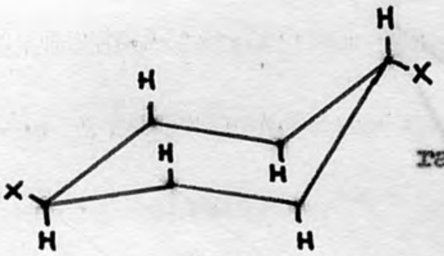

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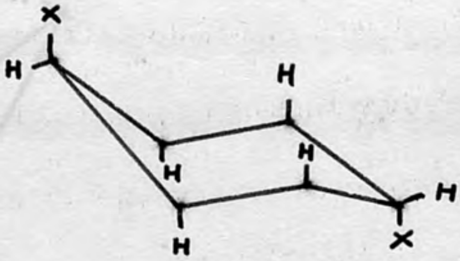
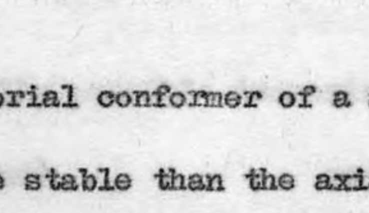


With more than two groups on the cyclohexane ring, the all-equatorial isomer becomes increasingly the more stable conformation because it places the groups the farthest apart.

It is possible, of course, that strong polar forces or H-bonding may preferentially stabilize the diaxial over the diequatorial conformation; for example, trans-1,2-dihalocyclohexanes, cis-1,3-cyclohexanediol, 2-chlorocyclohexanone etc exist as mixtures of the ee and aa conformations.

Although the equatorial conformer of a substituted cyclohexane is thermodynamically more stable than the axial form, the molecule may react in either conformation since the isomerization barrier is much less than the activation energies for most reactions. This also applies to the boat form, which is generally less stable because the hydrogen atoms at the "ends" of the boat would come closer together than in the chair form:



5.2) Number of isomers and conformations in 1,2,3,4-tetrachloroderivatives.

The same descriptive symbols and the same equilibrium relationships may be applied to the isomeric 1,2,3,4-tetrachlorocyclohexanes, benzene tetrachlorides and naphthalene tetrachlorides; the shape of the molecule of necessity will differ, depending on wheter a double bond is or is not present.

The ten theoretically possible isomeric forms are:

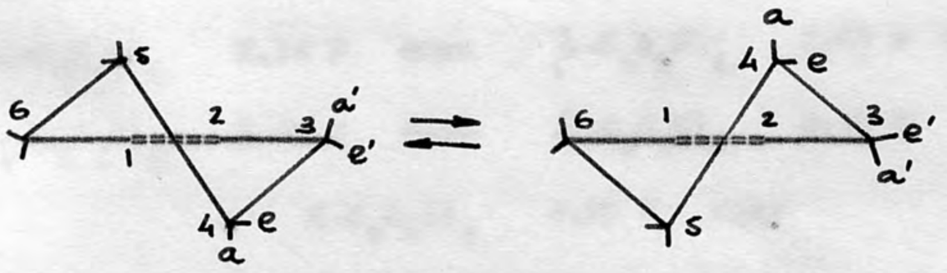
eeee $\rightleftarrows$ (aaaa)	eeea $\rightleftarrows$ (aaae)
eeae $\rightleftarrows$ (aaea)	eaae $\rightleftarrows$ aeea
eeaa (= aaee, identity)	eaea (= aeae, identity)

However, on the basis of ring conversion, the number capable of chemical separation is reduced to six. One would expect that the bracketted forms are less stable owing to 1a:3a repulsions.

The isomers eeee, eeea, eeae and aeea may exist in independent mirror image forms; the enantiomorphic forms of eeaa and eaea are transformed into each other by ring conversion and hence may not be separated chemically.

In a cyclohexene, the two carbons of the double bond (1 and 2), and the two carbon atoms attached to them (3 and 6) must be in the same plane (see section 5.4). The two remaining carbon atoms 4 and 5 take up a puckered or "half-chair" conformation:

which can be drawn schematically:



The valencies of C-3 and C-6 are in what might be called "quasi-equatorial" (e') and "quasi-axial" (a') positions. The valencies of C-4 and C-5 are equatorial and axial.

Unless fixed in some way by fusion to other rings, the two half-chair conformations are interconvertible like the two chair forms of a cyclohexane ring.

5.3) 3,4,5,6-Tetrachlorocyclohexa-1-enes (Benzene tetrachlorides).

The steric structures of the five known isomers of benzene tetrachloride have been established by photochlorinating the isomers individually and ascertainig which isomers of benzene hexachloride are formed[1].

The dipole moments of the five isomers were determined[2] and the results are in accordance with the results of chlorination. The values and conformations are:

α-$C_6H_6Cl_4$ 2.34 D eeaa β-$C_6H_6Cl_4$ 2.65 D aeea $\rightleftharpoons$ eaae

γ-$C_6H_6Cl_4$ 3.62 D eeea δ-$C_6H_6Cl_4$ 2.30 D eeee

ε-$C_6H_6Cl_4$ 2.19 D eeae

The chlorination of β-benzene tetrachloride has provided direct chemical evidence for ring conversion:

$$\beta\text{-}C_6H_6Cl_4\ (87\%\ \text{aeea} \rightleftharpoons 13\%\ \text{eaae}) + Cl_2 \longrightarrow$$

$$\longrightarrow 80\%\ \alpha\text{-}C_6H_6Cl_6\ (\text{aaeeee}) + 20\%\ \varepsilon\text{-}C_6H_6Cl_6\ (\text{eeaeea})$$

Despite the predominance of the form aeea in the initial material, 80% of the product was α-benzene hexachloride, providing that ring conversion was possible either in the original tetrachloride or in the resultant hexachloride.

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[1] Orloff et al, J. Am. Chem. Soc. 1953, 75 , 4243 .

[2] O. Bastiansen and J. Markali, Acta Chem. Scand. 1952, 6 , 442 .

5.4) 1,2,3,4-Tetrachloro-1,2,3,4-tetrahydronaphthalenes (Naphthalene tetrachlorides.

A naphthalene tetrachloride may be considered to be a hexasubstituted cyclohexene derivative in which a benzene ring is attached to the olefinic carbon atoms.

As shown by X-ray analysis the unsaturated and allylic carbons are coplanar; the two remaining carbons are situated one above and one below the plane of the ring.

Three of the six possible isomers have been separated and an attempt has been made by Schütz and Hahnfeld[1] to assign structures by study of their rates of dehydrochlorination with alkali. (These authors were unable to obtain again a fourth isomer described in the literature[2,3]).

Assuming vicinal elimination of hydrogen and chlorine[4] the rate must parallel the ratio of possibilities of trans-eliminations. From a con-

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1. F. Schütz and K. Hahnfeld, Chem. Ber. 1952, 85 , 131 .

2. E. Fisher, Ber. 1878, 11 , 735 .

3. M. Müller, Monatshefte 1953, 84 , 640 .

4. Cristol et al, J. Am. Chem. Soc. 1947, 69, 338 and 1951, 73, 676 .

sideration of the experimental data, the configurations have narrowed down as follows:

Dehydrochlorination of naphthalene tetrachlorides with alkali

Isomer	α	δ	γ
m.p.	181-2º	95-6º	133-4º
Rate coefficients:[a]			
1st stage	——	5.9	——
2nd stage	3.00	0.094	0.088
Number of possible trans-1,2-eliminations	2	1	0
Suggested orientation of chlorine atoms	eaea or aeea	eaee or eeea	eeee or eeaa
Products of hydrolysis	1,3- and 1,4- dichloronaphth.	60% 2,3- isomer	80% 1,4- isomer
Products of pyrolysis	?	?	2,3-$C_{10}H_6Cl_2$

([a] at 20º, in methanol-acetone 80-20%, by volume. Rate coefficients in l.mole^{-1}.min^{-1} ; 2nd stage of hydrolysis is faster than 1st for both α and γ-naphthalene tetrachlorides, hence only a coefficient k_2 is obtained).

One of the conformations, aeea, suggested for the α-isomer has been confirmed by X-ray analysis[1] :

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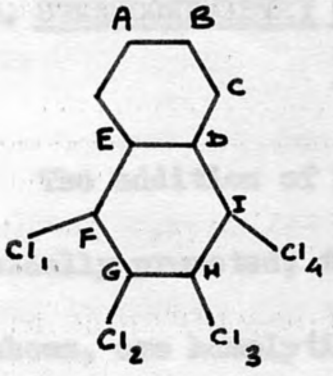
[1] M. A. Lasheen, *Acta Cryst.* 1952, 5 , 593 .



Bond lengths	Valency angles
AB = 1.386 A	ABC = 120°
BC = 1.407	BCD = 120°
CD = 1.405	CDE = 120°
DE = 1.386	CDI = 113°
EF = 1.549	EDI = 127°
FG = 1.551	$DICl_4$ = 105°
GH = 1.545	DIH = 106°
FCl_1 = 1.808	Cl_4IH = 108°
GCl_2 = 1.796	$IHCl_3$ = 111°
	IHG = 117°
	Cl_3HG = 113°

Projection of the molecule on the plane of the benzene ring.

These distances and angles may be compared with those of naphthalene (see section 3.1). The average length of the six C–C bonds in the aromatic ring, 1.40 A, is very close to the standard value (1.39) for the aromatic bond length. The bond common to both rings has the length 1.39 A, which implies that the attachment of the alicyclic ring has not changed the character of the aromatic bonds.

The average length of the other C–C bonds in the alicyclic ring is 1.55 A (standard value for aliphatic C–C bonds, 1.54 A).

6. STEREOCHEMISTRY OF SOME ADDITION REACTIONS [1,2,3].

The addition of halogens to olefinic substances may be photochemically promoted; these processes, as their high quantum efficency shows, are homolytic chain reactions.

The addition of chlorine to benzene is important because one of the five stereoisomeric 1,2,3,4,5,6-hexachlorocyclohexanes obtained has insecticidal properties. The quantum yields are 20 in the vapour phase and ca. 2500 in the liquid phase. The reaction involves three steps, and the final step (3,4,5,6-tetrachlorocyclohex-1-ene +

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[1] "Structure and Mechanism in Organic Chemistry", C. K. Ingold. Bell & Sons Ltd, London 1953. Pages 658-676.

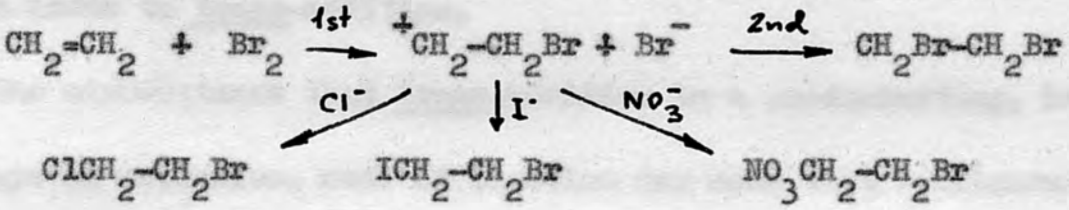
[2] "Mechanism and Structure in Organic Chemistry", E. S. Gould. Holt, Rinehart & Winston, Inc. New York 1959. Pages 489 ff.

[3] "Organic Chemistry", D. J. Cram and G. S. Hammond. 2nd edition. Mc Graw-Hill Book Company. New York, London 1964. Pages 390-395.

[4] "Free radicals in solution", C. Walling. John Willey & Sons, Inc. New York 1957, 308.

chlorine) has been shown to be definitely a radical-chain process, since the isomers are stable to chlorine in the dark but react rapidly on illumination. Each benzene tetrachloride yields two or three stereoisomeric hexachlorocyclohexanes; so radical addition occurs on either side of the double bond, and the final reaction with chlorine may be either cis or trans.

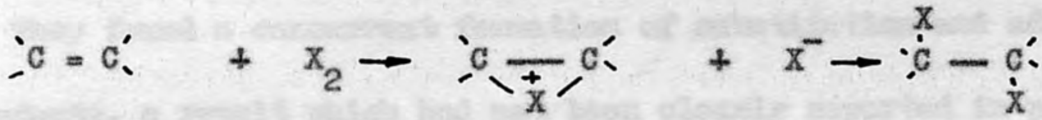
The thermal or "dark" additions of halogens (other than fluorine whose reactions seem to be entirely homolytic) need a polar environment and are heterolytic. These additions follow a two-stage mechanism; that is, they proced through intermediates in which only one of the two halogen atoms has become attached to the olefin; the second stage can be diverted by a source of active foreign anions, for example:



$$CH_2{=}CH_2 + Br_2 \xrightarrow{1st} {}^{+}CH_2{-}CH_2Br + Br^- \xrightarrow{2nd} CH_2Br{-}CH_2Br$$

$$\xrightarrow{Cl^-} ClCH_2{-}CH_2Br \qquad \xrightarrow{I^-} ICH_2{-}CH_2Br \qquad \xrightarrow{NO_3^-} NO_3CH_2{-}CH_2Br$$

Additions of halogens have generally been thought to be predominantly trans. Thus addition of halogens to maleic acid in hydroxylic solvents gives not less than 80% of racemic dihalogenosuccinic acid, which is predominating trans-addition. The corresponding additions to fumaric acid give meso-dihalogenosuccinic acids, which also is trans-addition. The two-stage mechanism allows trans-addition, but does not enforce it. The factor generally considered to be responsible for the prevalence of trans-addition is that the already bound halogen in the intermediate acts as a configuration-holding group:



$$>C=C< \; + \; X_2 \longrightarrow >C\underset{\overset{+}{X}}{-}C< \; + \; X^- \longrightarrow >\overset{X}{C}-\underset{X}{C}<$$

When, in the last stage of addition, a halide ion attacks the cation, it does so (equally or not, according to the symmetry of the former double bond in the olefin) at either carbon atom, and always produces an inversion of configuration at the atom attacked; provided that the configuration of the cation has been firmly held, such inversion leads to trans-addition.

The circumstance that trans-addition is a predominating, but not always an exclusive, mode of reaction may mean that configurations are not always firmly held.

7. PREVIOUS WORK IN SYSTEMS RELATED TO NAPHTHALENE [1].

De la Mare et al. have studied the chlorination of some aromatic hydrocarbons with molecular chlorine in anhydrous acetic acid, at 25º. They found a concurrent formation of substitution and addition products, a result which had not been clearly reported in previous works. In the addition products, chlorine adducts and acetoxychloride adducts were found:

	Percentages of reacted chlorine		
Hydrocarbon	Substitution	Chlorine adducts	Acetoxychloride add.
Biphenyl	76.5	17.5	2
Phenanthrene	44	42	14
Fluorene	80	11	5

Since, in the presence of added chloride ions, no less hydrogen chloride is produced than in its absence, a scheme involving only the carbonium ionic intermediates (see section 2) cannot adequately represent the reaction. The observations require a more elaborate

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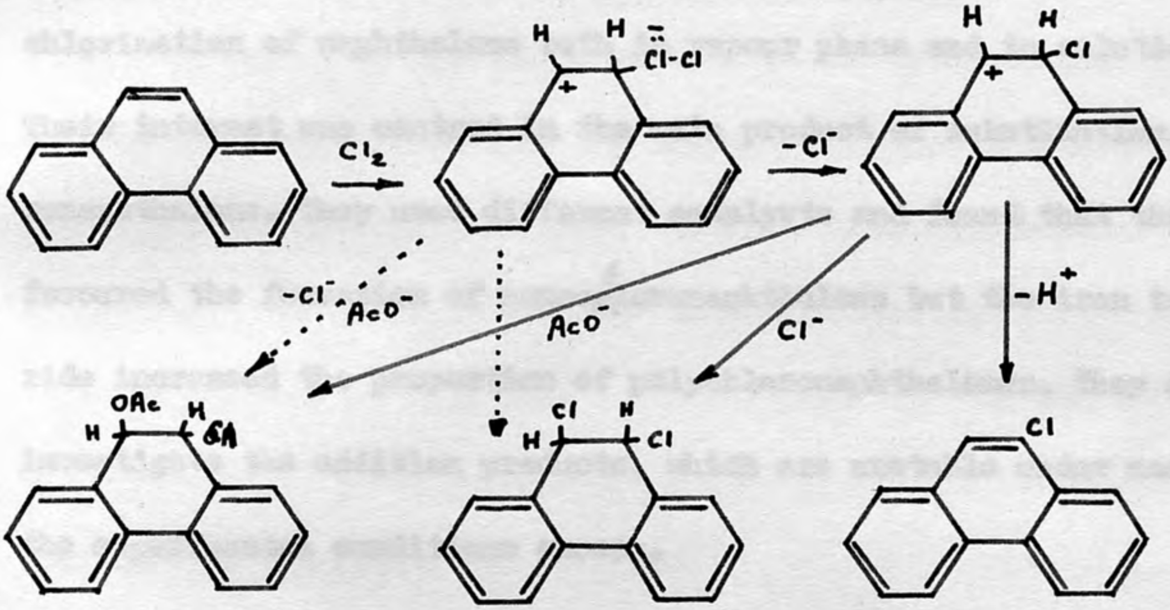
[1] P. B. D. de la Mare et al., J. Chem. Soc. 1961, 2749; 1961, 5285 and 1962, 988 .

scheme:



The analysis of the reaction mixture (in the example of the phenanthrene) is complicated by the fact that it seems that <u>cis-</u> and <u>trans-</u>isomers both of the dichloride adducts and of the acetoxychloride adducts are present (see part III).

8. PREVIOUS WORK ON NAPHTHALENE.

The chlorination of naphthalene has been studied over more than a century. Unfortunately very little systematic work has been done, and in many cases the exact experimental conditions are difficult to repeat.

a) Nuclear substitution products. Ferrero and coworkers[1] studied the chlorination of naphthalene both in vapour phase and in solutions. Their interest was centred in the main product of substitution, 1-chloronaphthalene. They used different catalysts and found that the iodine favoured the formation of monochloronaphthalene but the iron trichloride increased the proportion of polychloronaphthalenes. They did not investigate the addition products, which are unstable under most of the experimental conditions chosen.

The influence of the solvent was studied, carrying out the chlorinations in CCl_4, C_6H_6, C_6H_5Cl, o-$C_6H_4Cl_2$, $C_6H_5CH_3$, $C_{10}H_{18}$, $C_6H_5NO_2$, Et_2O, AcOH, AcOEt, $C_2H_2Cl_4$ and C_2HCl_5.

Some of the solvents were not convenient for different reasons: they were more or less attacked by chlorine ($C_6H_5CH_3$, $C_{10}H_{18}$), or it was difficult to separate the solvent from the products of chlorination ($C_6H_4Cl_2$), or the reaction was too slow ($C_2H_2Cl_4$, C_2HCl_5).

The experiments in AcOH produced 64% of 1-chloronaphthalene and

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[1] P. Ferrero et al., Hel. Chim. acta 1928, 11 , 416 ; 1929, 12 583 ; 1930, 13 , 1009 .

36% of dichloronaphthalenes and naphthalene chlorides (not investigated), at 18º. The proportions at 115º were 80 and 20% respectively.

A great number of references related to the chlorination of naphthalene have accumulated over the years, most of them describing industrial methods, uses and properties of 1-chloronaphthalene.

b) Adducts. The first description of the isomers of naphthalene tetrachloride was made last century[1,2,3]. Still in 1952 the configuration and knowledge of these isomers was uncertain. Müller[4] described again four isomers (including the β, which was found together with a naphthalene dichloride by Fisher[2]), but simultaneously Schütz and Hahnfeld[5] were unsuccesful in preparing it; they prepared the α-naphthalene tetrachloride by chlorination of the hydrocarbon in carbon tetrachloride, and the γ and δ-isomers by reaction between the naphthalene and liquid chlorine. Their experiments about rates and products of

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1. R. Grimaux, Bull. Soc. Chim. France 1872, (2) 18 205 .
2. E. Fisher, Ber 1878, 11 735 .
3. A. R. Leeds, J. Am. Chem. Soc. 1880, 2 205 .
4. M. Müller, Monatshefte 1953, 84 640 .
5. F. Schütz and H. Hahnfeld, Chem. Ber. 1952, 85 131 .

alkaline hydrolysis and the configurations assigned to them are described in section 5.4 .

c) Reactivity measurements.

Lauer and Oda[1] determined the rate of chlorination of benzene and naphthalene in acetic acid not very accurately as it was pointed out by Robertson and de la Mare[2] . The latter found that $k_2 = 6.5 \pm 0.5$ $l.mole^{-1}.min^{-1}$ in AcOH with 1% of water, at 24º. A slight autocatalysis thought to be the result of the formation of HCl was detected.

Dewar and Mole[3] measured the chlorination rates of naphthalene at 25º, in AcOH and in AcOH-CCl_4 (1:3 by volume); the reaction is faster in the former solvent:

$k_2 = 6.3 \times 10^{-2}$ and $k_2 = 1.9 \times 10^{-4}$ $l.mole^{-1}.sec^{-1}$ respectively.

d) Finally P. B. D. de la Mare, R. Koenigsberger and J. S. Lomas began to study the products of chlorination of naphthalene in acetic acid. Three kinds of products were found: substitution (1-chloronaph-

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1. Lauer and Oda, Ber 1936, 69 1061

2. P. W. Robertson and P. B. D. de la Mare, J. Chem. Soc. 1943, 279.

3. M. J. S. Dewar and T. Mole, ibid 1957, 342.

thalene), addition (α-naphthalene tetrachloride could be characterized, and at least other isomer was present), and an unidentified naphthalene acetoxytrichloride.

9. AIMS AND OBJECTS OF THE PRESENT INVESTIGATION.

The study of the chlorination of naphthalene has been chosen as a continuation of the studies on other hydrocarbons carried out in the Department of Chemistry of the Bedford College.

The literature describes many products of reaction of naphthalene with chlorine, especially products of substitution. The work described in this thesis has been done to establish as far as possible the structures, properties, and reactions of the products of addition of chlorine.

The kinetics of chlorination have also been looked at in solvents with different polarity, namely acetic acid and chloroform. In the latter case, as the kinetics found were irregular, the influence of different catalysts was studied and the anomalies explained.

However the study of the products has been emphasized. The knowledge of α, γ and δ-naphthalene tetrachlorides is now much better. The attempts to obtain the fourth isomer reported in the literature, the β-tetrachloride, have been unsuccesful. However a fifth isomer, which we designate the ε-tetrachloride, has been isolated and characterized for the first time.

Another hitherto unreported addition compound, a naphthalene acetoxytrichloride, is also described, and its hydrolysis has been studied.

Part II

EXPERIMENTAL

10. CHLORINATIONS IN ACETIC ACID.

10.1) Description of the reaction.

When a solution of chlorine in acetic acid is added to another of naphthalene in the same solvent, a fairly rapid reaction occurs, with formation of a mixture of products. The study of this reaction and of the products obtained is described in sections 10 to 15. The experimental procedure is exemplified in the following description.

Naphthalene, 7.68 g (75 mM), purified by crystallization from methylated spirit, m.p. 80-80.5º, was dissolved into 50 ml of acetic acid AnalaR (which was always used except where otherwise stated), contained in a conical flask protected from the light (to avoid its catalytic effect favouring homolytic reactions). A solution of chlorine in acetic acid was prepared by passing the gas from a comercial cylinder (ICI) through water (to remove hydrogen chloride) and concentrated sulfuric acid (for drying) into a volume of the solvent contained in a flask protected from the light with black paint or paper. After a while the passage of chlorine was stopped, and an aliquot part was pipetted into an aqueous solution of potassium iodide and titrated by the conventional method with standard sodium thiosulfate (BDH) 0.1 N, starch being added towards the end of the titration for determining the end-point.

A convenient volume, containing 75 to 100% of the number of moles of naphthalene, (60 ml in the run being described), was added to the solution of hydrocarbon; the mixture was stoppered and left overnight in the darkness.

The reaction proceeds quite speedly, with evolution of heat, and is complete in some minutes. Remaining chlorine was never found when the isolation of products was started.

In different runs the quantities of naphthalene employed ranged from 75 to 200 mM. The chlorine added was always between 75 and 100% (in moles) of the hydrocarbon; it was intended that the hydrocarbon should be present in excess to avoid the formation of di- or poly-chloronaphthalenes. (It should be remarked that, as the addition products formed by taking up 2 moles of the halogen for every mole of naphthalene are an important part of the total products, the hydrocarbon will be in excess even when the molar ratio of halogen to hydrocarbon is 1:1).

The total volume of acetic acid was from 150 to 500 ml in different runs.

10.2) Isolation and composition of the products.

The mixture of reaction products was poured into 700 to 1000 ml of water and extracted three times with ether. The ethereal extracts were collected and washed with water to remove the acetic acid (from 12 to 14 washings are necessary; when the stability of the products had been established, a 5% aqueous solution of sodium hydrogen carbonate was used, and the number of washings fell to 6 or 7).

The solution was dried with sodium sulfate and later the solvent removed at room temperature under reduced pressure. The residue was a brown liquid which sometimes contained a small quantity of crystals.

This liquid (if some crystals were present, 5 to 10 ml of benzene were added to disolve them) was adsorbed over 300 g of silica gel (M&B) contained in a column, in order to separate the products by chromatography. The elution was started with light petroleum, b.p. 40-60º, (this and all the solvents used for chromatography were commercial samples M&B without any purification) and changed gradually; for example, in the run being described the quantities employed were:

Volume (ml)	Light petroleum 4o-60º	Benzene	Ether
600	100%	——	——
400	75%	25%	——
250	50%	50%	——
250	25%	75%	——
200	——	100%	——
100	——	50%	50%
300	——	——	100%

About 40 fractions of 50 ml were collected, giving a perfect separation for three kinds of products: fractions 9 to 17 contained naphthalene and 1-chloronaphthalene (5.4 g), very easily detected because both products show blue fluorescence under ultarviolet light (the test is carried out evaporating a drop on a filter paper and examinig the spot; it can also be done by using a plate for thin-layer chromatography). These fractions have not been examined further.

Fractions 24 to 28 contained a mixture of naphthalene tetrachlorides (3.8 g), appearing under ultraviolet light as a spot with a weak violet fluorescence. The composition of this mixture, and the variation of this with conditions is described in sections 11 to 13.

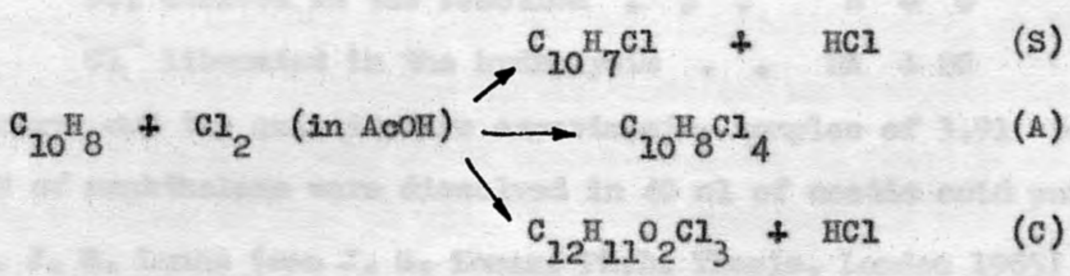
Finally, fractions 35 to 38 contained an acetoxytrichloride (0.9g) and coloured materials which made the test with ultraviolet light (which does not usually show any fluorescence) not necesary. The properties of the acetoxytrichloride are described in section 14.

10.3) Quantitative study of the reaction; influence of added electrolytes.

Knowing that the chlorination of naphthalene produced the three kinds of products described above, we then examined how these products were affected by the addition of some electrolytes in order to understand better the mechanism of the reaction and the intermediates involved.

The study was done using a technique devised in these laboratories by Dr. R. Koenigsberger, which reduced the errors to a minimum.

Considering the different products formed:



$C_{10}H_7Cl$ + HCl (S)

$C_{10}H_8$ + Cl_2 (in AcOH) → $C_{10}H_8Cl_4$ (A)

$C_{12}H_{11}O_2Cl_3$ + HCl (C)

and realising that the monochloronaphthalene and the acetoxytrichloro adduct (notation S and C, respectively) are formed in the same number of moles as the hydrogen chloride evolved, it was only necessary to determine carefully the initial chlorine (which produces both kinds of products and the adducts of chlorine, denoted A), and with the same care the hydrochloric acid produced, to have two equations in a system with three unknowns. The third equation comes from the determination of the chloride ions liberated in an alkaline hydrolysis of a sample of the products:

$$C_{10}H_7Cl \quad + \quad OH^- \not\longrightarrow \text{ no reaction}$$

$$C_{10}H_8Cl_4 \quad + \quad 2OH^- \longrightarrow C_{10}H_6Cl_2 \quad + \quad 2H_2O \quad + \quad 2Cl^-$$

$$C_{12}H_{11}O_2Cl_3 \quad + \quad 4OH^- \longrightarrow C_{10}H_7OCl + 4H_2O + CH_3CO_2^- + 2Cl^-$$

The substitution product does not react with the alkali but both kinds of adducts liberate a number of equivalents of chloride ions equal to the number of moles of chlorine used up when they were formed. Then the three equations become:

Initial chlorine . . . . $S + 2A + 2C$
HCl evolved in the reaction . . . $S + C$
Cl^- liberated in the hydrolysis . . $2A + 2C$

To carry out the quantitative experiments, samples of 3.91 to 5.86 mM of naphthalene were dissolved in 40 ml of acetic acid purified by Dr. J. S. Lomas (see J. S. Lomas, Ph.D. Thesis, London 1965) with less than 0.01% of water.

A solution of chlorine in the same solvent was prepared and diluted to give a convenient concentration such as 10 ml had a number of moles about 75% of that of hydrocarbon.

The solution of hydrocarbon was always prepared in a Quickfit conical flask of 50 ml, protected from the light.

To avoid errors produced by evaporation of chlorine, 4 flasks containing aqueous solutions of potassium iodide were prepared simultaneously; in a time as short as possible, two samples of 5 ml of the solution containing chlorine were pipetted into two flasks with potassium iodide; a third sample of 10 ml was pipetted into the flask with the hydrocarbon. The flask was stoppered immediately. Finally other two samples of 5 ml were pipetted into the remaining flasks with potassium iodide. The flask containing the reaction mixture was left overnight in darkness; the iodine liberated in the other flasks was immediately titrated with standard thiosulfate. Only if the four numbers obtained were in good agreement (for example, 24.0 , 23.9 , 23.9 and 24.0 ml in a run) was the determination considered valid.

The following day (or later) the flask containing the reaction mixture was opened, taking measures to avoid any lose of hydrochloric acid. A rubber tube was fitted round the neck of the flask and filled with distilled water. The stopper was then carefully freed, so that the water filled the dead-space in the flask but no hydrochloric acid escaped (this space is very small because a flask of about 50 ml is used for a volume of just 50 ml). The whole solution was poured into a mixture of ether and distilled water (also used to wash the flask), and extracted carefully.

The aqueous layer was extracted twice more and all the ethereal extracts were put together. The solvent was evaporated without heating and the semi-liquid residue containig all the organic products was dissolved in methanol and made up to 100 or 250 ml in a volumetric flask. Samples of 5 or 10 ml were then boiled under reflux for 3 hours with a solution of sodium methoxide in methanol; under these conditions the adducts are completely dehydrochlorinated and the alkali does not attack the substitution product. After the reaction, the whole solutions diluted with acetone were acidified with dilute nitric acid, lacmoid being used as indicator, and the Cl^- liberated in the reaction was titrated potentiometrically with 0.01 N silver nitrate (a volume between 6 and 10 ml was usually required).

Meanwhile the aqueous part derived from the extraction and containing the hydrochloric acid produced directly in the reaction between chlorine and the hydrocarbon, was distilled partially to eliminate about 10% of water and the dissolved ether (this distillate was shown to contain no HCl). The residue was made up to 250 or 500 ml with distilled water, and samples of 5 to 10 ml were added to excess of acetone and titrated potentiometrically with 0.01 N silver nitrate. Care was taken to ensure that all the reagents were free from chloride ions.

Three samples of each group were titrated, and every day the silver nitrate was standardized against standard hydrochloric acid.

The method was applied to the chlorination of naphthalene in pure acetic acid without any electrolyte, and the determination was carried out twice.

Afterwards more experiments were carried out with various added electrolytes.

First, LiCl was investigated to see if the presence of chloride ions increased the proportion of addition products. Then, NaOAc was employed as a basic salt able to fix the hydrogen chloride produced. It also provides a source of acetate ions, the rôle of which in the formation of the acetoxytrichloro adduct was to be investigated.

A new electrolyte, $HClO_4$, known to have important effects in the chlorination of other hydrocarbons, was also examined; as a strong acid it represses the ionization of the solvent and of hydrogen chloride produced in the reaction.

Finally $LiClO_4$ was used as a strong electrolyte without any ion common with the substances involved.

The influence of water, and of acetic anhydride, on the course of chlorination in presence of perchloric acid were also investigated.

The results are summarized in table I, page 59.

TABLE I. Influence of added electrolytes in the chlorination of naphthalene, at room temperature.

$C_{10}H_8$	Cl_2	Electrolyte	mM	mM HCl	% Reacted naphthalene			Other subs-
mM	mM			evolved	S	A	C	tances
3.91	2.27	——		1.41	66.1	25.5	8.4	——
3.91	2.39	——		1.45	64.6	26.6	8.8	——
5.47	2.67	LiCl	4.77	1.56	68.9	27.2	4.0	——
5.47	3.51	NaOAc	5.0	2.19	71.2	24.2	4.5	——
5.47	3.26	$LiClO_4$	5.0	2.29	74.2	18.6	7.1	——
5.47	3.56	$HClO_4$	4.72	2.77	80.8	13.3	6.0	11 mM Ac_2O
5.86	5.30	"	5.0	4.05	80.8	13.9	5.2	——
5.47	2.63	"	24.0	2.21	83.5	9.2	7.2	42 mM H_2O
3.91	2.30	"	25.0	1.93	86.6	9.0	4.4	——

Reaction volume 50 ml .

11. THE α-NAPHTHALENE TETRACHLORIDE.

The α-1,2,3,4-tetrachloro-1,2,3,4-tetrahydronaphthalene is the main component of the mixture of addition products obtained by chlorination of naphthalene in acetic acid; as was pointed out in section 10.2, these products are eluted by benzene, after 1-chloronaphthalene and before naphthalene acetoxytrichloride and coloured materials. After the solvent had been evaporated, it was possible, by crystallization from light petroleum (b.p. 60-80º or 80-100º), to obtain a crop of crystals of α-naphthalene tetrachloride, m.p. 181-2º, comprising 90% of the original mixture. The remaining product had a melting range 90-150º and further chromatography resulted in no purification.

The α-isomer is the most stable and is relatively insoluble in a variety of solvents including benzene, acetone and methanol; these properties allow its easy isolation. Its infrared spectrum was recorded (see Appendix) and compared with that of the remaining mixture, which, of course, showed more peaks belonging to other isomers.

As a test of purity its alkaline hydrolysis was followed kinetically in the conditions employed by Schütz and Hahnfeld[1]. The hydrolysis of this isomer has two steps, and because the reaction follows second-order kinetics without any obvious disturbances, the first

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[1] F. Schütz and K. Hahnfeld, Chem. Ber. 1952, 85, 131.

stage is considered to be rate-determining:

$$\alpha\text{-}C_{10}H_8Cl_4 + OH^- \xrightarrow{\text{SLOW}} C_{10}H_7Cl_3 + Cl^- + H_2O$$

$$\xrightarrow[\text{FAST}]{OH^-} C_{10}H_6Cl_2 + H_2O + Cl^-$$

The results can be seen in table II :

TABLE II. Alkaline hydrolysis of α-naphthalene tetrachloride in acetone-methanol (20-80%, by volume) at 25º.

Run	t(min)	100(b-x)	100(a-x)	100x	k_2
A	0	1.47	1.92	—	-
A	25	0.38	0.84	1.09	4.6
A	50	0.18	0.64	1.29	4.4
B	0	1.63	1.98	—	-
B	10	0.82	1.17	0.81	4.6
B	20	0.50	0.85	1.13	4.7
B	30	0.38	0.73	1.25	4.3

$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$; $a = \frac{1}{2}[NaOH]$, $b = [C_{10}H_8Cl_4]_0$, x = tetrachloride reacted at time t . The average value of k_2 is 4.5 $l.mole^{-1}.min^{-1}$.

Schütz and Hahnfeld found $k_2 = 3.00$ at 20º.

12. THE γ-NAPHTHALENE TETRACHLORIDE.

12.1) Synthesis and properties.

Because it was supposed that the residue, m. range 90-150º (obtained after separating pure α-naphthalene tetrachloride from the addition mixture obtained in the chlorination of naphthalene which has been described in the preceding section) might contain the γ-isomer, the synthesis of this compound was attempted following again Schütz and Hahnfeld.

Naphthalene, 7 g., was slowly added to 80 ml. of liquid chlorine, the mixture being shaken occasionally. The excess of chlorine (used in a molar ratio 68:1) was allowed to evaporate and the waxy residue was dissolved in 4 to 5 ml. of hot benzene and allowed to cool. A crop of white crystals, 2 g., was obtained; recrystallized from methylated spirit, they melted at 123-150º.

The attempt was repeated three times without succes. Crystallization from different solvents failed to give a pure substance; for example, the m. ranges were : 128-150º from ethanol, 118-136º from methanol, 122-9º from light petroleum b.p. 80-100º, and 122-130º from benzene. Adsorption on a column packed with silica gel followed by elution with light petroleum (b.p. 40-60º) did not give further purification. This experiment led to the discovery that the γ-naphthalene tetrachloride shows a yellow fluorescence under ultraviolet light; the other isomers show a very weak violet fluorescence.

The equivalent weight of the impure γ-isomer was determined by alkaline hydrolysis. The values obtained, 132.0 and 132.1, were in good agreement with the theoretical value, 135, and showed that the impurity was also a naphthalene tetrachloride. When the hydrolysis was followed kinetically, it could be seen that the product was a mixture of both α and γ-isomers. As their rates of hydrolysis are very different (at 20º, $k_2 = 0.088$ and 3.00 $l.mole^{-1}.min^{-1}$ for the γ and α, respectively), an attempt was made to destroy the α-tetrachloride by partial hydrolysis. This method gave only very small quantities of pure γ-isomer.

Finally, this isomer could be obtained succesfully and in reasonable yield by a modification of the same method. The reaction was made under direct sunlight, in order to catalyse a homolytic reaction, at -34º, the boiling point of the chlorine, and a device for addition of naphthalene without opening the flask was employed: a two-necked flask was used for the chlorine; a second flask connected to it by a rubber tube permited the hydrocarbon to be added without condensation of moisture; a calcium chloride tube fitted in the other neck allowed the chlorine to evaporate. Starting with 10 g. of naphthalene and proceeding as has been described, 3 g. of γ-naphthalene tetrachloride could be isolated; after crystallization from methylated spirit, white needles m.p. 133-4º were obtained and no further purification was necessary.

The product was analysed by Dr. A. Bernhardt (who also has made all the other analyses described in this thesis) :

	C	H	Cl
Found	44.36	3.01	52.61
$C_{10}H_8Cl_4$ requires	44.44	2.98	52.59

The infrared spectrum was recorded and it could be seen that this isomer was not present in the mixture obtained from the chlorination in acetic acid.

12.2) Study of thermal decomposition.

A sample of 0.35 g. of pure γ-naphthalene tetrachloride was heated without solvent, at 220º during 90 minutes. The compound became black, a gas (probably HCl) was evolved and the residue was crystallized from methylated spirit to give a small quantity of white needles m.p. 178-180º, identified by its infrared spectrum as α-naphthalene tetrachloride; we had no succes in attempting to isolate the bulk of the product, which should be 2,3-dichloronaphthalene:

$$\begin{tikzcd}
 & (\text{2,3-}C_{10}H_6Cl_2 + 2HCl)\ \text{expected product} \\
\gamma\text{-}C_{10}H_8Cl_4 + \text{heat} \arrow[ur] \arrow[dr] & \\
 & 5\%\ \alpha\text{-}C_{10}H_8Cl_4
\end{tikzcd}$$

The isomerization indicates the stability of the α-isomer.

13. THE δ-NAPHTHALENE TETRACHLORIDE.

13.1) Attempts of synthesis and purification.

As it has been pointed out in sections 11 and 12, the mixture of addition products obtained by chlorination of naphthalene in acetic acid contained mainly α-naphthalene tetrachloride with a small proportion of another isomer which was not the γ-tetrachloride.

It seemed probable that the unknown product was the δ-isomer, the third clearly described in the literature.

In an attempt to obtain a greater proportion of this isomer, the chlorination of naphthalene was repeated with two different electrolytes added to the solvent; as a consequence of the quantitative studies of chlorination described in section 10.3, LiCl and $HClO_4$ were choosen as the electrolytes with the most pronounced effects on the proportion of addition products, thinking that at least one of them could influence the mechanism of the reaction and hence might change the proportion of the naphthalene tetrachlorides.

The results of the experiments undertaken confirmed that the $HClO_4$ lesesns the proportion of addition products, and that LiCl has a smaller effect in the same direction.

The products obtained, compared with those of the run described in section 10.2 , without electrolyte, can be seen in Table III (experi-

ments A, B and C), page 67.
α-Naphthalene tetrachloride was separated by crystallization and the infrared spectra of the remaining mixtures showed peaks at that time unidentified.

The alkaline hydrolysis of these mixtures was followed kinetically at 25º, (as has been described in section 11 for the α-tetrachloride), values of k_2 about 7.4 $l.mole^{-1}.min^{-1}$ being obtained for times of reaction of 2 or 3 minutes. (In fact no constants were obtained, the values ranging from 7.7 at t = 2 min. to 0.7 at t = 160 min.). The values given by Schütz and Hahnfeld at 20º were :

α-$C_{10}H_8Cl_4$ $k_2 = 3.00$; γ-$C_{10}H_8Cl_4$ $k_2 = 0.088$ and δ-$C_{10}H_8Cl_4$ k_2 (first stage) = 5.9 and k_2 (second stage) = 0.094 .

We have found $k_2 = 4.50$ (at 25º) for the α-tetrachloride, therefore the δ-isomer (or, less probably, a new isomer also able to be hydrolysed faster than the α-tetrachloride) should be present.

Experiments D, E and F, which can also be seen in Table III, were carried out to obtain the δ-isomer.

The remaining 3.4 g. of the addition mixture in D (after crystallizing the α-isomer) were rechromatographed, light petroleum, b.p. 40-60º, being used for elution of fractions of 50 ml. which gave: from fractions 1-10, 0.1 g. of m.p. 115-123º (α + γ-tetrachlorides); from fractions 11-18, 0.2 g. of m.p. 182-4º (pure α-isomer); from fractions 19-48, 1.1 g. of m.p. 95-6º (δ-tetrachloride); and finally from fractions 49-56, eluted with ether, only coloured materials (tars). This

TABLE III. Chlorinations of naphthalene in acetic acid.

Experiment		A	B	C	D	E	F
Starting materials:							
Naphthalene, g.		7.68	9.6	9.6	25.6	25.6	25.6
Chlorine, g.		3.86	4.97	4.56	11.1	18.6	17.7
Added electrolyte		None	LiCl	$HClO_4$	LiCl	LiCl	LiCl
Concentration, N		—	0.127	0.127	0.57	0.40	0.40
Acetic acid, ml.		110	180	170	349	500	500
Products:							
$C_{10}H_8 + C_{10}H_7Cl$, g.		5.4	10.3	9.0	27.7	27.0	26.7
Addition mixtures, g.		3.8	2.8	0.9	3.6	7.2	10.5
α-isomer crystallized, g.		3.2	0.9	0.5	0.2	0.35	2.2
Acetoxytrichloro add. g.		0.9	1.2	1.0	0.9	3.5	2.0
% Reacted naphthalene	substitution	54.0	73.4	88.4	-	-	-
	α-isomer	35.0	9.5	3.6	-	-	-
	δ-isomer	2.9	9.5	2.0	-	-	-
	acetoxyadduct	8.0	7.6	6.1	-	-	-
	γ-isomer	Traces			-	-	-

It must be pointed out that the chromatographic separation of the chlorine and acetoxychloro adducts was not perfect in experiments E and F.

The percentages of naphthalene tetrachlorides (in the addition mixtures) were estimated preparing mixtures of the isomers and recording their infrared spectra for comparing with those of their obtained mixtures.

has been the only time that pure δ-tetrachloride has been isolated. When the same method was applied to the mixtures from experiments E and F, only impure δ-isomer was isolated, with a m.p. 86-91°. We have not been able to clarify the reasons for this irreproducibility; several attempts to purify these fractions by rechromatography were without success.

It is concluded that as this isomer is the most soluble, small proportions of the other isomers which cannot be removed by crystallization, can influence the melting point and prevent complete purification.

The equivalent weight of the slightly impure δ-tetrachloride was determined by alkaline hydrolysis. Values of 134.0 and 133.8 were obtained; naphthalene tetrachloride requires 135.0 .

The analysis of the slightly impure specimen was:

	C	H	Cl
Found	44.43	3.16	52.63
$C_{10}H_8Cl_4$ requires	44.44	2.98	52.59

Further purification was attempted by various methods, without succes, as follows:

a) Slow crystallization from methanol, the solution being seeded with a crystal of the pure compound (in this solvent the differences of solubility are the greatest); gave crystals m.p. 90-3°.

b) Sublimation at 100° and reduced pressure (4 mm). Crystals apparently very pure but with a m.p. 90-3°; samples taken at different times of the sublimation gave always the same melting point.

c) Zone melting (by courtesy of Dr. E. A. Johnson in the Medical Research Council laboratories) gave material m.p. 88-96º, not improved by recrystallization. The infrared spectra of different samples taken from different parts of the column used for the zone melting were identical and also coincident with that of the starting material; only a very small peak was slightly increased.

13.2) Stability and thermal decomposition.

It was supposed that the δ-tetrachloride was not stable to the heat, because of its behaviour in the attempted purification by zone melting; so the following test was carried out: the whole sample, 1.3 g. m.p. 88-96º, was heated for some time at a certain temperature; after this period its infrared spectrum was recorded and when no variation was observed, the sample was heated at a higher temperature and the process repeated; the results found were:

Temperature	Time of heating	I.R. spectrum showed:
110º	3 hours	No change
135º	5 hours	No change
185º	3 hours	No change
210º	4 hours	Total decomposition

In the last test a black liquid residue was obtained, which after chromatographic purification gave only about 0.1 g. of a colourless liquid, with a very complicated infrared spectrum. This material was supposed to be a mixture of dichloronaphthalenes.

14. NAPHTHALENE ACETOXYTRICHLORIDE AND NAPHTHALENE HYDROXYTRICHLORIDE.

During a period of time extending over 9 months, while the naphthalene tetrachlorides described in sections 11 to 13 were being investigated, the third group of products (see section 10.2) was accumulated and stored from many chlorinations in acetic acid. When this stored mixture, weighing 12 g., was crystallized from light petroleum (b.p. 80-100°), 5 g. of pure white needles were isolated, m.p. 124-5°.

Its infrared spectrum (see Appendix) showed the characteristic stretching vibration of a C=O bond at 1740 cm^{-1}. A sample gave the following analysis:

	C	H	O	Cl
Found	49.03	3.77	10.68	36.15
$C_{12}H_{11}O_2Cl_3$ requires	49.06	3.75	10.90	36.29

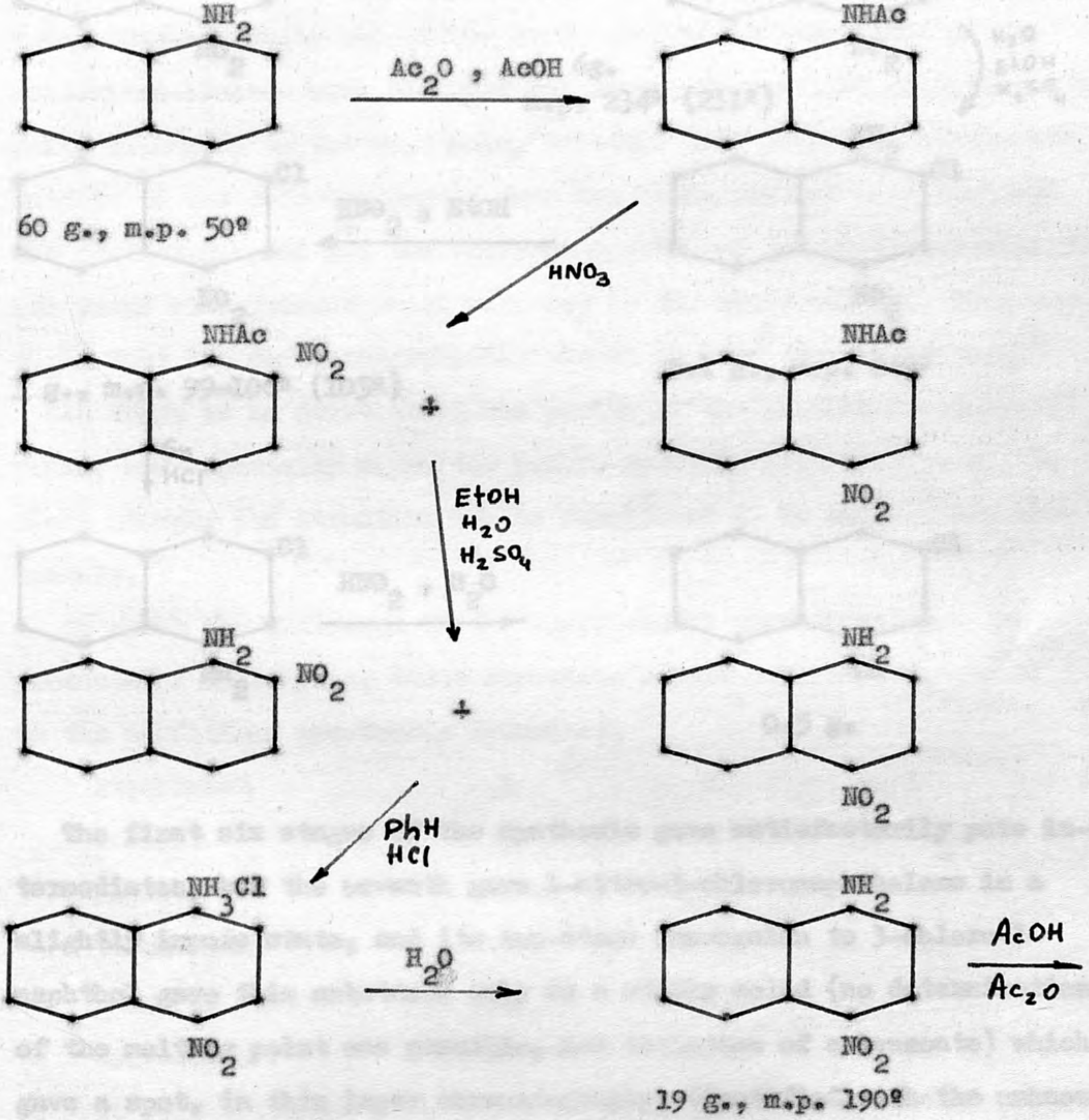
The uncrystallized residue, which made up to 54% of the starting mixture, was a coloured, very viscous liquid, which resisted any further attempt of crystallization or purification. Its infrared spectrum showed the peaks of the pure acetoxytrichloride as well as many others.

It has been found in several experiments carried out in other solvents (which will be described in sections 17 and 18) that this coloured part eluted from the chromatographic column with ether, has an infrared spectrum with peaks where the vibrations C=O and O-H are expected; this suggests the presence of naphthols and quinones, partially derived by oxidation sequences and partially by hydrolysis on the column, because the final elution with ether, which can contain water, is strongly exothermic. The weight of these residues in experiments made in other solvents is about 1 to 5% of the total products.

The pure 1-acetoxy-2,3,4-trichloro-1,2,3,4-tetrahydronaphthalene was shown to have this structure through its acid and alkaline hydrolysis; this result was confirmed by its proton magnetic resonance spectrum (see section 20).

A sample (0.2 g., m.p. 124-5º) was boiled in aqueous alcoholic sodium hydroxide during three hours. The solution became coloured in red; after that time it was allowed to cool, acidified and extracted with ether, and this solution was examined by thin layer chromatography. The plates (made with silica gel Merck), were developed with benzene, and were sprayed with a freshly prepared mixture of p-nitroaniline hydrochloride, sodium nitrite and aqueous sodium carbonate. Two spots of naphthols were visible after the development process. The first was 1-chloro-4-naphthol, as was shown by comparison with the spot derived from an authentic specimen. This result establishes the position of the acetoxy group. The only reasonable structure for the second product of hydrolysis is therefore 2-chloro-4-naphthol (3-chloro-1-naphthol).

This compound was synthesised as is summarized in the scheme in page 72; when pure products were isolated, the melting points and weights are given. The bracketted numbers are the melting points given in the literature[1,2] (when different from those found):



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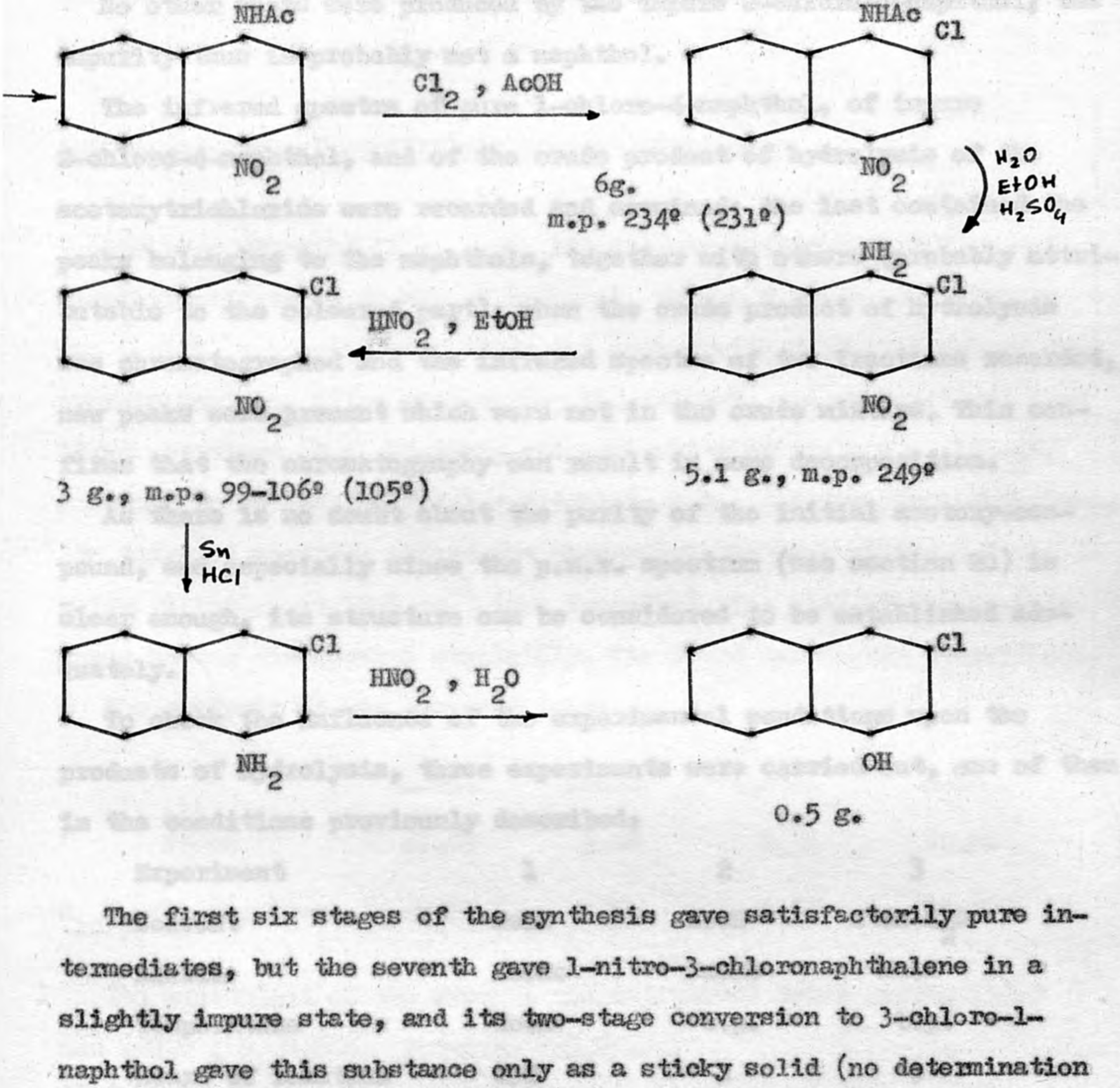
1. H. H. Hodgson and J. Walker, <u>J. Chem. Soc.</u> 1933, 1205 .

2. H. H. Hodgson and R. L. Elliot, <u>ibid</u> 1934, 1705 .



The first six stages of the synthesis gave satisfactorily pure intermediates, but the seventh gave 1-nitro-3-chloronaphthalene in a slightly impure state, and its two-stage conversion to 3-chloro-1-naphthol gave this substance only as a sticky solid (no determination of the melting point was possible, nor isolation of a benzoate) which gave a spot, in thin layer chromatography, identified with the unknown product proceding from the hydrolysis of the acetoxy compound.

No other spots were produced by the impure 2-chloro-4-naphthol; the impurity thus is probably not a naphthol.

The infrared spectra of pure 1-chloro-4-naphthol, of impure 2-chloro-4-naphthol, and of the crude product of hydrolysis of the acetoxytrichloride were recorded and examined; the last contained the peaks belonging to the naphthols, together with others (probably attributable to the coloured part); when the crude product of hydrolysis was chromatographed and the infrared spectra of two fractions recorded, new peaks were present which were not in the crude mixture. This confirms that the chromatography can result in some decomposition.

As there is no doubt about the purity of the initial acetoxy-compound, and especially since the p.m.r. spectrum (see section 20) is clear enough, its structure can be considered to be established adequately.

To check the influence of the experimental conditions upon the products of hydrolysis, three experiments were carried out, one of them in the conditions previously described:

Experiment	1	2	3
Solvent	MeOH	MeOH	EtOH-H_2O
Alkali	NaOMe	NaOMe	NaOH
Temperature	Room	b.p.	b.p.
Hours of reaction	192	3	3
Appearance	Colourless	Yellow	Red

Each of the samples showed two spots on thin layer chromatography; probably the difference in colour proceeds from small amounts of quinones or other oxidation products which are formed easily at higher temperatures.

Acid hydrolysis of naphthalene acetoxytrichloride.

The pure compound (1 g., m.p. 124-5º) was boiled with 1.5 ml. of dimethyl sulfate in 40 ml. of methanol, during 4 hours; the mixture was cooled, extracted with ether and washed with distilled water. The organic residue, after evaporating the solvent, was crystallized from light petroleum, b.p. 80-100º, and gave white crystals m.p. 113-4º, supposed to be 1-hydroxy-2,3,4-trichloro-1,2,3,4-tetrahydronaphthalene. Its infrared spectrum showed the characteristic peak of the O-H stretching vibration at 3505 cm^{-1} (see Appendix), the peak of the acetate group having dissapeared completely. The yield was nearly theoretical.

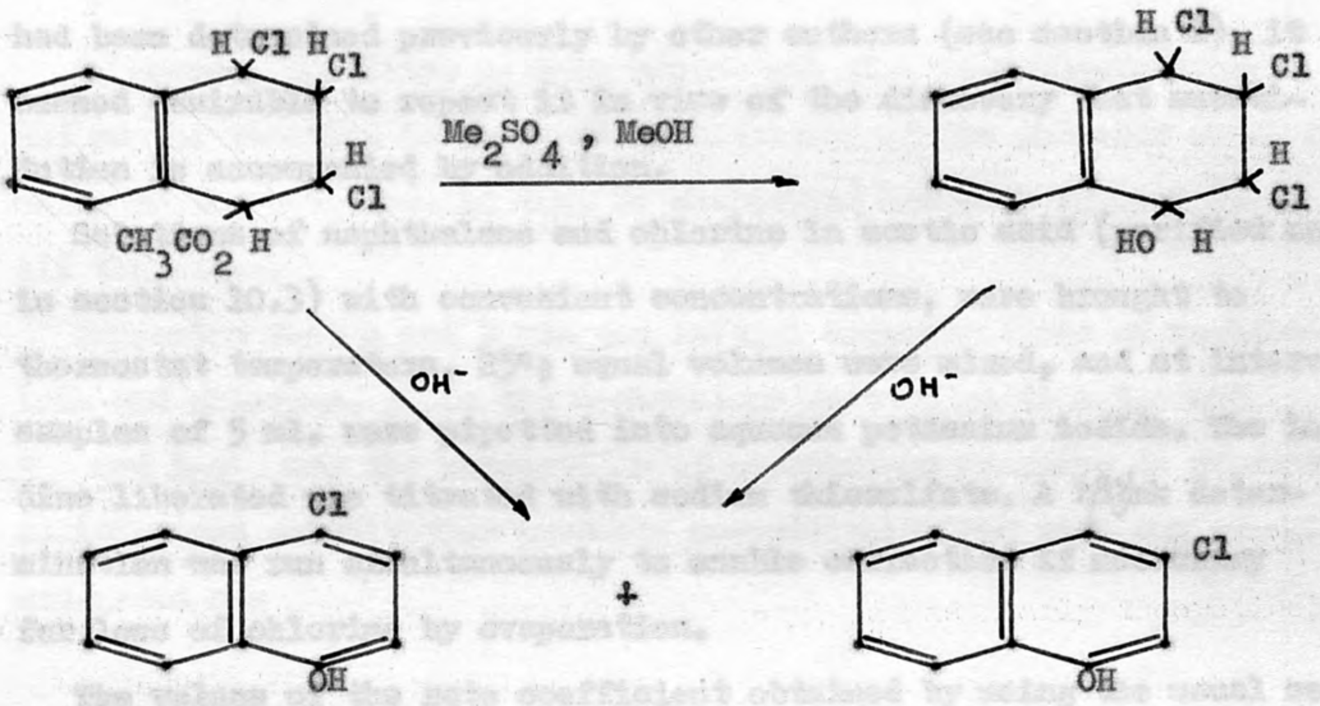
The analysis of the compound gave:

	C	H	O	Cl
Found	47.63	3.48	6.51	42.26
$C_{10}H_9OCl_3$ requires	47.70	3.60	6.36	42.21

The equivalent of the alcohol was determined twice giving 119.7 and 120.0 ; $C_{10}H_9OCl_3$ requires 125.7 .

If sulfuric acid is employed instead of dimethyl sulfate, the hydrolysis is slower and the yield of alcohol is poorer.

A sample of the alcohol was hydrolysed with sodium methoxide in methanol, the products, when examined by thin-layer chromatography, were the 1-chloro- and 2-chloro-4-naphthols already described. The following scheme thus summarises the reactions:



15. KINETICS OF CHLORINATION OF NAPHTHALENE IN ACETIC ACID.

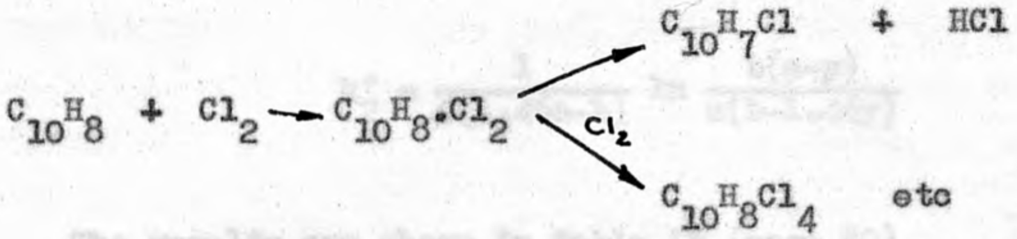
Although the rate of chlorination of naphthalene in acetic acid had been determined previously by other authors (see section 8), it seemed desirable to repeat it in view of the discovery that substitution is accompanied by addition.

Solutions of naphthalene and chlorine in acetic acid (purified as in section 10.3) with convenient concentrations, were brought to thermostat temperature, 25°; equal volumes were mixed, and at intervals samples of 5 ml. were pipetted into aqueous potassium iodide. The iodine liberated was titrated with sodium thiosulfate. A blank determination was run simultaneously to enable correction if necessary for loss of chlorine by evaporation.

The values of the rate coefficient obtained by using the usual second-order rate-equation:

$$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)}$$

where a = initial concentration of naphthalene, b = initial chlorine and x = reacted chlorine at time t, increased slowly but clearly with the course of the reaction. This effect had been observed before, and had been attributed to a small catalysis by the hydrogen chloride produced in the reaction. But the experiments and studies described in sections 10 to 14 established the necessity of using another equation which could allow for the important addition products formed by taking up more chlorine:



$$C_{10}H_8 + Cl_2 \rightarrow C_{10}H_8.Cl_2 \begin{cases} \rightarrow C_{10}H_7Cl + HCl \\ \xrightarrow{Cl_2} C_{10}H_8Cl_4 \quad \text{etc} \end{cases}$$

Of course, the first step is slower and then rate-determining, but as the reaction is followed by titration of the chlorine which remains in the reaction, it must be considered how much is used up in all the steps.

Supposing that a and b are the initial concentrations of naphthalene and chlorine, y is the naphthalene reacted at time t, and α and $1-\alpha$ are the proportions of naphthalene reacting to produce addition and substitution products respectively, the rate can be expressed as:

$$\frac{dy}{dt} = k_2' (a-y)(b-y-\alpha y)$$

which after integration gives :

$$k_2' = \frac{1}{t((1+\alpha)a-b)} \ln \frac{b(a-y)}{a(b-y-\alpha y)}$$

For naphthalene with no added electrolyte, the substitution products are 54.0% of the reacted naphthalene, the tetrachloride adducts 38.0% , and the acetoxytrichloro adduct 8.0% , so $\alpha = 0.46$, and the equation becomes:

$$k_2^* = \frac{1}{t(1.46a-b)} \ln \frac{b(a-y)}{a(b-1.46y)}$$

The results are shown in Table IV (page 80).

Values of k_2^* show no trend with the initial concentrations or with the progress of the reaction.

The volume of thiosulfate is equivalent to the chlorine which remains in the reaction, $b - x$ or $b - 1.46y$, in each of the equations.

TABLE IV. <u>Kinetics of chlorination of naphthalene in acetic acid, at 25º.</u>

Naphthalene	Chlorine	Time (min)	Sodium thiosulfate		k_2	k_2'
			ml	N		
0.050 M	0.027 M	0	2.4	0.02	——	——
		5	1.05		3.8	2.5
		12	0.25		3.7	2.3
0.050 M	0.026 M	0	5.20	0.02	——	——
		2	3.75		3.6	2.5
		4	3.00		3.2	2.1
		6	1.90		3.8	2.6
		8	1.40		4.4	2.7
		10	1.05		4.4	2.8
		12	0.85		4.3	2.6
		14	0.65		4.4	2.6
		16	0.55		4.9	2.5
0.050 M	0.0237 M	0	4.75	0.02	——	——
		1	4.05		3.3	2.2
		3	2.75		4.2	3.2
		4	2.45		3.9	3.3
		5	2.00		4.2	3.1
		7	1.85		4.1	2.9
		8	1.30		4.2	2.9
		9	1.15		4.2	3.0
0.014 M	0.014 M	0	5.60	0.01	——	——
		2	4.45		4.7	3.4
		4	3.95		4.0	2.5
		6	3.25		4.3	2.7
		8	2.95		3.9	2.5
		10	2.45		4.1	2.6
		14	2.30		3.2	2.0
		17	1.65		3.9	2.4
		18	1.55		3.9	2.4
		20	1.50		3.6	2.2

k_2 and k_2' in $l.mole^{-1}.min^{-1}$

Average k_2' : 2.4 , 2.5 , 2.9 and 2.5 respectively.

16. CHLORINATION OF NAPHTHALENE IN CHLOROFORM.

16.1) Study of the products.

Different chlorinations have been carried out following a method similar to that used with acetic acid.

A quantity of naphthalene was dissolved in pure chloroform, freshly distilled (after purification by washing with concentrated sulfuric acid and water, and drying with calcium chloride); a sample of the solvent was saturated with chlorine (in a flask protected from the light) and the halogen was titrated with sodium thiosulfate after pipetting an aliquot part into aqueous solution of potassium iodide; no starch is needed for the end-point because the iodine remains in the small volume of non-aqueous solvent.

Convenient volumes of the solutions of naphthalene and chlorine were mixed and the flask was left under the chosen conditions, with or without added catalyst.

After one or two days, the solvent and the hydrogen chloride produced were removed by distillation under reduced pressure, and the residue was chromatographed over silica gel and eluted as usual.

When it was possible, some pure α-naphthalene tetrachloride was removed by crystallization before the chromatographic separation.

If crystallization was employed, the mother liquors were chromatographed together with the uncrystallizable part.

The results can be seen in Table V , page 83.

The time which was necessary for completing the chlorinations varied widely; reaction B was exothermic, with violent evolution of hydrogen chloride and boiling of the solvent; all the halogen reacted in less than three minutes. Reactions A, C and D were carried out in flasks protected from the light, and therefore it was impossible to wacht the mixtures; however, from kinetic studies, A should be a very slow reaction and in this case no heating was observed. C and D should be more rapid and accordingly it was noticed that the solutions became warm.

TABLE V. Products of chlorination of naphthalene in chloroform.

Experiment		A	B	C	D
Naphthalene (g.) :		12.8	12.8	12.8	12.8
Chlorine (g.) :		7.1	7.1	5.3	5.3
Conditions :		Dark	Light	Dark	Dark
Catalyst (conc.) :		——	——	I_2 0.0001M	HCl 0.14 M
Volume of solvent (ml.):		170	170	175	175
Products isolated:					
α-$C_{10}H_8Cl_4$ cryst. g.		3.1	1.15	——	——
$C_{10}H_8$ + $C_{10}H_7Cl$ after chromatography (g.):		10.6	12.7	11.6	11.1 [a]
Addition products after chromatography (g.) :		4.8	4.3	5.3	5.0
Estimation of products[aa]:					
Unreacted naphthalene, g.		4.4	5.1	5.2	4.4 [a]
Monochloronaphthalene, g.		6.2	7.6	6.4	6.7
N. tetrachlorides, g.		7.9	5.45	5.3	5.0
% Reacted naphthalene	Substitution	56.6	69.4	69.1	66.8
	Addition	43.4	30.6	30.9	33.2
Composition of addition mixtures (%) [aaa]	α-isomer	50.6	32.8		
	γ-isomer	6.5	13.9		
	δ-isomer	35.2	43.8	[aaa]	[aaa]
	ε-isomer	6.5	7.9		
	$C_{10}H_7Cl_5$	1.2	1.6		

a) Perhaps some naphthalene was lost by sublimation.

aa) The difference between the chlorine used up to form the addition products and the initial chlorine was attributed to substitution; by allowing the mixtures of unreacted naphthalene and monochloronaphthalene to lose the hydrocarbon by sublimation at room temperature during 2 to 3 weeks, the weight of the substitution product could be determined experimentally and it was found in a very good agreement with the calculated number shown in the Table, the differences being smaller than 0.1 g.

sss) Dr. M. D. Johnson (see section 20) made an estimation of the different isomers by examining the proton magnetic resonance spectra of these mixtures. Samples from experiments C and D showed a composition between those of A and B, but unfortunately they are not representative because it was not possible to dissolve all the α-naphthalene tetrachloride present. The ε-naphthalene tetrachloride and the naphthalene pentachloride will be described in sections 17 and 18.

16.2) Kinetics of chlorination of naphthalene in chloroform (without Catalyst) at 25°.

First, it was necessary to adopt a new method of titration. The one employed for the kinetics in acetic acid was unsatisfactory because when a sample is pipetted into aqueous solution of potassium iodide, the iodine liberated goes preferentially to the chloroform, catalysing the chlorination and producing meaningless results. Following preceding methods [1], the samples were pipetted into aqueous solutions of buffered sodium arsenite, and the remaining reagent (after destruction of the chlorine by vigorous shaking) was titrated with standard solution of iodine in potassium iodide.

Blanks were run to observe, as usual, the behaviour of the halogen in chloroform and it was immediately found that in the light the chlorine disappeared speedly according to the reaction :

$$CHCl_3 + Cl_2 + \text{light} \longrightarrow CCl_4 + HCl$$

New solutions of chlorine kept in flasks protected from the light remained with a constant concentration of the halogen.

The kinetic measurements were made in flasks protected from the light and in a thermostat placed in a dark room with a red bulb which gave a very weak illumination.

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[1] P. B. D. de la Mare, R. A. Scott and P. W. Robertson, J. Chem. Soc. 1945, 509 .

The rate coefficient was calculated as in section 15, with the ordinary equation

$$k_2 = \frac{1}{t(a-b)} \ln \frac{b(a-x)}{a(b-x)} \quad \text{or} \quad k_2 = \frac{x}{at(a-x)} \text{ if } a = b$$

and the modified one

$$k_2' = \frac{1}{t(1.43a-b)} \ln \frac{b(a-y)}{a(b-1.43y)}$$

In this case as substitution = 56.6% and addition = 43.4% of the reacted naphthalene, the coefficient $\alpha = 0.43$.

The meaning of the symbols is the same as in section 15.

The titration was made pipetting samples of 5 ml. into 10 ml. of 0.104 N buffered aqueous sodium arsenite, and back titration with 0.102 N iodine in potassium iodide; the volume of iodine plus that of chlorine remaining in the reaction is a constant quantity equivalent to the volume of sodium arsenite; from this number the chlorine used up (x or $1.43y$ in each of the equations) and finally the rate coefficients can be calculated.

The results are in Table VI, page 87.

Blanks were run during the first experiments, until it was realized that the reaction was very slow and therefore a point at $t = 1$ or 2 minutes gives the initial concentration; no chlorine is lost by evaporation during a whole run.

When the ratio of chlorine to naphthalene is small, both equations give a constant. When the ratio is nearly 1, the modified equation gives much better results but these are still far from perfect constancy.

The explanation for the variation of the coefficients will be described in section 16.4 ; a similar anomaly can be seen in next section.

TABLE VI. <u>Kinetics of chlorination of naphthalene in chloroform at 25º.</u>

Naphthalene	Chlorine	Time (min.)	Iodine (ml.)	k_2	k'_2
0.1 M	0.047 M	0	5.7	—	—
		120	8.1	0.056	0.018
		200	9.25	0.126	0.079
		284	9.95	0.120	0.073
0.1 M	0.1 M	0	0.45	—	—
		120	6.10	0.111	0.066
		200	8.10	0.166	0.082
		285	9.45	0.334	0.111
0.1 M	0.037 M	0	6.7	—	—
		110	8.3	0.057	0.039
		170	9.1	0.066	0.047
		228	9.4	0.069	0.046
0.1 M	0.0815 M	0	2.25	—	—
		110	6.60	0.098	0.059
		170	8.30	0.137	0.077
		228	9.35	0.194	0.097
0.05 M	0.0225 M	0	8.15	—	—
		120	8.8	0.062	0.042
		220	9.15	0.060	0.041
		300	9.45	0.067	0.044
		400	9.8	0.084	0.054
0.05 M	0.0225 M	0	8.15	—	—
		120	8.9	0.074	0.050
		220	9.35	0.081	0.054
		300	9.5	0.073	0.048
		400	9.75	0.078	0.051

16.3) Kinetics of chlorination of naphthalene in chloroform, in presence of iodine as catalyst.

The method used was the same as it has been described in the preceding section, but initially a small concentration of iodine (obtained by consecutive dilutions) was present together with the hydrocarbon. This concentration is so small that it does not influence the titration.

Samples of 5 ml. were pipetted into 10 ml. of buffered sodium arsenite (0.011 N), and the excess of reagent back titrated with 0.0118 N iodine.

Again k_2 and k'_2 were calculated. In this case as substitution = 69.1% and addition = 30.9% of the reacted chlorine, the coefficient α becomes equal to 0.31 .

The results can be seen in next page; all the symbols in Table VII as in Table VI.

The first values for the rate coefficients are influenced by greater errors because the times of reaction are very small and about 20 seconds are necessary for quenching the reaction.

The order of the reaction in iodine is 1, because when its concentration was made 50 and 25%, the values for the rate coefficient decreased approximately in that proportion.

The inconstancy of the rate coefficients, found also in the preceding section, was attributed to the cumulative effect of the hydrogen chloride produced in the reaction and this was proved as it will be seen in next section.

TABLE VII. Kinetics of chlorination of naphthalene in chloroform at 25°, in presence of iodine as catalyst.

Naphthalene 0.01 M in all the experiments

Chlorine	Iodine	t(min.)	ml. iodine	k_2	k_2'
0.01 M	0.00008 M	0	0.3	—	—
		2	1.3	6.8	5.2
		4	3.1	11.5	8.4
		6	4.45	14.3	9.9
		8	5.45	16.3	11.1
		10	6.1	17.9	11.5
		12	6.45	17.7	10.9
		14	7.0	20.2	11.8
		16	7.25	20.4	11.6
		18	7.65	23.7	12.5
0.01 M	0.00004 M	0	0.3	—	—
		3	1.1	3.4	2.7
		6	2.85	6.6	4.9
		9	3.85	7.2	5.1
		12	4.8	8.2	5.7
		15	5.4	8.6	5.7
		18	5.8	8.5	5.6
		21	6.25	9.1	5.8
		24	6.7	10.0	6.0
		27	6.95	10.1	6.1
0.00462M	0.00002 M	0	5.5	—	—
		5	6.0	3.0	2.3
		10	6.55	3.4	2.5
		15	6.9	3.4	2.5
		20	7.3	3.6	2.6
		25	7.65	3.8	2.8
		30	7.85	3.7	2.7
		36	8.1	3.8	2.8
		40	8.35	4.2	3.0
		45	8.5	4.3	3.0

16.4) Kinetics of chlorination of naphthalene in chloroform, in presence of hydrochloric acid as catalyst.

Small quantities of water were shown in preliminary experiments to influence the effect of hydrogen chloride. The kinetic measurements were therefore made by using chloroform which was either dried or saturated with water, and then saturated with hydrogen chloride.

Naphthalene and chlorine were then dissolved in it and the kinetics were followed as usual; extra sodium hydrogen carbonate was added to the buffered sodium arsenite to neutralize the hydrochloric acid.

As substitution = 66.8% and addition = 33.2% of the reacted naphthalene, the coefficient α is 0.33 ; all symbols employed in Table VIII (page 91) are the same as in the preceding ones.

Samples of 5 ml. were pipetted into 10 ml. of 0.1005 N sodium arsenite, and its excess titrated with 0.098 N iodine. In these experiments only k_2^* has been calculated.

The starting concentration of halogen was determined by separate experiments.

TABLE VIII. Kinetics of chlorination of naphthalene in chloroform, at 25°, in presence of hydrochloric acid as catalyst.

Naphthalene	Chlorine	t(min.)	Iodine (ml.)	k'_2	Hydrogen chl.	Water
0.2 M	0.0704 M	0	(3.72)	——	0.225 M	Satur.
		2	6.55	1.13		
		4	8.00	0.90		
		6	8.85	0.84		
		8	9.7	0.91		
		10	10.05	0.87		
		12	10.35	0.86		
		14	10.45	0.79		
		16	10.8	0.94		
		18	11.0	1.14		
0.1 M	0.055 M	0	(5.25)	——	0.125 M	55% of saturation
		3	6.30	0.45		
		6	6.65	0.29		
		9	7.2	0.31		
		12	7.6	0.30		
		15	7.85	0.28		
		18	8.1	0.27		
		21	8.7	0.31		
		24	8.8	0.29		
		27	9.05	0.29		
0.1 M	0.12 M	0	(8.0)	——	0.225 M	None [a]
		5	3.0	1.03		
		10	5.0	0.94		
		15	6.25	1.14		
		20	7.05	1.01		
		25	7.65	1.05		
		30	8.1	1.04		
		35	8.5	1.15		
		40	8.65	1.07		
0.2 M	0.09 M	0	(9.95)	——	0.225 M	None [a]
		2	5.3	1.35		
		4	6.7	1.09		
		6	7.5	0.96		
		9	8.65	1.00		
		11	8.90	0.93		
		13	9.25	0.95		
		15	9.5	0.99		

TABLE VIII. (Continuation)

a) In these two kinetic experiments, dry chloroform was saturated with dry hydrogen chloride. When the results were compared with those from the first experiment in which chloroform saturated with water was saturated with hydrogen chloride, it was noticed inmediately that the rate coefficients were identical; this led to discover that the solutions of hydrogen chloride in chloroform are so hygroscopic that they become saturated inmediately with water taken from the atmosphere. In the second experiment, the naphthalene was dissolved in 25 ml. of chloroform saturated with hydrogen chloride (instead of in 45 ml. which were employed in the fisrt, third and fourth experiments), adding later 20 ml. of pure chloroform. The halogen was always added dissolved in 5 ml. of chloroform.

The variation of the rate coefficient with the concentration of hydrogen chloride and of water, suggests that the kinetic order of the reaction in each of these substances is 1 . In all cases there is no trend of k_2' with the initial concentration of chlorine or with the progress of the reaction.

17. CHLORINATION OF NAPHTHALENE IN CARBON TETRACHLORIDE AND ISOLATION OF ε-NAPHTHALENE TETRACHLORIDE.

Naphthalene (12.8 g.) was mixed with chlorine (14 g.) in carbon tetrachloride. There was no apparent reaction during three hours but on exposure of the solution to weak sunlight, a smooth reaction occurred, and in less than thirty minutes the colour of chlorine had disappeard. The solvent was distilled off under reduced presure, and a mixture of crystals and liquid was obtained. The crystals (3 g.), separated by filtration, gave a m.p. 133-4º, after recrystallization from methylated spirit. They were identified as γ-naphthalene tetrachloride. The remaining liquid was chromatographed as usual. The following fractions were obtained:

a) Unreacted naphthalene, together with monochloronaphthalene (16.6 g.)

b) A mixture of tetrachlorides (3.8 g.) m.p. 85-115º. The p.m.r. spectrum of this, kindly examined by Dr. M. D. Johnson (see section 20), showed clearly the presence of a new naphthalene tetrachloride, now designated the ε-tetrachloride. The ratio of γ:ε in this sample was <u>ca</u>. 2:3 .

c) Coloured tars (0.5 g.).

A second chlorination was made with 0.1 mole of naphthalene and 0.15 moles of chlorine in 125 ml. of carbon tetrachloride. An ultraviolet lamp was used to catalyze the reaction, but its effect (probably because the flask was an ordinary one made of glass) was small and the reaction very slow as in the preceding case.

In a third experiment, naphthalene (12.8 g.) was allowed to react with chlorine (14 g.) in carbon tetrachloride (200 ml.), in presence of a trace of benzoyl peroxide and under direct sunlight. The reaction was very rapid and exothermic; the solvent boiled and all the chlorine had disappeard in less than three minutes. The solvent was removed by distillation under reduced pressure. The residue (a mixture of crystals and liquid) was crystallized from methanol and gave crystals m.p. 133-4º of pure γ-naphthalene tetrachloride (4.2 g.). Concentration of the mother liquor gave a second crop of γ-isomer (1.7 g.). Further concentration of the residue gave a crop m.p. 65-73º (5.9 g.); after seven recrystallizations from light petroleum (b.p. 60-80º and 80-100º) and finally from cyclohexane, pure crystals (1.8 g., m.p. 85-7º) of ε-naphthalene tetrachloride were isolated. This material was characterised by its infrared (see Appendix) and p.m.r. spectra; the latter showed it to be free from isomeric impurities.

A sample gave the following analysis:

	C	H	Cl
Found	44.59	3.11	52.45
$C_{10}H_8Cl_4$ requires	44.44	2.98	52.59

The remaining uncrystallized residue (after separating the three crops described) was chromatographed as usual and 9.8 g. of a mixture of the γ and ε-tetrachlorides, and 1.8 g. of impure δ-isomer, were isolated.

It is noteworthy that in this reaction very little, if any, substitution occurred.

18. OTHER CHLORINATIONS.

Chlorination of naphthalene was examined in outline also under certain other conditions, as described below.

The main purpose of these experiments was to attempt to establish wheter other naphthalene tetrachlorides are formed.

18.1) In nitromethane.

Naphthalene (12.8 g.) was allowed to react with chlorine (14 g.), in a total volume of 250 ml. of nitromethane, in the dark. The reaction was exothermic and probably very fast. The solvent was distilled under reduced pressure and the products were separated by chromatography as usual. There was obtained:

a) Naphthalene and monochloronaphthalene (9.5 g.)
b) 1,4-Dichloronaphthalene (0.4 g., m.p. 64-6º)
c) γ-Naphthalene tetrachloride (0.5 g., m.p. 133-4º)
d) The impure γ-isomer, m.p. 105-110º (perhaps with ε-isomer), 0.9 g.
e) α-Naphthalene tetrachloride, m.p. 181-3º (1.9 g.)
f) Unidentified tars (1.3 g.)

18.2) In hydrochloric acid with potassium chlorate.

This kind of chlorination was made to attempt to repeat the experimental procedure described by Fisher[1] who reported the formation of β-naphthalene tetrachloride, m.p. 116-8°.

Naphthalene (12.8 g.) and potassium chlorate (6 g.) were carefully powdered with a small quantity of water. When the mixture was homogeneous, it was added insmall proportions to concentrated hydrochloric acid (65 g.); chlorine was evolved according to the equation:

$$KClO_3 + 6\,HCl \longrightarrow 3\,Cl_2 + KCl + H_2O$$

The reaction-mixture was left overnight, and the following day was extracted with ether. The solvent was evaporated, and the liquid residue was chromatographed as usual. There was recovered unreacted naphthalene and monochloronaphthalene (6.2 g.), and α-naphthalene tetrachloride (3.0 g.); but no other isomers or products could be detected.

A second attempt was equally unsuccesful; a small quantity of monochloronaphthalene tetrachloride (see section 18.4) was also detected.

A modification was introduced in a third attempt: naphthalene (6.4 g.) was dissolved in acetic acid (200 ml.); concentrated hydrochloric acid (37 g.) was then added without precipitation of the hydrocarbon, and followed by potassium chlorate (4 g.). The mixture became orange-coloured and was treated as usual. After the chromatography, monochloronaphthalene (6 g.), a mixture (1.3 g.) of α and δ-tetrachlorides and naphthalene pentachloride (identified by its infrared spectrum), and a mixture (2.8 g.) of naphthalene acetoxytrichloride and tars,

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[1] E. Fisher, Ber. 1878, 11 , 735 .

were isolated.

A fourth attempt was made with a suspension of naphthalene (12.8 g.) in acetic acid (165 ml.) and concentrated hydrochloric acid (65 g.); potassium chlorate (6 g.) was added with vigorous stirring. The isolation of products after the chromatography gave: monochloronaphthalene (11.2 g.); a mixture (0.6 g.) of $C_{10}H_7Cl$ and $C_{10}H_7Cl_5$; a mixture (0.3 g.) of α and δ-tetrachlorides together with naphthalene pentachloride; a mixture (0.6 g.) of α and δ-tetrachlorides and acetoxytrichloride and tars (0.5 g.).

In a fifth experiment, naphthalene (12.8 g.) was dissolved in acetic acid (200 ml.), and bleaching powder (47.3 g., equivalent to 0.2 moles of chlorine) was added.The mixture was very heterogeneous; the products were isolated by adding water, extracting with ether, and chromatographing the residue. Naphthalene and monochloronaphthalene (9 g.), and α-naphthalene tetrachloride (1.5 g.) were isolated.

18.3 Without solvent (in liquid naphthalene).

Naphthalene (25.6 g.) was melted and a slow flow of chlorine was passed through it. After three hours the mixture was quite viscous and the produced solids made the flow of the halogen difficult. The passage of chlorine was stopped, and the mixture was poured into light petroleum (250 ml., b.p. 40-60°); the insoluble solid was boiled with light petroleum (200 ml., b.p. 80-100°), and the still insoluble residue was filtered off. The first solution, after evaporating the solvent, gave a liquid residue of 1-chloronaphthalene; the second gave a crop of crystals m.p. 130-170° (5.5 g.); and the insoluble residue, after recrystallization from benzene, gave pure α-naphthalene tetrachloride (7.2 g., m.p. 188-191°), identified by its infrared spectrum.

The mixture m.p. 130-170° contained α-naphthalene tetrachloride and a monochloronaphthalene tetrachloride. By digestion with chloroform, it was possible to separate this component; after recrystallization from that solvent it had a m.p. 127-130°. This is evidently the monochloronaphthalene tetrachloride m.p. 129°, described by Schütz and Hahnfeld[1].

A sample gave this analysis:

	C	H	Cl
Found	39.60	2.40	58.16
$C_{10}H_7Cl_5$ requires	39.40	2.29	58.29

Its proton magnetic resonance spectrum, reported by Dr. M.D.Johnson, shows that it is, as expected, a 1,1,2,3,4-pentachloro-1,2,3,4-tetrahydronaphthalene.

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1. F. Schütz and K. Hahnfeld, Ber 1952, 85 , 131 .

19. DETERMINATION OF SOME DIPOLE MOMENTS.

The usual method for determining dipole moments from dielectric constant, density and refractive index measurements on dilute solutions, has been applied to some naphthalene tetrachlorides. To begin with the dipole moment of the α-benzene tetrachloride, known to be 2.34 D [1], was redetermined to check the procedure.

Following this determination, the dipole moments of α and γ-naphthalene tetrachlorides were measured. In every case four dilute solutions of the compound to be studied, in about 60 ml. of benzene dried oversodium, were prepared. The solutions, each with a different concentration, were used as dielectric to fill the experimental cell, the capacity of which was compared with that of a condenser using the heterodyne method.

In every determination, the aparatus was calibrated with the solvent and the refractive index of it and those of the solutions as well as their densities, were determined.

Each complete determination was done in duplicate. A whole determination was done in one day to avoid contamination by moisture or losses by evaporation. The temperature was 25º. The experimental values can be summarized as follows:

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[1] O. Bastiansen and J. Markali, Acta Chem. Scand. 1952, 6 , 442 .

α-Benzene tetrachloride

	PhH	1	2	3	4
Weight solute g.	——	0.3388	0.5906	0.9007	1.1185
Weight solution	——	52.7870	53.0445	53.2811	53.6035
100 w	——	0.6418	1.1134	1.6905	2.0866
x	25.00	19.23	15.79	11.64	8.73
$\Delta\varepsilon$	——	0.01853	0.03141	0.04695	0.05784
n	1.4969	1.4970	1.4971	1.4972	1.4973
Weight pyc.	7.2186	7.2381	7.2524	7.2652	7.2815

α-Naphthalene tetrachloride (1st time)

W. solute	——	0.2893	0.5397	0.9001	1.0903
W. solution	——	52.7370	53.0026	53.3233	53.4948
100 w	——	0.5486	1.0182	1.6880	2.0381
x	25.00	19.69	14.25	5.95	1.86
$\Delta\varepsilon$	——	0.02339	0.04372	0.07473	0.09002
n	1.4979	1.4981	1.4985	1.4989	1.4989
W. pycnomet.	7.2323	7.2510	7.2639	7.2846	7.2933

α-Naphthalene tetrachloride (2nd time)

W. solute	——	0.2387	0.5147	0.7567	1.0295
W. solution	——	52.6953	52.9834	53.4016	53.6369
100 w	——	0.4530	0.9714	1.4170	1.9194
x	25.00	19.73	16.16	10.35	4.11
n	1.4980	1.4982	1.4984	1.4988	1.4991
$\Delta\varepsilon$	——	0.02359	0.03698	0.05877	0.08217
W. pyc.	7.2330	7.2465	7.2629	7.2757	7.2918

γ-Naphthalene tetrachloride (1st time)

W. solute	——	0.2532	0.5210	0.7693	1.0137
W.solution	——	52.7347	52.9915	53.2821	53.4941
100 w	——	0.4801	0.9832	1.4438	1.8950
x	25.00	21.41	16.95	11.32	7.88
$\Delta\varepsilon$	——	0.01519	0.03184	0.05285	0.06570
n	1.4979	1.4981	1.4983	1.4986	1.4989
W. pyc.	7.2316	7.2461	7.2576	7.2747	7.2887

γ-Naphthalene tetrachloride (2nd time)

	PhH	1	2	3	4
Weight solute	——	0.2735	0.5277	0.6998	1.0950
Weight solution	——	52.6394	53.8840	53.0708	53.5179
100 w	——	0.5196	0.9793	1.3186	2.0460
x	25.00	20.64	16.35	13.19	6.68
$\Delta\varepsilon$	——	0.01721	0.03340	0.04533	0.06989
n	1.4978	1.4980	1.4983	1.4987	1.4989
Weight pyc.	7.2312	7.2452	7.2616	7.2707	7.2934

w, molecular fraction of the solutions; x, reading in a small condenser; n, refractive index.

Two different methods of calculation were used to work out the experimental values: the first one the conventional method, and the second one the simplified method by Dr. J. W. Smith[1], in which the densities are not used :

<u>Exact method</u> <u>Simplified method</u>

$$P = \left[\frac{3\alpha v_o}{(\varepsilon_o + 2)^2} + \frac{\varepsilon_o - 1}{\varepsilon_o + 2}(v_o + \beta) \right] M$$

$$_{\mu}P = \frac{3v_o\left(\alpha - \frac{\Delta n^2}{w}\right)}{(\varepsilon_o + 2)^2} M$$

$$R = \left[\frac{3\frac{\Delta n^2}{w} v_o}{(n_o^2 + 2)^2} + \frac{n_o^2 - 1}{n_o^2 + 2}(v_o + \beta) \right] M$$

$$_{\mu}P = P - R$$

In both methods : $\mu = 0.2212\sqrt{_{\mu}P}$ at 25º. Symbols:

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1. J. W. Smith, Transactions of The Faraday Society, 1950, 46, 5, 394.

v_o = specific volume of benzene

ε_o = dielectric constant of benzene

n_o = refractive index of benzene

n = refractive index of the solutions

w = molecular fraction of the solute

Coefficients α and β defined by the equations $\varepsilon = \varepsilon_o + \alpha w$ and $v = v_o + \beta w$, where ε and v are the dielectric constants and the specific volume of the solutions.

P = molecular polarization

R = molecular refraction (in cubic centimetres)

$_{\mu}P$ = orie ntation polarization

μ = dipole moment, in Debyes .

The values found were:

	1st determination		2nd determination	
Compound	Exact method	Simplified	Exact method	Simplified
α-$C_6H_6Cl_4$	——	——	2.33	2.34
α-$C_{10}H_8Cl_4$	3.23	3.23	3.23	3.23
γ-$C_{10}H_8Cl_4$	2.83	2.83	2.84	2.84
δ-$C_{10}H_8Cl_4$	4.1 ± 0.2 [a]			

a) The determination of the dipole moment of this isomer was a courtesy of J. Jenkins. The pure specimen avaible was only 0.26 g.; the determination was made once by sucesive dilutions of a first solution. The refractive index of the first solution was equal to that of benzene, and hence the molecular refraction had to be calculated. The coefficient β was a little greater than expected (as compared with those from the other isomers), hence the allowance of 0.4 Debyes for the value obtained.

20. PROTON MAGNETIC RESONANCE SPECTRA AND STRUCTURES OF SOME NAPHTHALENE CHLORODERIVATIVES.

Dr. M. D. Johnson has determined in the University College, London, the p.m.r. spectra of four naphthalene tetrachlorides, of a naphthalene pentachloride and of naphthalene acetoxytrichloride.

These measurements have enabled their structures to be assigned (only that of α-naphthalene tetrachloride was previously known).

Their proportions in different mixtures have also been estimated as stated in preceding sections.

In Table IX, page 104, cam be seen all the results found for the compounds examined;

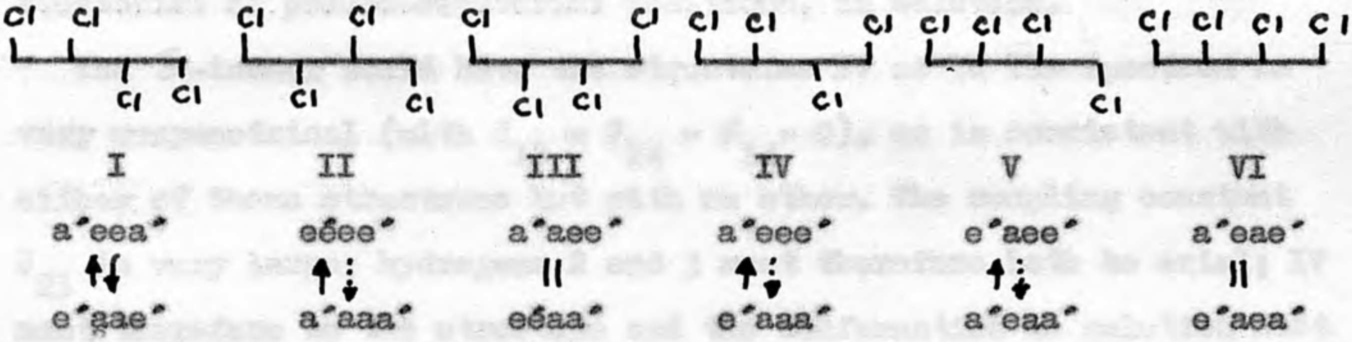
TABLE IX. Proton magnetic resonance spectra of some naphthalene adducts.

Compound	α-tetrachloride	γ-tetrachloride	δ-tetrachloride	ε-tetrachloride	acetoxytrichloride
m.p.	182º	134º	96º	86º	124º
Spectrum type	A_2X_2	A_2X_2	ABCD	A_2X_2	ABCD
τ-Values (p.p.m.):					
Aromatic	2.48 Single	2.26 Single	2.2–2.7 Unsymm.	2.4 Single	Unsymm.
1 – H	4.28	4.48	4.56	4.53	4.48
2 – H	4.93	5.42	5.53	5.08	4.60
3 – H	4.93	5.42	5.08	4.96	4.53
4 – H	4.28	4.48	4.60	4.53	3.56
Acetoxy.	—	—	—	—	7.75
Coupling constants (c/sec):[a]					
$J_{1,2}$:	3.5	8.0	3.2	5.8	2.9
$J_{2,3}$:	11.0 [aa]	8.0	10.9	3.5	11.0
$J_{3,4}$:	3.5	8.0	7.6	5.8	7.0
Chlorine positions (in solution) :					
	a´eea´	e´eee´	a´eee´	eéaa = a´aee	aéee´ (AcO in e´)

[a] All values plus minus 0.6 $c.sec^{-1}$

[aa] This value is for tetrahydrofuran as solvent; this isomer is very insoluble in deuterochloroform (used for all the spectra).

The six possible stereoisomers of naphthalene tetrachloride (see sections 5.2 and 5.4), their structures and conformations, are :



The α-naphthalene tetrachloride was known to have the structure I, in the conformation with chlorines in positions a'eea' in the solid state (see section 5.4).

The γ-isomer could be II or III (see again section 5.4); its p.m.r. spectrum shows that the environment of the hydrogens 1 and 4 (and likewise those of hydrogens 2 and 3) are the same (an A_2X_2 spectrum); all the coupling constants are large. Karplus' relationship[1] between coupling constants and angles may be tabulated as follows:

Dihedral angle		0º	30º	60º	90º	120º	150º	180º
Coupling constants (c/sec)	Theoretical	8.2	6.0	1.7	-0.28	2.2	6.9	9.2
	Experimental			2 to 4				5 to 8

In the γ-isomer, therefore, there must be a large angle between each pair of hydrogens (the possibility of a small angle between the

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1. M. Karplus, J. Chem. Phys. 1959, 30 , 11 .

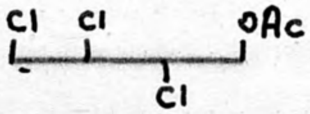
C-H bonds can be excluded by examination of models). The only possible conformation is that having all the four hydrogens axial or pseudo-axial; hence the structure is II, and all four chlorine atoms are in equatorial or pseudo-equatorial positions, in solution.

The δ-isomer could have the structures IV or V. The spectrum is very unsymmetrical (with $J_{13} = J_{24} = J_{14} = 0$), as is consistent with either of these structures but with no other. The coupling constant J_{23} is very large; hydrogens 2 and 3 must therefore both be axial; IV must therefore be the structure and the conformation in solution must be that with chlorine atoms in a'eee' positions.

The p.m.r. spectrum of the new isomer, ε-tetrachloride, shows that like the α and γ-isomers, the environment of hydrogens 1 and 4 (and likewise of 2 and 3) are magnetically equivalent. Of the remaining possibilities having this symmetry, VI and III, the former should, in either of its possible conformations, have low coupling constants for each pair of protons. This does not accord with the experimental data; the latter should be an equilibrium containing the conformations a'aee' = e'eaa' in equal amounts. Each of these should have a large coupling constant (note the large angle between C_1-H and C_2-H bonds in e'eaa') for one pair of the outer hydrogens and a small coupling constant for the other. The rapidly equilibrating mixture should have coupling constants J_{12} and J_{34} equal and intermediate between a high value of about 8 or greater and a low value of about 3. The observed value, 5.8 , is consistent with this and only this structure.

The p.m.r. spectrum of the naphthalene acetoxytrichloride shows that the most strongly deshielded hydrogen atom is in the 4-position, to which the electron-withdrawing acetoxyl group must therefore be attached. The pattern of coupling constants then establishes first that the 2- and 3-hydrogen atoms must be axially disposed, to give the large coupling constant, $J_{23} = 11$; secondly, that the 1-hydrogen atom must be in the pseudo-equatorial position; and thirdly, that the 4-hydrogen atom must be pseudo-axially situated.

The structure is



analogous with that of δ-naphthalene tetrachloride.

Part III

DISCUSSION

21. PREPARATIVE PROCEDURES FOR ISOMERIC NAPHTHALENE TETRACHLORIDES AND FOR NAPHTHALENE ACETOXYTRICHLORIDE.

Four naphthalene tetrachlorides, nominated with the Greek letters α , β , γ and δ were described last century. Despite this early description, their structures and properties were almost unknown up to 1952. The α-isomer is referred many times as "naphthalene tetrachloride" without further distinction. This isomer is the most insoluble and stable (as our experiments suggest), reasons which explain its facile isolation.

In 1952, a paper by Schütz and Hahnfeld[1] reported the preparation of this isomer, m.p. 181º, by passage of chlorine through a solution of naphthalene in carbon tetrachloride, together with a naphthalene pentachloride m.p. 129º, 1,4-dichloronaphthalene m.p. 68º, and a trace of γ-naphthalene tetrachloride, m.p. 133º. When these authors allowed naphthalene to react with liquid chlorine (ratio 1:68), γ-tetrachloride (yield 55%), liquid products not investigated and the δ-isomer

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[1] F. Schütz and K. Hahnfeld, Chem. Ber. 1952, 85 , 131 .

(yield 1%) m.p. 96º, were isolated. They did not isolate the β-isomer m.p. 114º, described by Fisher[1].

A year later Müller[2] reported again four isomers (he inverted the notation for the γ and δ-tetrachlorides), preparing the β by the action of nascent chlorine (produced by reaction of potassium chlorate with concentrated hydrochloric acid) on naphthalene, and checked that the four isomers possesed the four chlorine atoms in the same ring of the molecule.

We have not found any later references to preparative procedures for naphthalene tetrachlorides.

The structure of α-naphthalene tetrachloride is known from X-ray difraction experiments[3]. Schütz and Hahnfeld had given two possible structures for the α, γ and δ-isomers, deduced from experiments of alkaline dehydrochlorination. Nothing is known about the structure of the β-tetrachloride.

When we started to study the chlorination of naphthalene in a polar solvent like acetic acid (with a limited quantity of chlorine which never was greater than 100%, in moles, of that of hydrocarbon), we

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[1] E. Fisher, Ber. 1878, 11, 735.
[2] M. Müller, Monatshefte 1953, 84, 640.
[3] M. A. Lasheen, Acta Cryst. 1952, 5, 593.

found among the products 1-chloronaphthalene, α-naphthalene tetrachloride and naphthalene acetoxytrichloride as has been described in part II.

A small quantity of another tetrachloride, which was identified as the δ-isomer, was also found. When the reaction was made in presence of lithium chloride, the substitution product increased slightly, the acetoxytrichloride did not change and the proportion of α and δ-tetrachlorides changed with a notable increase of the latter.

Perchloric acid produced a greater increase in proportion of the substitution product, no change in that of the acetoxytrichloride, and an increase in the proportion of δ-tetrachloride, but not as notable an increase as in the preceding case.

It must be emphasized that the proportion of acetoxytrichloride did not change much when sodium acetate was present in the solution. Its influence on the proportion of tetrachlorides has not been investigated.

When the chlorination of naphthalene was attempted in liquid chlorine, α and γ-tetrachlorides were isolated. Schütz and Hahnfeld reported that this simultaneous formation of both isomers is a function of the rate of addition of naphthalene. We didnot find any influence in this direction; however, when the reaction was made under the catalytic effect of sunlight, the γ-isomer could be isolated in pure condition.

We studied later the chlorination of naphthalene in chloroform with a quantity of chlorine of about 100% (in moles) of that of hydrocarbon. 1-Chloronaphthalene, α, γ and δ-naphthalene tetrachlorides were first characterized.

In carbon tetrachloride, chosen as a non-polar solvent, with 100 to 200% moles of chlorine and under the catalytic effect of sunlight, 1-chloronaphthalene, the γ-tetrachloride and a new isomer which we designate ε, m.p. 85-7°, were isolated. When the reaction was made in presence of a trace of benzoyl peroxide and with stronger illumination, the yield of tetrachlorides was increased, a small quantity of the δ-isomer was detected and the amount of 1-chloronaphthalene formed was very small.

No α-tetrachloride has been detected in our experiments in carbon tetrachloride; probably in Schütz and Hahnfeld's experiments it was formed by a dark chlorination with excess of chlorine.

We studied the chlorination of molten naphthalene by passing an excess of chlorine over it; this led to the isolation of 1-chloronaphthalene, α-naphthalene tetrachloride and naphthalene pentachloride. The excess of chlorine produces the addition of two moles of the halogen to the molecule of 1-chloronaphthalene, a reaction favoured by the higher temperature and the longer time of reaction.

By examining the products obtained from the reaction in chloroform by p.m.r. spectroscopy, the pentachloride and the ε-tetrachloride could be detected together with the α, γ and δ-isomers, which were also shown to be present by infrared spectroscopy.

The chlorination of naphthalene in nitromethane with 200% moles of chlorine led to the isolation of 1-chloronaphthalene, 1,4-dichloronaphthalene, and the α and δ-tetrachlorides.

We have been unsuccesful in our attempts to repeat the synthesis of β-naphthalene tetrachloride. When the reaction was made following Fisher, only the α-isomer was isolated. If acetic acid was added to the hydrochloric acid to help to dissolve partially or completely the hydrocarbon, the α-tetrachloride was isolated with the δ-isomer (as well as acetoxytrichloride), but no β or other isomers were found. Probably the formation of the δ-isomer was favoured by the presence of potassium chloride produced by reduction of potassium chlorate.

In all our experiments, some quantities of unidentified tars were isolated. The acetoxytrichloro adduct is isolated as an oil which crystallises easily with any solvent. In our experiments only about 50% of the product was converted into white crystals, but this result could be produced by the long storage (see section 14) of its mixtures. Freshly prepared, the acetoxytrichloride crystallizes in greater proportions. At the moment, after new experiments by Dr. J. S. Lomas, it seems probable that other isomers of naphthalene acetoxytrichloride are produced also.

When we made chlorinations in chloroform, carbon tetrachloride, nitromethane and aqueous hydrochloric acid, different proportions of tars were isolated and could never be crystallized. Their infrared spectra suggested the presence of naphthols and quinones (O-H and C=O vibrations) partially produced by oxidation favoured in exothermic reactions, and partially as decomposition products from the processes of isolation.

The isolation of naphthalene tetrachlorides in pure condition is quite tedious and difficult in some cases. The fact that the α-isomer is the most insoluble makes facile its crystallization and purification. Despite this, its melting point is sometimes influenced by traces of other isomers and by the solvent used for the crystallization.

The γ-isomer, if free of α-tetrachloride, does not offer difficulties for purification.

The δ-isomer is more soluble than its γ and α-isomers. Any impurity of these isomers makes very difficult to obtain a good melting point. Sublimation does not help because the vapour pressure of all the isomers must be similar. Chromatography and zone melting were unsuccesful. The isomeric impurities were present in very small proportion because they could not be detected by infrared spectroscopy.

The very good yield in the synthesis of γ and ε-tetrachlorides made possible to obtain small quantities completely pure after several crystallizations, but the bulk of the reaction products could be isolated only as impure isomers.

22. STRUCTURES OF NAPHTHALENE TETRACHLORIDES AND ACETOXYTRICHLORIDE.

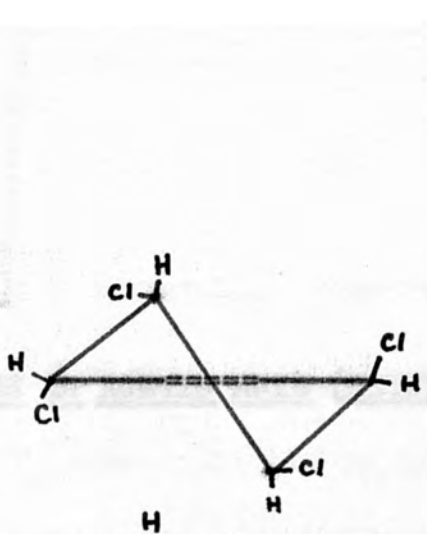
As it has been stated in part II (section 20), the p.m.r. spectra of the adducts isolated leads to the establishment of their structures, which are shown in next page.

In all the schematic formulae, the aromatic ring, not drawn, is attached to the double bond.

The stereochemistry of these addition products allows discussion of the possible mechanisms of reaction between chlorine and naphthalene.

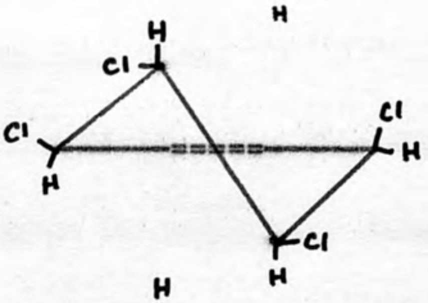
α -naphthalene tetrachloride

(solid state and in solution)



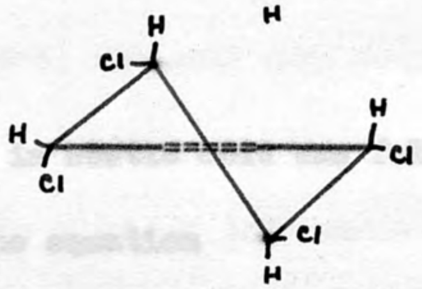
γ-naphthalene tetrachloride

(in solution)



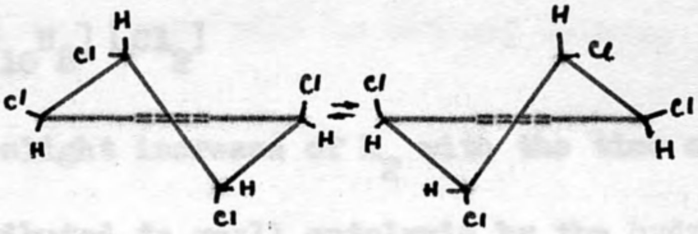
δ -naphthalene tetrachloride

(in solution)



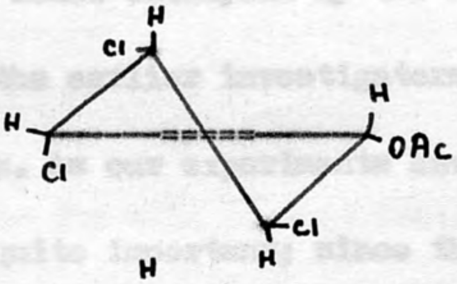
ε -naphthalene tetrachloride

(in solution)



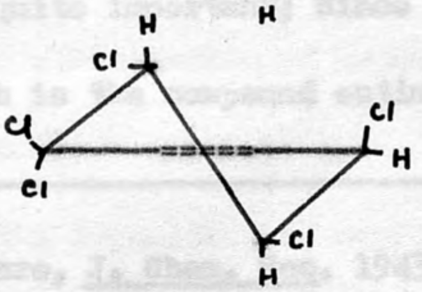
-naphthalene acetoxytrichloride

(in solution)



-naphthalene pentachloride

(in solution)



23. <u>COURSE OF CHLORINATION OF NAPHTHALENE IN ACETIC ACID</u> (<u>HETEROLYTIC REACTION</u>.

23.1) <u>Kinetics</u>.

When the chlorination of naphthalene in acetic acid was followed kinetically, the rate was found to obey the equation

$$v = k_2 [C_{10}H_8] [Cl_2]$$

Earlier studies[1,2] found a slight increase of k_2 with the time of reaction. This effect was attributed to small catalysis by the hydrogen chloride produced by the reaction, but the earlier investigators neglected completely the addition products. As our experiments have showed, the proportion of addition products is quite important; since they are formed by taking up more chlorine (which is the compound estimated in

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[1] P. W. Robertson and P. B. D. de la Mare, <u>J. Chem. Soc</u>. 1943, 279.

[2] M. J. S. Dewar and T. Mole, <u>J. Chem. Soc</u>. 1957, 342.

following the progress of the reaction), a correction (described in section 15) was necessary in calculating the rate-coefficients. With the modified equation, the coefficient k_2 showed no marked trend with initial concentration or progress of the reaction.

The kinetic expression suggests a slow first stage for the chlorination (rate-determining) with one or more intermediates formed by union of a molecule of naphthalene to one, and only one, molecule of chlorine.

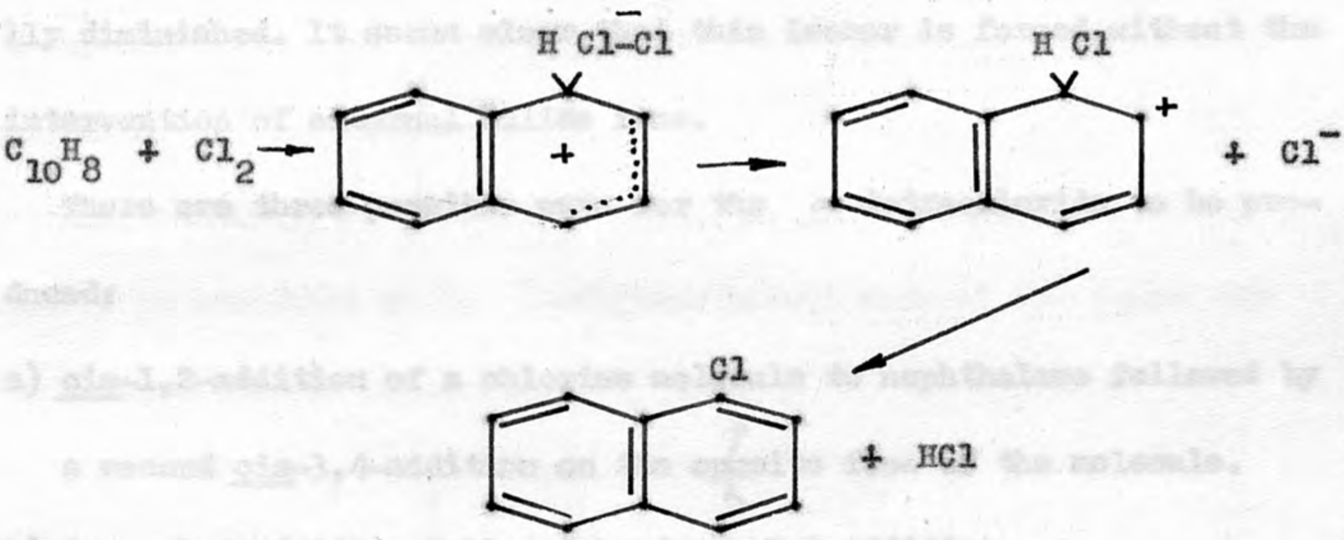
It cannot be demonstrated if there is only one intermediate for all the products. Some reasonable hypotheses will be set out below.

23.2) The mechanism of substitution.

1-Chloronaphthalene is presumed to be the main product isolated, without further investigation, from the chlorination of naphthalene in acetic acid. (See references in section 8).

The fact that the chlorine attacks the 1-position of naphthalene is in good agreement with theoretical predictions and experimental results for other reactions (see sections 1, 2 and 8).

The path of the reaction probably involves these steps:



On this mechanism, it is possible to interpret why added electrolytes promote substitution at the expense of addition; if proton-loss is determined at a relatively late stage on a reaction path in which the transition state is more polar than the reactants, then added electrolytes may be expected to favour this process.

23.3) The mechanisms of heterolytic addition in acetic acid.

The main product of addition of chlorine to naphthalene in acetic acid in the absence of added electrolytes is the α-tetrachloride (chlorine atoms in positions a'eea'). When chloride ions are added to the reaction mixture, however, the proportion of this isomer is substantially diminished. It seems clear that this isomer is formed without the intervention of external halide ions.

There are three possible ways for the α-tetrachloride to be produced:

a) cis-1,2-addition of a chlorine molecule to naphthalene followed by a second cis-3,4-addition on the opposite face of the molecule.

b) trans-1,4-addition followed by trans-2,3-addition

c) trans-1,2-addition followed by cis-S_Ni rearrangment, followed by trans-2,3-addition.

The first stage in mechanisms b and c cannot be formulated as one-stage processes, hence route a seems more reasonable.

The second stage in route a (or also in b or c) is obviously very fast because we have been unable to isolate a naphthalene dichloride even in chlorinations with excess of naphthalene. This result also accords with the intermediacy of a 1,2-dichloride rather than with a 1,4-dichloride. (The 1,2-adduct is thermodynamically more stable than that derived from 1,4-addition but it cannot be assumed without question that 1,2-addition would be kinetically favoured since it is known[1]

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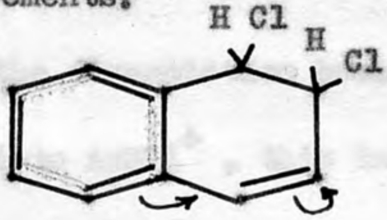
[1] De la Mare, Hughes and Ingold, J. Chem. Soc. 1948, 17 .

that kinetically controlled addition of halogens or hydrogen halides to conjugated systems often gives the thermodynamically less stable isomer in preponderant amount).

Theoretically, electrophilic attack on such 1,2-dichloro adduct should be initiated at the 3-position rather than at the 4-position since the electron movements:



should be the dominant directing influence.

The chlorine in the 2-position would be expected to hinder attack on the same side of the ring plane, both sterically and by its polar effect, and the α-tetrachloride (a'eea') is obtained but not the isomer a'eae'.

With added chloride ions, the most marked change is the decrease in the proportion of the α-tetrachloride and the corresponding increase in the proportion of the δ-isomer (a'eee'). Apparently the stereochemistry of the first stage of the addition has not been interfered with, but that of the second now in part involves a <u>trans</u>-process, with intervention by external ions. Again the attack initiated at the 3-position must be in the opposite face of the molecule, leading to the δ-isomer and not to the tetrachloride with the structure a'eaa'.

These results accord with the view developed in earlier studies[1] of chlorination of phenanthrene, that cis-addition is determined at an early stage in the reaction path and is essentially an internal capture of chloride ions during the course of attempted dissociation of a complex $ArH.Cl_2$; if the dissociation becomes complete to give the carbonium ionic intermediate $ArHCl^+$, this intermediate can be captured by external nucleophiles, but then this stage proceeds in the trans-sense.

The naphthalene acetoxytrichloride has a configuration which corresponds with that of the δ-tetrachloride, and it can be also produced by trans-addition in the second stage of the reaction, initiated by attack of chlorine at the 3-position, again on the opposite face of the molecule to that taken by the first molecule of halogen. As the acetate ions or the perchloric acid do not affect the proportion of acetoxy adduct, it can be supposed that only the molecules of acetic acid play an important rôle in the formation of the adduct.

The effect of the perchloric acid is generally similar to that of

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[1] De la Mare et al., J. Chem. Soc. 1961, 5285 ; 1964, 5327 .

chloride ions; the first stage is not interfered with, but the more ionising conditions favour *trans*-processes for the second stage and the δ-tetrachloride increases at expense of the α-isomer.

The δ-naphthalene tetrachloride and the acetoxytrichloride can be also produced through other paths, for example:

d) *trans*-1,2-addition followed by *cis*-3,4-addition

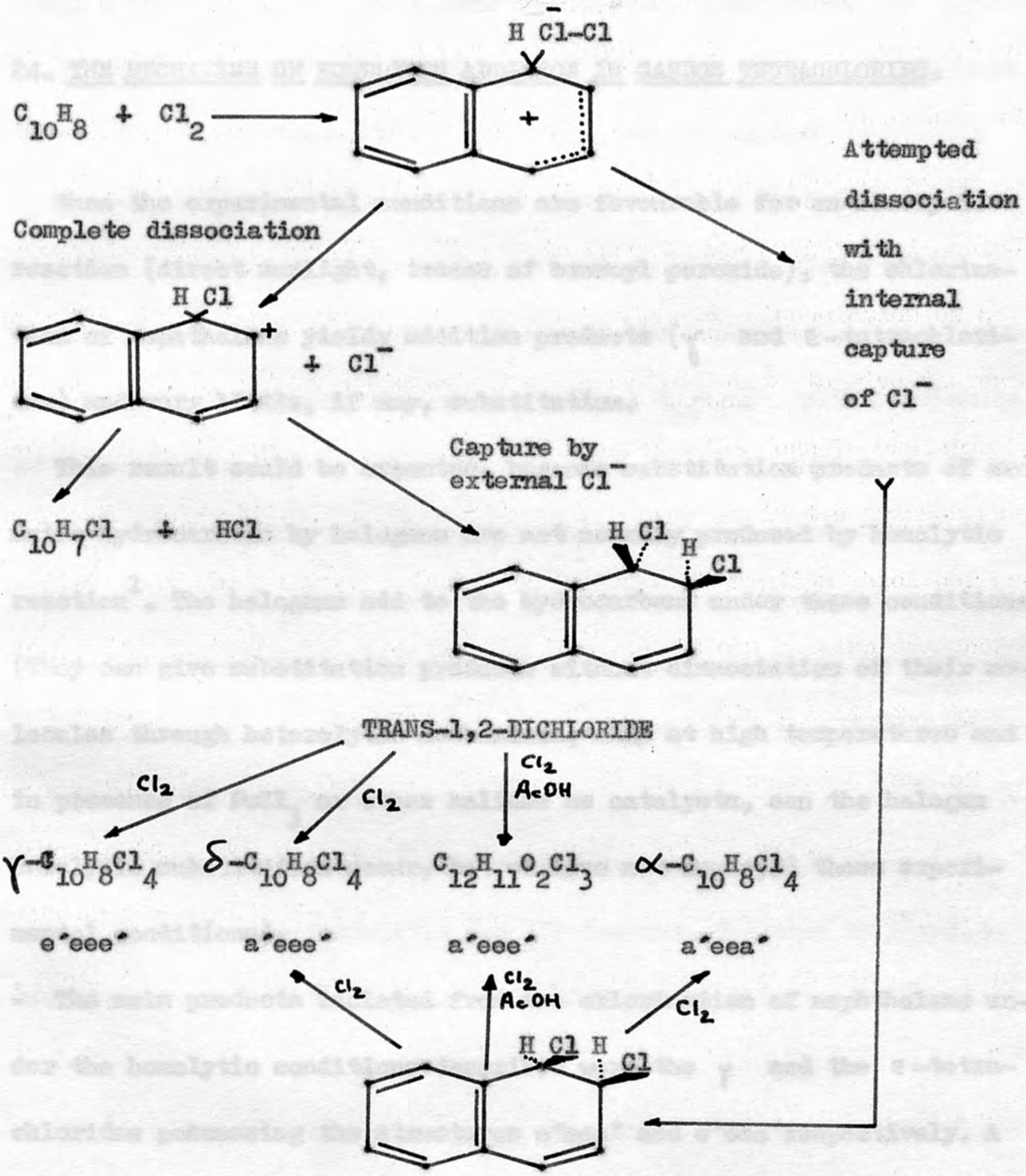
e) *cis*-1,4-addition followed by *trans*-2,3-addition.

Route *d* could be initiated from the same intermediate as the substitution product (see scheme, next page).

The γ-naphthalene tetrachloride (e'eee') is produced only as traces when the chlorination of naphthalene is carried out in acetic acid.

Its formation is not possible through the 1,2-naphthalene dichloride intermediate postulated for both α and δ-tetrachlorides, but it can be produced from route *d* (see scheme):

Some mechanisms of chlorination of naphthalene in acetic acid:



24. THE MECHANISM OF HOMOLYTIC ADDITION IN CARBON TETRACHLORIDE.

When the experimental conditions are favourable for an homolytic reaction (direct sunlight, traces of benzoyl peroxide), the chlorination of naphthalene yields addition products (γ and ε-tetrachlorides) and very little, if any, substitution.

This result could be expected, because substitution products of aromatic hydrocarbons by halogens are not usually produced by homolytic reaction[1]. The halogens add to the hydrocarbons under these conditions. (They can give substitution products without dissociation of their molecules through heterolytic mechanisms; only at high temperatures and in presence of $FeCl_3$ or other halides as catalysts, can the halogen homolytic substitution occur, but we have not employed these experimental conditions).

The main products isolated from the chlorination of naphthalene under the homolytic conditions described were the γ and the ε-tetrachlorides possessing the structures e'eee' and e'eaa'respectively. A

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[1] "Homolytic Aromatic Substitution", B. H. Williams. Pergamon Press. London 1960, page 120.

small proportion of the δ-isomer (a'eee') was also found.

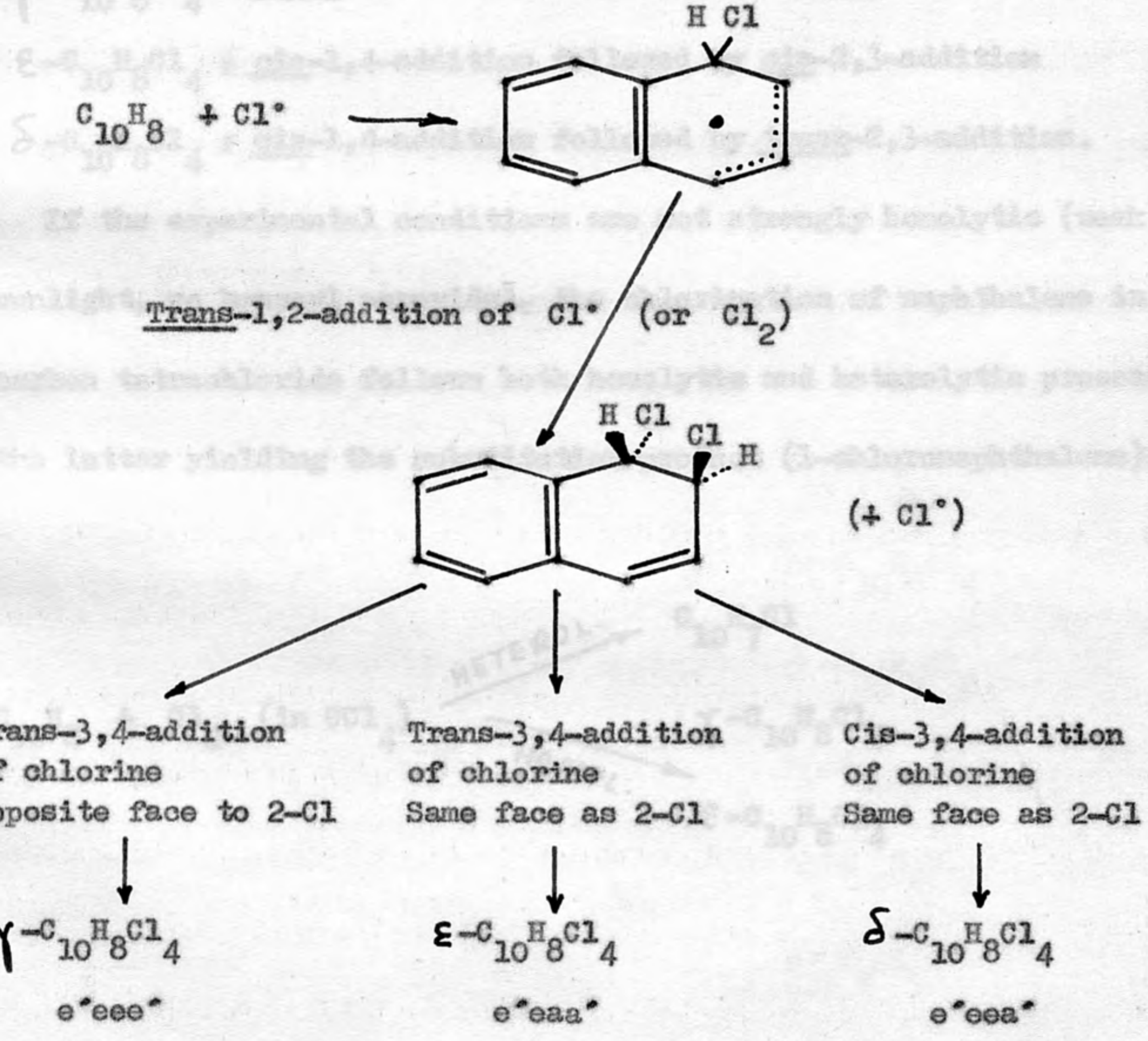
It seems reasonable to attribute the formation of the main isomers to two trans-additions. In a first stage, common to both isomers, a trans-1,2-addition of a molecule of chlorine would lead to a naphthalene dichloride with the chlorine atoms in positions e'e, probably formed by attack of a chlorine radical at the 1-position of the hydrocarbon, followed by reaction of the radical $C_{10}H_8Cl^\bullet$ with a molecule of chlorine (or with a second radical $Cl^\bullet$). The second stage would be a trans-3,4-addition of a second molecule of chlorine on either side of the molecule to yield a mixture of the two isomers. Perhaps the homolytic dissociation of the molecule of chlorine allows to initiate the attack at the 4-position, thus avoiding the steric and polar interference of the 2-chlorine.

The small quantity of δ-tetrachloride could proceed through the same 1,2-dichloride postulated for its isomers, followed by cis-3,4-addition started at the face of the molecule opposite to the 2-chlorine (see scheme, next page).

Other mechanisms involving trans or cis-1,4-additions as the first stage would not allow explanation of the formation of γ and ε-tetrachlorides from the same intermediate, but they cannot be rejected

Mechanism of homolytic addition of chlorine to naphthalene, in carbon tetrachloride :

$$Cl_2 + h\nu \longrightarrow 2\,Cl^\cdot$$



because very little is known about homolytic reactions except that they usually proceed through chain reactions.

The naphthalene tetrachlorides require, if a 1,4-dichloride is formed in the first stage, these routes:

γ-$C_{10}H_8Cl_4$: trans-1,4-addition followed by trans-2,3-addition

ε-$C_{10}H_8Cl_4$: cis-1,4-addition followed by cis-2,3-addition

δ-$C_{10}H_8Cl_4$: cis-1,4-addition followed by trans-2,3-addition.

If the experimental conditions are not strongly homolytic (weak sunlight, no benzoyl peroxide), the chlorination of naphthalene in carbon tetrachloride follows both homolytic and heterolytic processes, the latter yielding the substitution product (1-chloronaphthalene):

$$\begin{tikzcd}
 & C_{10}H_7Cl \\
C_{10}H_8 + Cl_2 \text{ (in } CCl_4\text{)} \arrow[ur, "\text{HETEROL.}"] \arrow[dr, "\text{HOMOL.}"'] & \gamma\text{-}C_{10}H_8Cl_4 \\
 & \varepsilon\text{-}C_{10}H_8Cl_4
\end{tikzcd}$$

25. THE MECHANISMS AND KINETICS OF CHLORINATION OF NAPHTHALENE IN CHLOROFORM.

This reaction produces the widest variety of products. Not only the substitution product but the four naphthalene tetrachlorides as well as a naphthalene pentachloride are produced.

As the absence or presence of light only changes a little the proportion of the tetrachlorides (especially the α-isomer), it must be deduced that independentely of the experimental conditions chosen, both heterolytic and homolytic processes coexist, the former being predominant:

$$C_{10}H_8 \;+\; Cl_2 \quad (\text{in } CHCl_3) \quad \begin{array}{c} \nearrow \\ \\ \searrow \end{array} \quad \begin{array}{l} C_{10}H_7Cl \\ \alpha\text{-}C_{10}H_8Cl_4 \\ \delta\text{-}C_{10}H_8Cl_4 \\ \gamma\text{-}C_{10}H_8Cl_4 \\ \varepsilon\text{-}C_{10}H_8Cl_4 \\ C_{10}H_7Cl_5 \end{array}$$

The dark reaction is much slower than that in acetic acid, because the smaller polarity of the solvent makes difficult the formation of a polar transition state necessary for the heterolytic reaction.

The kinetic expression for the rate of reaction is not

$$v = k_2 [C_{10}H_8][Cl_2]$$

as for the reaction in acetic acid, because the coefficient k_2 increases with the time of reaction and it is also influenced by the initial concentration of chlorine.

If a trace of iodine is present, its big molecule makes more facile the formation of a different transition state with a molecule of each, naphthalene, chlorine and iodine. However, the expression

$$v = k_2^{*} [C_{10}H_8][Cl_2][I_2]$$

is not complete because k_2^{*}, which is much greater than k_2, increases with the extent of reaction.

Hydrogen chloride and water (or hydrochloric acid if preferred) have also a catalytic effect, but a relatively great concentration is necessary in order to increase the polarity of the solution.

In this case the correct expression for the rate is

$$v = k_2^{**} [C_{10}H_8][Cl_2][HCl.H_2O]$$

and no trend of k_2^{**} with the progress of the reaction or with the initial concentration of chlorine was observed. The iodine is a better catalyst than the hydrochloric acid (see below), but the reaction, despite its speed, is still under the influence of the HCl produced:

Kinetics of chlorination of naphthalene at 25°

Solvent	Catalyst	Order	Rate coefficient ($l.mole^{-1}.min^{-1}$)
AcOH	——	2	$k_2 = 2.6$
$CHCl_3$	——	>2	$k_2 = 0.03$ to 0.1
$CHCl_3$	I_2 0.00008 M	>3	$k_2' = 11.7$
$CHCl_3$	I_2 0.00004 M	>3	$k_2' = 5.6$
$CHCl_3$	I_2 0.00002 M	>3	$k_2' = 2.7$
$CHCl_3$	HCl 0.22 M *	3	$k_2'' = 1.0$
$CHCl_3$	HCl 0.12 M **	3	$k_2'' = 0.29$

* Water about 2% (saturation). ** Water about 1% (50% saturation)

Schonken et al.[1], and Andrews and Keefer[2] found similar effects for these catalysts in the chlorination of liquid hydrocarbons, with and without solvent, as well as the fact that the order of the reaction fell to 2 in acetic acid or other polar solvents where neither iodine

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[1] P. Schonken, J. L. Page and J. C. Jurgens, Bull. soc. chim. France 1957, 5 , 1394 .

[2] L. J. Andrews and R. M. Keefer, J. Am. Chem. Soc. 1957, 79, 5169.

nor hydrogen chloride have catalytic effect.

None of the catalysts we have employed changed fundamentally the coexistence of heterolytic and homolytic mechanisms, the same products being obtained.

When the reaction was catalyzed by light, and hence homolytic mechanism was favoured, the proportion of α-tetrachloride decreased slightly but those of γ and ε-isomers increased in a much smaller proportion, the δ-tetrachloride and the substitution product being favoured. This result proves that the heterolytic reaction is still predominating; probably the light catalyzes the chlorination of chloroform and the hydrogen chloride produced favours the heterolytic reaction.

The small quantity of chloronaphthalene tetrachloride detected in all these cases was probably produced by addition of two molecules of chlorine to 1-chloronaphthalene.

26. OTHER ATTEMPTED CHLORINATIONS.

Without any doubt the chlorination of naphthalene is a very complicated reaction which can occur through many mechanisms of which several have been set out above.

The fact that processes described in the literature fail to give the expected products or lead to others, as well as the enormous influence of catalysts, confirm the plurality of mechanisms.

The facts accumulated by our experience recommend to be very cautious when trying to explain or to draw practical consequences of a reaction influenced by so many factors.

We have not studied extensively other chlorinations but it must be emphasized that the chlorination of naphthalene in nitromethane (solvent more polar than acetic acid) gives a behaviour similar to that found in chloroform, with formation of 1-chloronaphthalene, three or four naphthalene tetrachlorides and the chloronaphthalene tetrachloride.

When molten naphthalene was chlorinated with excess of chlorine, 1-chlornaphthalene, α-naphthalene tetrachloride and chloronaphthalene tetrachloride were produced. These experimental conditions were supposed to lead to some homolytic reaction but no γ or ε-tetrachlorides were detected. The higher temperature and the excess of chlorine are responsible of the formation of the chloronaphthalene tetrachloride. The 1-chloronaphthalene (much less reactive than naphthalene) reacts by addition of two moles of chlorine to give the pentachloride.

27. REPRODUCIBILITY OF THE EXPERIMENTAL CONDITIONS EMPLOYED AND POSSIBLE INFLUENCE OF SEVERAL FACTORS.

As stated in section 9, our object on carrying out the investigations described in this thesis, was to study the products of addition of chlorine to naphthalene, in different solvents and experimental conditions.

Many results (for example the quantitative estimation of products, section 10.3, and the kinetic experiments, sections 15 and 16) have been reproduced several times. But the preparative experiments can be influenced (and probably are) by factors whose study has not been yet made.

First of all it must be considered that the quantitative and kinetic experiments have been carried out in highly purified solvents, in dilute solutions and at temperatures not higher than 25°. The preparative synthesis have been made in solvents not so purified (for example glacial acetic acid) with greater concentrations of reactants. As the reactions are quite exothermic, the temperature ~~rised~~ rose without any control.

The influence of weak illumination on chlorinations in acetic acid has been neglected without further investigation and perhaps is responsible for the traces of γ-tetrachloride produced.

The kinetic expressions are influenced by the factor α (see sections 15 and 16) calculated from preparative experiments. It seems that this factor does not change notably under very different experimental conditions (the variation is from 1.46 for acetic acid to values between 1.33 and 1.43 in chloroform according to the catalyst employed) but perhaps the rate-coefficient values are affected by some error.

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APPENDIX

INFRARED SPECTRA OF SOME ADDUCTS FROM NAPHTHALENE

These were determined by using a Grubb-Parsons D.B.$_2$ grating infrared spectrophotometer. The results are shown below. They refer to Nujol mulls and the Nujol absorptions at 1375 and 1450 cm^{-1} have been omitted.

<u>Infrared absorption bands</u> (cm^{-1}; range 650-2000 cm^{-1}) <u>of some adducts from naphthalene.</u>

Tetrachlorides				Hydroxytri-chloride	Acetoxytri-chloride
α	γ	δ	ε		
597 m	601 m	697 m	606	600	603
	611	613		618	620 s
633 m			642 m	667 sh	667 sh
686 vs	691	667 s	670 s	680 s	675 vs
		706 s	713 s		
736	723 vs			732 m	734 s
	737 m	741	741 s		
774 s	779 s	775 m	776 s	759 s	762 s
781 sh				795 s	787 s
	802	794 m	805 m	817	808
832 m	835 m	826 sh			
845 m		836 m	832 s	839 m	831 m
		872	881	870	873
902	902 m	901 m	901 m	895	899
952 m	966		962 m		925
		980		984	989 m
1020 m				1015 m	
		1037	1037	1050	1033 s
	1062	1062		1071 m	1080
		1089		1090	1095

Tetrachlorides				Hydroxytrichloride	Acetoxytrichloride
α	γ	δ	ε		
1110			1112 m	1122	1117
1174				1158	
1190		1189	1190 m	1176	1188
				1186	
1202	1211 m	1214	1225	1205 m	1224 s
				1212	1232 sh
1261	1235 m	1239 m	1256	1259	
		1263	1269	1287	
1294		1295		1311	1294
	1318				1307
1351		1342	1351	1339	1344
					1488
					1730 s
				[a]	1745 sh

vs = very strong
s = strong
m = medium
sh = shoulder
All others weak

[a] Also has a medium absorption band at 3540 cm^{-1}.