STEREOCHEMISTRY OF DIPHENYLS

A thesis submitted to the University of London for the
degree of Doctor of Philosophy

by

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ABSTRACT.

This thesis is divided into two sections.

Part 1 describes the synthesis of various alkyldiphenyls. The ultraviolet absorption spectra of these diphenyls were examined in order to study the relation between configuration and conjugation. The diphenyls prepared include 2-ethyl-, 2:2'-diethyl-,3:3'-diethyl- and 4:4'-diethyldiphenyl; 2-*iso*-propyl-, 2:2'-di-*iso*propyl-, 4:4'-di-*iso*propyl, & 2:2':4:4'-tetra-*iso*propyldiphenyl. 6:6'-Di-*iso*propyldiphenyl-3:3'-dicarboxylic acid and 2'-*iso*propyldiphenyl-2-carboxylic acid were obtained as intermediaries and the optical properties of these two acids were studied in an attempt to correlate the evidence of steric hindrance as shown through optical activity with the evidence shown by the ultraviolet absorption spectra. 2'-(*α*-Hydroxy*iso*propyl)-diphenyl-2-carboxylic acid was initially used as starting material in the synthesis of the latter compound and the mode of its dehydration under different conditions studied. Under acid conditions 9:9-dimethylfluorene-4-carboxylic acid was obtained and from this 9:9-dimethylfluorene, 4-*iso*propenyl-, and 4-*iso*propyl-9:9-dimethylfluorene were prepared and the ultraviolet absorption spectra determined.

Part 11 describes the preparation of 2:2'-dimethyl-6-aminodiphenyl. The first method tried led to 2:2'-dimethyl-5-aminodiphenyl. 2:2':4:4'-Tetramethyl-6-aminodiphenyl was also prepared

and converted into 2:4:5:7-tetramethyl-9-(p-nitrophenyl)-phenanthridine, spectroscopic evidence being used to confirm its structure. Finally the phenanthridine was reduced to 2:4:5:7-tetramethyl-9-(p-aminophenyl)-phenanthridine. It has not yet been possible to obtain this compound in an optically active condition.

The author wishes to express her thanks to Professor E.E.Turner, F.R.S. for all his help and encouragement, and to Dr. D.Muriel Hall for many helpful discussions. She is indebted to the Department of Scientific and Industrial Research for a maintenance grant.

P.M.E.

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PART 1.

INTRODUCTION.

When the collinear structure for diphenyl was first accepted, it was thought that the preferred configuration would be planar. Dhar (*Indian J. Physics*, 1932,*7*,43) by X-ray methods showed that diphenyl was in fact planar in the crystal. Maximum resonance would be obtained for a planar configuration. If *ortho* substituents were present in the diphenyl molecule, then if these substituents were sufficiently large the two rings could no longer be coplanar or rotate freely about the 1:1'- bond. In some cases the restricted rotation conferred measurable optical stability on the rotational enantiomorphs. In such cases resonance between the two rings was considered impossible.

More recent evidence suggests that the preferred configuration in diphenyl itself is not however planar. e.g.Karle and Brockway (*J.Amer.Chem.Soc.*,1944,*66*,1974) from electron diffraction measurements of the vapour favour a non-planar structure and Bastiansen (*Acta Chem. Scand.*,1949,*3*,408) gives the angle between the rings as 45° ± 10°. In the crystal strong intermolecular cohesive forces will operate and in solution an intermediary value for the angle between the rings is to be expected. Other workers have pointed out that partial loss of coplanarity is not necessarily associated with complete loss of resonance. Coulson and Longuet-Higgins (see, Braude and Forbes, J.Chem.Soc.,1955,3776) have calculated that the decrease in repulsion energy between the ortho hydrogen atoms in diphenyl and the decrease in resonance energy resulting from non-planarity are practically balanced for interplanar angles up to about 20°.

Apart from X-ray and electron diffraction methods which give information about the configuration of the molecule in the solid and gaseous states respectively, and optical resolution or optical activation of diphenyls containing suitable ortho substituents, other methods which have been used for determining the configuration of diphenyls are the measurement of dipole moments and ultraviolet absorption spectra.

A study of the ultraviolet absorption spectra of diphenyls gives direct information about the extent of the conjugation between the rings and from this conclusions involving the relation between resonance and coplanarity of the phenyl rings have been drawn. This method is very useful since it can be applied to dilute solutions and the experimental techniques are quite simple and rapid. It is also more sensitive than the methods mentioned above. The smallest significant wavelength displacement is approximately 50 Å and this corresponds to an energy difference of only 1-2 K.cal.mol.$^{-1}$, whereas the existence of isolable optical isomers requires an energy barrier of not less than 15 $K.cal.mol.^{-1}$ between the two stereoisomers. In addition optical resolvability is a function of the molecule in the ground state, whereas the spectral properties depend on both the ground and excited states. The excited states are more influenced by steric effects than the ground state and therefore much less steric overlap is required to produce spectral phenomena than optical effects.

The absorption of light energy causes transition of a molecule from the ground state (energy E_o) to an ionic electronically excited state (E_1). The difference in energy of these two states determines the frequency (ν) of the light absorbed.

$$E_1 - E_o = h\nu$$ where h is Planck's constant.

Hence the smaller the energy difference between the ground and excited states, the lower the frequency and the greater the wavelength (λ) of the light absorbed. Transitions between different electronic levels are usually accompanied by simultaneous changes in the vibrational and rotational levels and hence do not result in a single spectral line but give rise to a large number of individual lines which in the case of a complex molecule are generally broadened so that they overlap giving rise to an absorption band. The intensity of the absorption is related to the probability of the transition, the energy of the transition being determined by the wavelength of the light absorbed. Maxima correspond to the most probable transitions and the absorption properties of a compound are often expressed in terms of the intensity and wavelength of the maxima.

Absorption in the near ultraviolet region (λ, 2000-4000 Å) corresponds to energy increases of 70-140 K.cal.mol.$^{-1}$ and quanta of this magnitude are involved in the ordinary displacement of the π or 'unsaturation' electrons. A study of the light absorbing properties of a molecule in this region should therefore give some information about the distribution of unsaturated linkages in the molecule.

When a molecule contains two or more ethylenic bonds which are well separated they behave as separate absorbing groups and the effect on the spectrum is largely additive. If however thet are separated by only one single bond a conjugated system results giving rise to markedly different chemical and physical properties which can be explained by the concept of resonance or mesomerism. The structure of the molecule cannot be represented satisfactorily by any of the classical formulae but may be represented by several structures of approximately equal potential energy which differ only in the distribution of the electron pairs amongst the atomic nuclei. These structures have no separate existence but resonance between these different structures gives rise to a stable structure of energy content lower than any of the contributing forms.'Ionic' resonance structures contribute chiefly to the excited state and hence tend to resonance-stabilise the excited state more than the ground state, thus lowering the energy of the excited state more than that of the ground state. This affects the molecular spectrum in two ways.

1) A resonance 'hybrid' will require less energy for excitation and therefore absorption will take place at longer wavelengths.

11) Since resonance crowds the energy levels, transitions between the different energy levels are more probable and therefore the intensity of the absorption is increased.

In the case of benzene, each carbon atom in the ring has one π orbital perpendicular tq the plane of the ring and interaction between the carbon atoms is possible so that a resonating system of bonds results. Maximum interaction i.e. overlap of orbitals, will result when the orbitals are parallel to each other.

The spectrum of benzene has two main absorption bands. (see e.g. Henri, *J.phys.radium*,1922,3,189.)

a) A high intensity band near 1980 Å (ε ca. 8000), which is therefore outside the range of the normal quartz spectrophotometer.

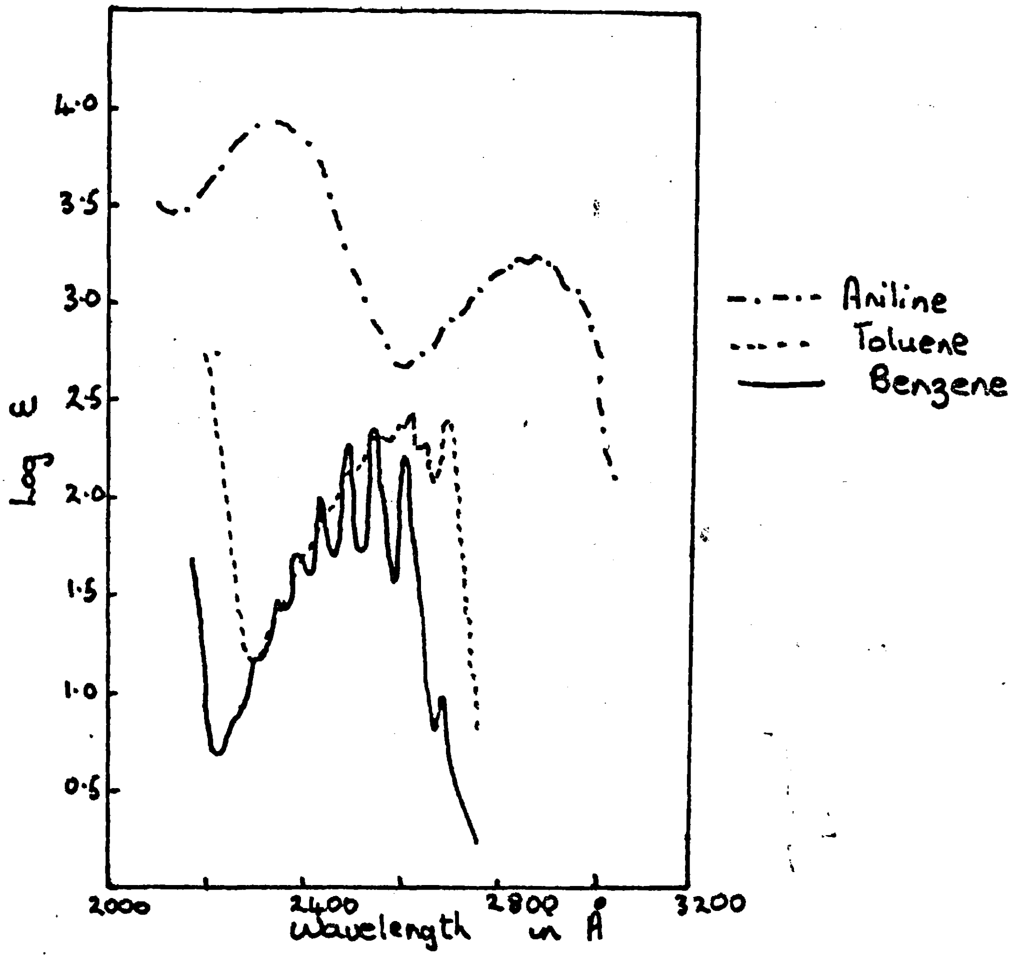
b) A lower intensity band between 2,300-2,700 Å

(ϵ c.a.230), which therefore lies well in the range of the quartz spectrophotometer.

Substituents such as alkyl groups which do not interact strongly with the ring usually give a small increase in the intensity of the absorption, together with small shifts to longer wavelengths. The characteristic fine structure of the bands is not lost. If however groups which interact more strongly with the ring are present, e.g. -OH, -OMe, -NH_2, a much larger increase in intensity is observed and the fine structure is lost.

(See Friedel + Orchin, Catalogue of U.V. Spectra of Aromatic Compounds)

FIG.1



Jones (J.Amer.Chem.Soc.,1945,67,2128) reviewed the effect of substituents on the spectra of polynuclear aromatic hydrocarbons. These effects fall roughly into four classes.

1) Bathochromic Effect (B Effect).

The 'B Effect' corresponds to a shift to longer wavelengths and results when a substituent with no unshared electrons on the atom attached to the ring is substituted in the nucleus, e.g. alkyl groups, $-NH_3^+$. This shift must result from a decrease in the energy difference between the ground and excited states. The introduction of alkyl groups cannot give rise to any new resonance structures and Mulliken and co-workers (J.Amer.Chem.Soc.,1949,63,41),suggested that 'hyperconjugation' of the alkyl groups with the ring was responsible for the lowering of the excitation energy. The increased intensity and long-wave shifts observed for para alkyl substituted diphenyls arise in this way.

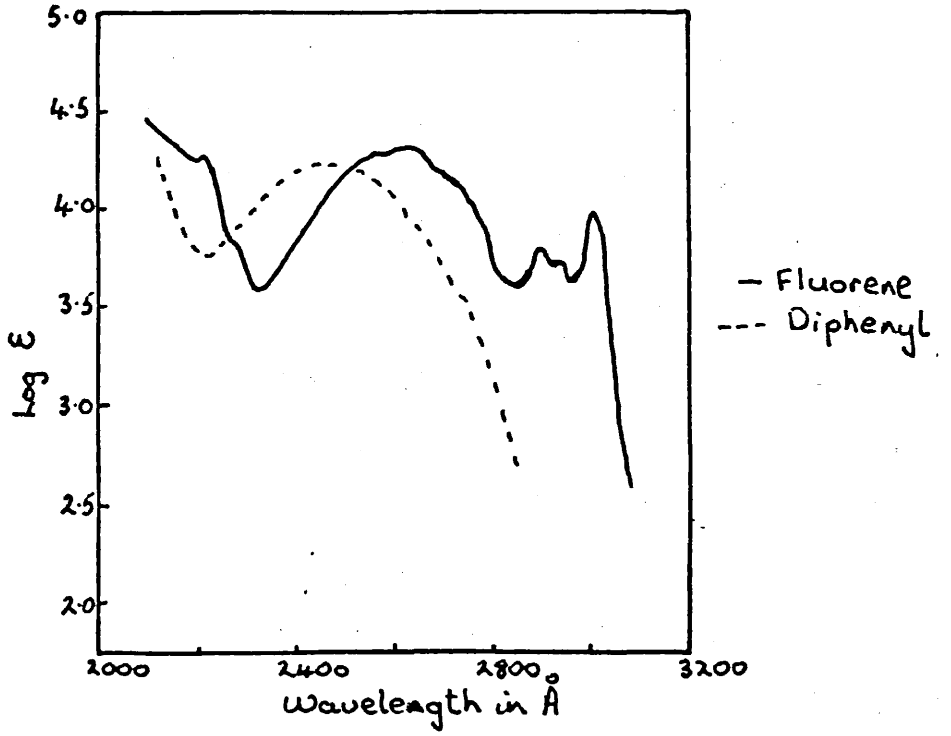
11) Fine-Structure Effect (Fs Effect).

The 'Fs Effect' is the splitting of the spectral bands which results for example when a saturated methylene group is introduced across a polynuclear aromatic hydrocarbon,e.g. fluorene. Fluorene contains a strained 5-membered ring and the spectrum has much fine structure. This is attributed to vibrational activations of the molecule.

Spectra of Diphenyl and Fluorene for comparison.

(Friedel and Orchin, Catalogue of U.-V.-Spectra of Aromatic Compounds.)

FIG. 2.



111) Conjugation Effect (C Effect).

In the case of the 'C Effect' in some or all of the spectral bands we may get:-

a) A large bathochromic shift.

b) A decrease in fine structure.

c) An increase in intensity.

This effect is produced by unsaturated hydrocarbons (or nonhydrocarbon groups containing an atom with unshared electrons e.g.-NH_2), in which the unsaturated link is in a position to conjugate with the aromatic ring. The effect produced is usually large.

As a result of the conjugation, resonance between the various 'structures' is possible and by increasing the length of the conjugated system the number of possible resonance forms is increased, the excitation energy is decreased and the wavelength shifted to longer wavelengths. Phenyl groups produce a much greater effect than other hydrocarbon substituents because of the much more extensive conjugation, and diphenyl shows an intense band arising as a result of conjugation between the two rings at λ c.a. 2500 Å, ε c.a. 20,000. (see Fig. 2). The spectrum has no fine structure and is quite unlike that of benzene.

It was generally considered that if resonance or conjugation in diphenyl is to operate the π orbitals of the 1:1'-C-C bond must be parallel and this means that the two rings must be coplanar. London (J. Chem. Physics, 1945, 13, 396) assuming a planar configuration for diphenyl, constructed wave functions for diphenyl from linear combinations of the benzene molecular orbitals and computed the numerical values of the energy levels in diphenyl. The agreement between the theoretical electronic transitions and the observed ultraviolet absorption spectrum was good and this he concluded favoured the planar model. However a complete review of the literature shows that it is more accurate to speak of near planarity rather than coplanarity as a condition of effective resonance.

Rodebush and Feldham (J.Amer.Chem.Soc., 1946,68,896) conclude that 'all that can be stated with certainty from spectroscopic studies is that in unsubstituted diphenyls the configuration is near enough to coplanarity to allow a resonance energy of several large calories'.

Braude and Forbes, (J.Chem.Soc.,1955,3776), suggest that since fluorene must be practically planar to accomodate the methylene bridge and since fluorene shows diphenyl-type absorption more intense than that of diphenyl itself, then this supports the assumption that diphenyl itself is near planar in solution. Thus fluorene is considered by these workers as a planar o:o'-disubstituted diphenyl, the intense increase in intensity being attributed to the normal substitution effect of alkyl groups being comparable with that of p:p'-ditolyl. However in fluorene (unlike diphenyl) the phenyl rings are not collinear, and the molecule must be strained. These two are therefore not strictly comparable.

1V) Steric Effect (S Effect).

Steric effects often exert a considerable influence on spectra acting in opposition to the conjugation effect. The 'S Effect' produces:-

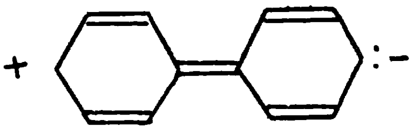
a) Short-wave shifts.

b) Decreased intensity.

C) Increased fine structure.

In the case of diphenyls with small *ortho* substituents although some conjugation may still be present there is interference with resonance with the above results.

Calvin (*J.Org.Chem.*,1939,**4**,256) pointed out that if pure states of the type X are to contribute to the ground state of diphenyl, it must be possible for the two rings to become coplanar. (see also, Mulliken,*J.Chem.Phys.*,1939,**7**,121).



X

If the contribution of types X to the ground or excited states is reduced or eliminated, the spectrum should be very similar to that of the two single ring structures. In the extreme case, when sufficiently large groups are present in the *ortho* position to prevent the rings becoming coplanar the spectrum of the diphenyl should correspond to that of the two benzene components, the effect being additive. If however the coplanar structure was possible the fine stucture should be lost and a great increase in intensity would result, i.e. diphenyl-type spectrum would result. All this has been confirmed experimentally. However from the data so far collected a complete correlation of the geometry of the molecule with the evidence of steric hindrance as observed from the spectrum has not been possible. A satisfactory quantitative treatment of the factors determining the extent of steric interference with resonance is lacking.

Guy (*J.Chim.phys.*,1949,*46*,469), calculated that for an angle (θ) between the two rings in diphenyl,

$\theta = 0^\circ - 22.5^\circ$, resonance unaffected.
$\theta = 45^\circ - 67.5^\circ$, resonance practically zero.
$\theta = 67.5 - 90^\circ$, resonance impossible.

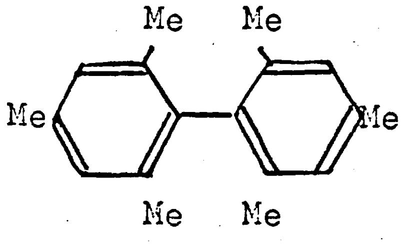
Braude and Sondheimer (*J.Chem.Soc.*,1955,3754) pointed out that steric effects in conjugated systems may be divided into two types.

In type 1 there is a decrease in the intensity of absorption only. This type results when the steric hindrance is slight, transitions taking place between non-planar ground states and uni-planar (or nearly planar) excited states. e.g. alkylated acetophenones, 9:10-dihydrophenanthrene. In these cases it is considered that the transitions are restricted to the vibrational states of the molecule in which a sufficient degree of planarity is retained. The transition probability is thus decreased but the transition energy remains unchanged.

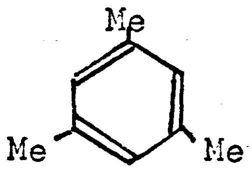
In type 11 the intensity change is accompanied by a shift in wavelength. This type is observed in the case of *ortho* substituted diphenyls; the steric effects here are larger and the transitions take place between non-planar ground and excited states.

After the above general account of ultraviolet absorption spectra it is of interest to summarise the results obtained for the spectra of alkyl substituted diphenyls.

In an attempt to explain the experimental results of Pickett, Walter and France, (J. Amer. Chem. Soc., 1936, 58, 2296) Kistiakowsky seems to have first suggested that the marked effect of ortho substituents on the spectrum of diphenyl was a result of steric effects. These workers first showed that diphenyls in which rotation about the 1:1' C:C bond was restricted had very different light absorbing properties from those capable of free rotation. Methyl groups were known not to show selective absorption in the region studied and to produce only small modifications in the spectrum of benzene. They therefore compared the spectra of dimesityl(A) and mesitylene (B).



(A)



(B)

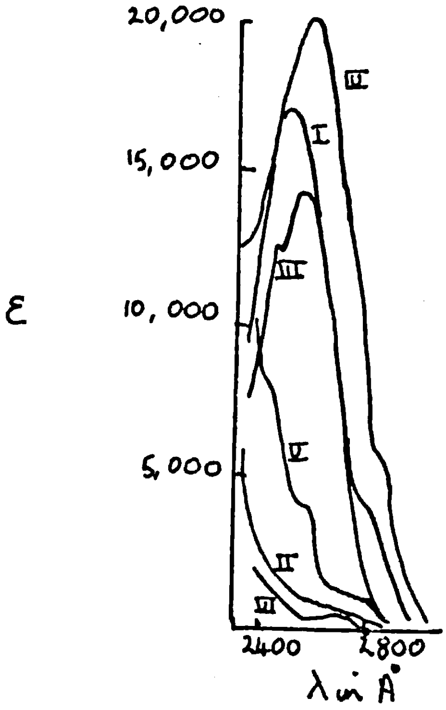
It was found that the ultraviolet absorption spectra of (A) and (B) were very similar but the most intense bands in

(B) were shifted towards shorter wavelengths in (A). In the diphenyl compound the values of the extinction coefficient were 2-3 times those in the benzene compound. 3:3'-Ditolyl and 4:4'-ditolyl however showed no fine structure corresponding to that of toluene. In the case of the *p:p'*-compound the absorption intensity was increased considerably and the absorption curves resembled those of diphenyl. Similar results were obtained for the corresponding chloro compounds.

Pestemer and Meyer-Pitsch (*Monatsh.*, 1937, *70*, 104) studied some mono substituted diphenyls and again showed that *ortho* substituted compounds absorb ultraviolet light with reduced intensity as compared with diphenyl itself and *meta* and *para* substituted derivatives.

O'Shaughnessy and Rodebush, (*J.Amer.Chem.Soc.*, 1940, *62*, 2906) carried out a general investigation of the spectra of substituted diphenyls and concluded that the ultraviolet absorption spectra promised to serve as a test for restricted rotation in diphenyls and similar molecules where coplanarity was necessary for resonance. Some of their results are given in fig. 3. In 2:2'-ditolyl there was a surprising reduction in intensity and it was concluded that the methyl groups interfered with the 6:6' H atoms to such an extent that the rings were turned well out of the plane and all resonance between them was destroyed. In the case of 2:2'-4:4'-tetramethyldiphenyl the increased absorption was thought to arise because the *para* substituents promote the ionic state and planar configuration.

FIG. 3.



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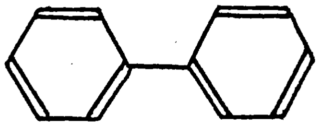

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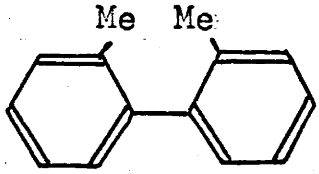

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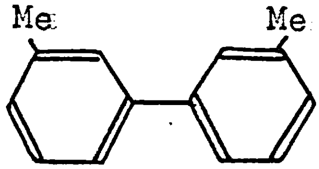

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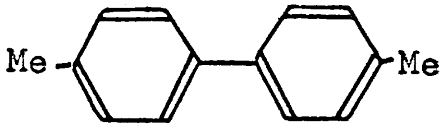

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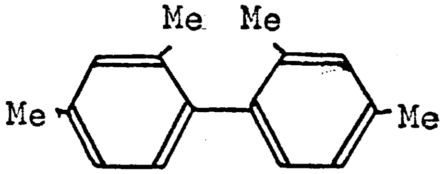

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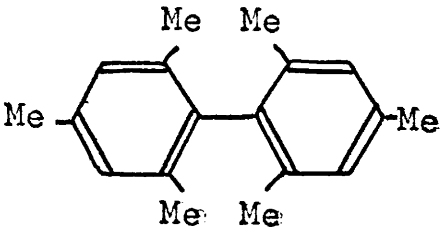


Williamson and Rodebush (J.Amer.Chem.Soc.,1941,63, 3018) obtained evidence for increased departure from coplanarity as the size of the ortho substituents was increased; the nature of the substituent apart from its size was however very important. They compared the absorption curves of the diphenyl with that of the corresponding benzene. 2:2'-Ditolyl showed greater absorption than 2 times toluene and it was suggested that the ortho-para directing properties of the methyl group would tend to concentrate electrons in the 1:1' C:C bond and thus favour ionic structures even when the phenyl rings were not in the same plane.

Sherwood and Calvin(J.Amer.Chem.Soc.,1942,64,1350) showed that when nitro groups were introduced in the para-para' position in 2:2'-ditolyl, the spectrum reverted to the diphenyl type, again emphasising the importance of the nature of the substituent group. It thus seems that in some cases the interaction of a substituent with the ring may be more important in determining the nature of the spectrum than the steric effects.

Friedel, Orchin and Reggel (J.Amer.Chem.Soc.,1948,70, 199) compared the spectra of various dinaphthyls and diphenyls. They showed that even in 2-methyldiphenyl there was a reduction in intensity and a short-wave shift as compared with diphenyl itself.

Beaven,Hall,Lesslie,Turner and Bird (J.Chem.Soc.,1954, 131) re-examined the ultraviolet absorption spectrum of

2:2'-ditolyl. They found more fine structure in the 2650-2850 Å region arising from the partial benzene chromophores, than previous workers, and on comparing the spectrum with that of toluene there was found to be more absorption on the short wave side if the fine structure than would be expected for the additive absorption of two toluene chromophores. The inflection at c.a. 2300 Å was regarded as a vestigial conjugation band which had been displaced to shorter wavelengths.

Braude and Forbes (J.Chem.Soc.,1955,3776) compared the spectra of a number of ortho substituted diphenyls. (see also Braude et al. Nature,1954,173,117). In the series of mono orthoalkyldiphenyls there was a marked decrease in absorption and short-wave shift of λ as compared with diphenyl.

Where,

Alkyl = Me-,Et-, n-Propyl, iso-Propyl, n-Butyl.

The shift in λ was greater for 2-ethyldiphenyl (λ 2330 Å, ε 10,500) than 2-methyldiphenyl (λ 2350 Å , ε 10,500) but did not differ appreciably for the other alkyl substituents. All but the CH_2- attached directly to the ring can orientate so that they cause little or no additional steric interference.

It appears then that even in diphenyls in which the preferred configuration must be appreciably non-planar significant conjugation is still present which can be detected spectroscopically. In the planar configuration the resonance energy must be a maximum but introduction of ortho substituents will oppose the diphenyl resonance by virtue of the steric effect of the groups and will either oppose or enhance the diphenyl resonance as a result of electronic interactions of the substituent with the ring. Both these factors must be taken into account. In a recent review of this subject Beaven,Hall,Lesslie and Turner,(*J.Chem.Soc.*,1952,854) conclude that, 'caution is necessary in interpreting the effect of substitution on the 'configuration' of diphenyl as indicated by its ultraviolet absorption spectrum.'

Beaven et al (*J.Chem.Soc.*,1954,131) had shown that in 2:2'-ditolyl, in spite of the steric effect of the *ortho* methyl groups, slight conjugation between the two benzene rings was still present. It was therefore decided in this work to prepare other *ortho* substituted diphenyls with larger substituents to see if traces of a vestigial conjugation band still remained. Alkyl substituted diphenyls were particularly suitable since alkyl groups interact only slightly with the phenyl rings and effects other than steric are thus small.

2:2'-Diethyldiphenyl and 2:2'-di-*iso*propyldiphenyl were therefore chosen as suitable compounds to study. 2;2'-Di*tert*.butyldiphenyl was being studied by Lesslie and Turner (private communication) and in this case the steric interference should be very large and might confer measurable optical stability on the rotational enantiomorphs. In the case of 2:2'-di-*iso*propyldiphenyl, models show that the molecule can rotate about the 1:1' C:C bond, the methyl groups of the *iso*propyl groups can orientate so that they confer little or no extra interference and in this case there may be no measureable optical stability. However a synthetic route to 2:2'-di-*iso*propyldiphenyl was chosen so that salt-forming groups were present in the hope that the compound could be optically activated.

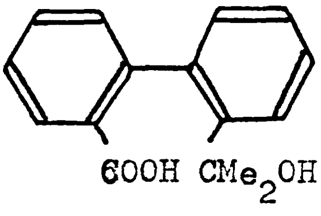
3:3'-Diethyldiphenyl and 4:4'-diethyldiphenyl were also to be studied and compared with the data for the corresponding ditolyls. The spectrum of 3:3'-diethyldiphenyl should be very similar to that of diphenyl whereas the *para* substituted compound would be expected to show a characteristic bathochromic shift and increased absorption intensity.

m-Di-*iso*propylbenzene was available and it was hopedto synthesise 2:2':6:6'-tetra*iso*propyldiphenyl and 2:2':4:4'-tetra*iso*propyldiphenyl in order to see in the first compound how far the diphenyl absorption approximated to 2 times *m*-di-*iso*propylbenzene, and in the second compound to determine how great the enhanced absorption due to the *para* substituents would be.

Although 2-ethyldiphenyl and 2-*iso*propyldiphenyl have been studied by other workers the values given for $\varepsilon_{max.}$ differ by amounts well outside the limits of experimental error and it was intended to reinvestgate these compounds.(Braude etal., *Nature*,1954,*173*,117, Braude and Forbes,*J.Chem.Soc.*,1955,3776, American Petroleum Institute, Research Project No 44, Ultraviolet Spectral Data, Serial No's 284,285).

With a view to obtaining some correlation between steric effects as manifested in the spectra and by optical activity, it was decided to prepare 2'-*iso*propyldiphenyl-2-carboxylic acid. Considering steric effects, then this acid would probably be less optically stable than 2:2'-di-*iso*propyldiphenyl-5:5'-dicarboxylic acid (which was prepared as an intermediate in the synthesis of 2:2'-di-*iso*propyldiphenyl) owing to the smaller blocking effect of a carboxyl as compared with an *iso*propyl group. (see e.g. Adams and Hale, *J. Amer. Chem. Soc.*, 1939, *66*, 2825).

Similar compounds which have been studied optically are 2'-(α-hydroxy*iso*propyl)-diphenyl-2-carboxylic acid (1) and 2'-*iso*propenyldiphenyl-2-carboxylic acid (11).



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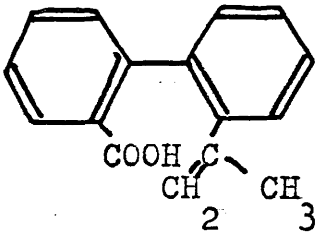


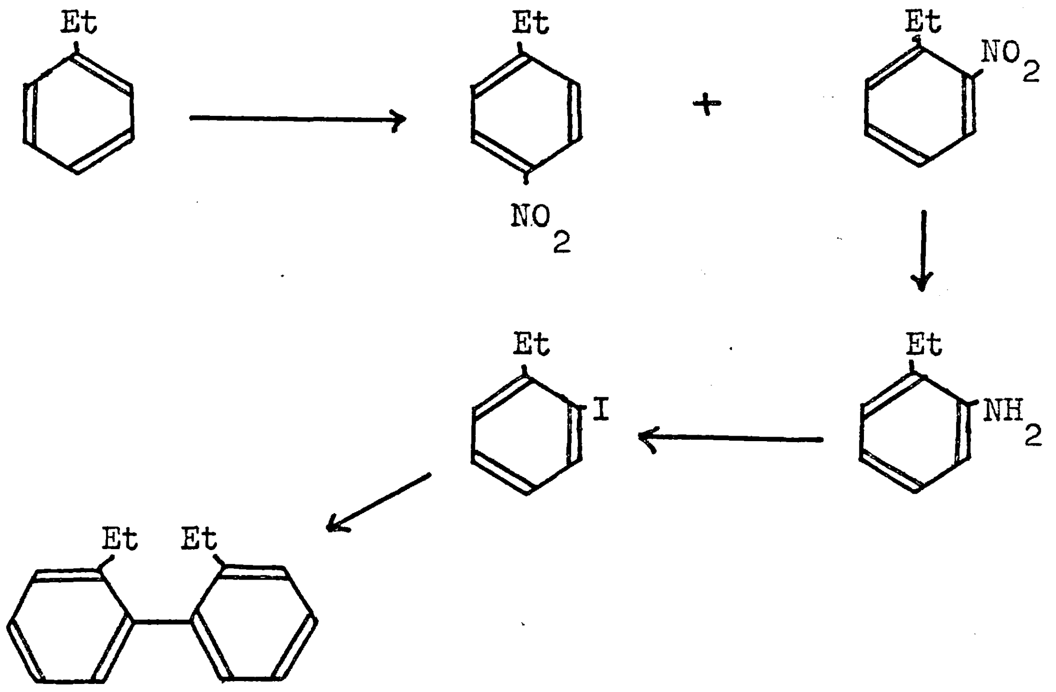
(11)

Corbellini and Angeletti, (*Atti, R, Accad. Lincei.*, 1932, *15*, 968) showed that (1) underwent a second order transformation with brucine in ethanol. Re-examination of this compound by Jamison and Turner (*J. Chem. Soc.*, 1942, 437) provided the first example of a compound undergoing both first and second order transformations with the same alkaloid (brucine) in the same solvent (chloroform). Ridgwell (unpublished) attempted optical activation of (11) with brucine and cinchonidine without success.

DISCUSSION.

a) Mono and di-ethyldiphenyls.

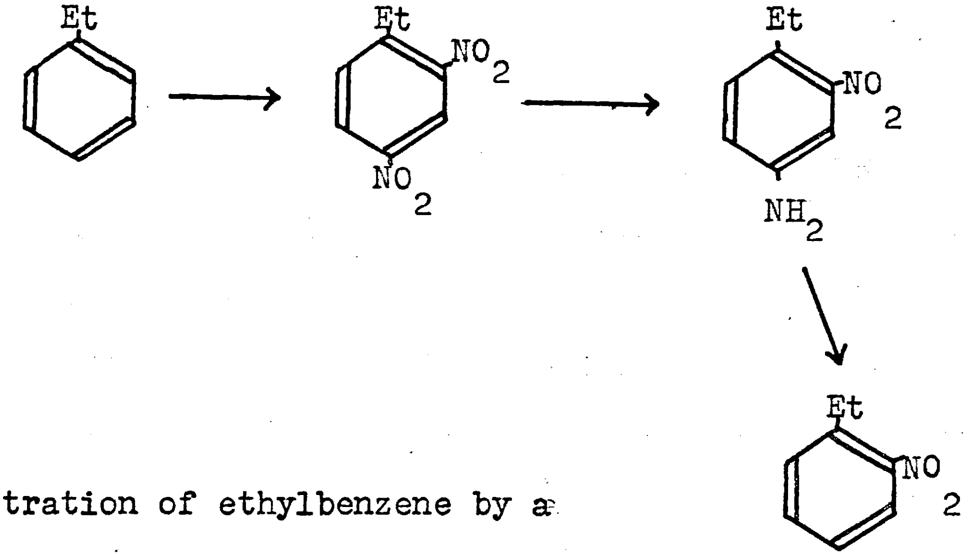
Three routes to 2:2'-diethyldiphenyl were investigated.



It was prepared in 34% overall yield from o-nitroethylbenzene via o-ethylaniline and o-iodoethylbenzene, followed by an Ullmann reaction.(cf. Mascarelli and Longo, Gazzetta, 1941,71,397).

Initially o-nitroethylbenzene was prepared by the nitration of ethylbenzene. (Cline and Reid, J.Amer.Chem.Soc., 1927,49,3150, Ford-Moore and Rydon, J.Chem.Soc.,1946,679.) It was obtained in 32% yield, $n_D^{25^\circ}$ 1.5329.

Separation of the two isomers required very efficient fractionation and the purity of the product was not certain owing to the different values recorded in the literature for the refractive index of o-nitroethylbenzene. An alternative route was therefore used in an attempt to obtain o-nitroethylbemzene in a high degree of purity and check its refractive index.



Dinitration of ethylbenzene by a modified method of Weisweiller, (Monatsh.,1900,21,39) using an excess of nitric acid and warming on a boiling water bath to complete the reaction, instead of heating at 125-130° which caused the emmision of copious nitrous fumes, gave an improved yield of 2:4-dinitroethylbenzene.

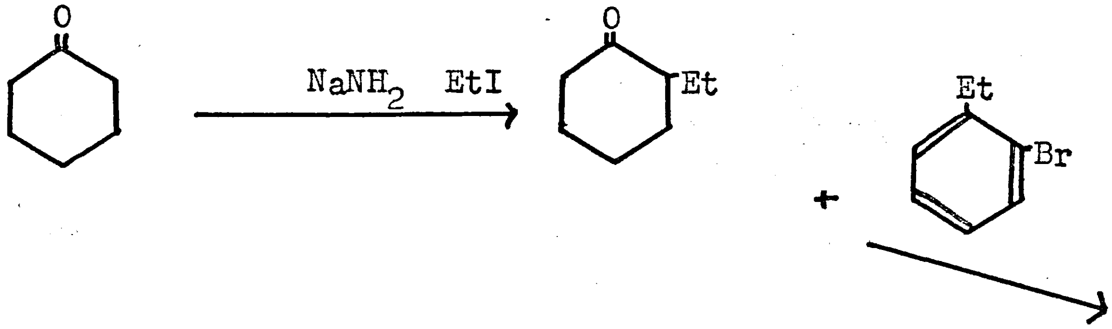
Partial reduction to 2-nitro-4-aminoethylbenzene was effected in 47% yield using sodium disulphide. Reduction with ammonium hydrogen sulphide (Schultz, Ber.,1901,42,2633, Cline and Reid, loc.cit.) gave only a 32% yield but this method was preferred since isolation of the product was easier. The low melting point given by Schultz,(43° and acetyl derivative 101°) was shown by Cline and Reid (45° and acetyl derivative 110°) to be due to the presence of the isomeric 2-amino-4-nitroethylbenzene. In our case m.p. 45-46° was obtained for the pure 2-nitro compound and m.p. 110° for the acetyl derivative. Deamination by the action of hypophosphorous acid on the diazo compound gave o-nitroethylbenzene, $n_D^{25^\circ}$ 1.5339. This route proved tedious for the preparation of large quantities of material as the overall yield of o-nitroethylbenzene was only 16 to 24%. Later o-nitroethylbenzene was obtained commercially and after purification by steam distillation had $n_D^{25^\circ}$ 1.5340.

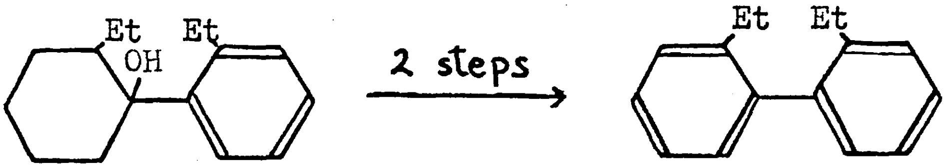
Mascarelli and Longo (loc.cit.) used stannous chloride and hydrochloric acid for the reduction to o-ethylaniline and obtained as by product 5-chloro-2-aminoethylbenzene. Various other reducing agents were therefore tried to avoid nuclear substitution by chlorine. Cline and Reid (loc.cit.) reported that the yield of o-ethylaniline obtained by reduction with iron filings and 10% hydrochloric acid was poor. A 50% yield was however obtained by this method and finally by carrying out the reduction in alcohol,(West,J.Chem.Soc.,1925, 127,494) a 70% yield of pure base was obtained after purification via the acetyl derivative. Although catalytic reduction with platinum oxide catalyst gave satisfactory yields this method was not suitable for large scale work.

o-Ethylaniline was diazotised in sulphuric acid and aqueous potassium iodide added; this gave o-iodoethylbenzene in 80% yield. Treatment with copper powder at ca. 240° for three hours gave 2:2'-diethyldiphenyl. This proved a very convenient route for preparing 2:2'-diethyldiphenyl and a total of 150g. were prepared by this method. Although analytically pure, 2:2'-diethyldiphenyl showed on gas chromotography that it contained appreciable quantities of impurities not removable by further fractional distillations. For spectral purposes a sample was purified by three crystallisations from ethanol at ca. -35°, and then redistilled.

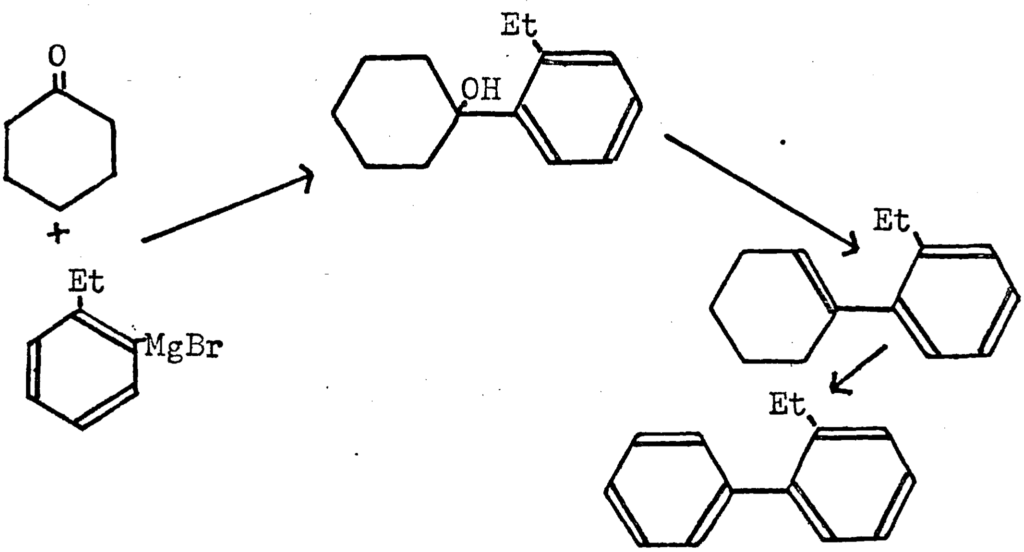
Alternatively o-ethylaniline was converted into the bromo compound by the Gattermann, or more conveniently by the Sandmeyer reaction. The best yields were obtained when the diazotisation was carried out in hydrobromic acid. A Grignard reagent was prepared from the bromo compound and anhydrous cupric chloride added slowly. (Method of Krizewsky and Turner, J. Chem. Soc., 1919, 115, 559). The overall yield by this method based on o-nitroethylbenzene was 10%.

An entirely different route to 2:2'-diethyldiphenyl was then attempted so that a check could be made on its spectrum.





*cyclo*Hexanone was ethylated with ethyl iodide in the presence of sodamide. Only a 12% yield of 2-ethyl*cyclo*hexanone was obtained after purification as the semicarbazone. Some 2:2-diethyl*cyclo*hexanone was formed which was identified as its semicarbazone, together with a high boiling residue which presumably consisted of self-condensation products of the *cyclo*hexanone. Conia (*Bull.Soc.chim.*, 1950,*175*,33) obtained similar results using ethyl iodide and diethyl sulphate. Because of the difficulty encountered in the prepatation of 2-*ethyl*cyclohexanone, it was decided to prepare some 2-ethyldiphenyl by a similar method to that outlined above for 2:2'-diethyldiphenyl, to work out the conditions and then apply this method to diethyldiphenyl. 2-Ethyldiphenyl was also of interest for spectral purposes.

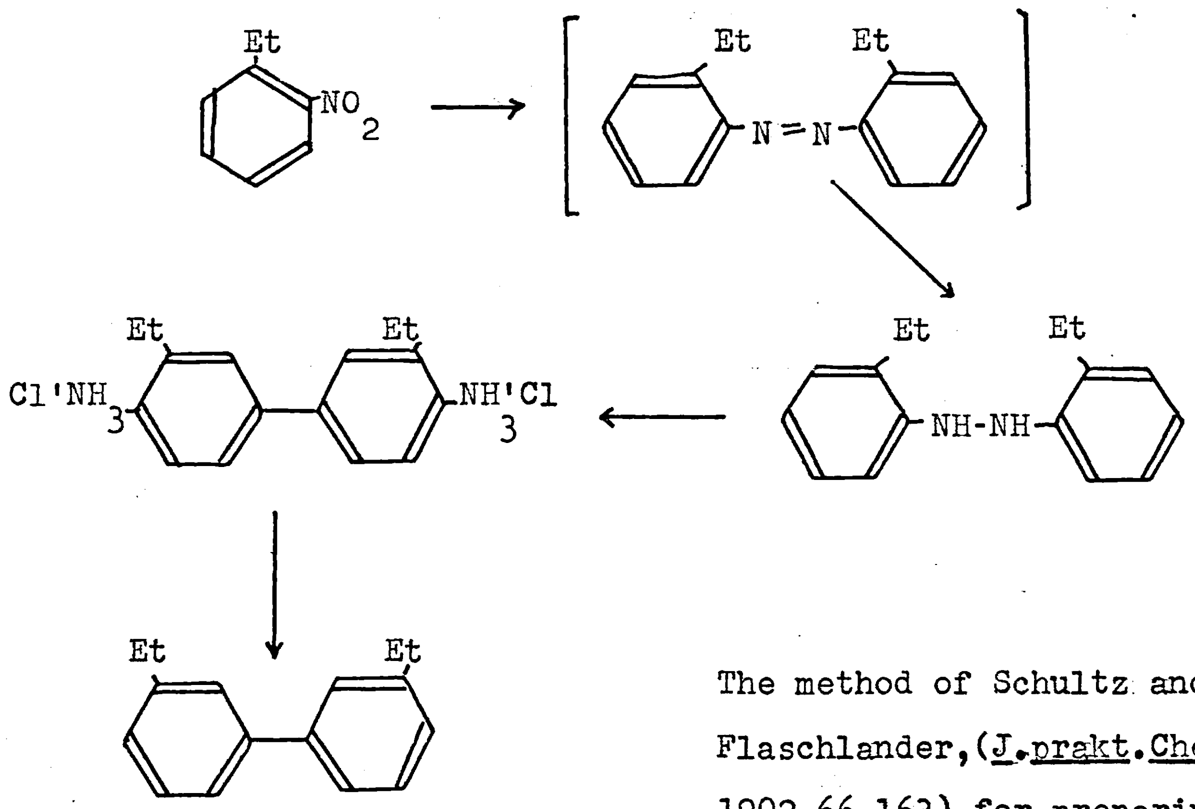


This method was similar to that used by Orchin,(*J.Amer.Chem.Soc.*,1946,*69*,571) who treated 2-phenyl*cyclo*hexanone with ethylmagnesium iodide, dehydrated the product and then dehydrogenated.

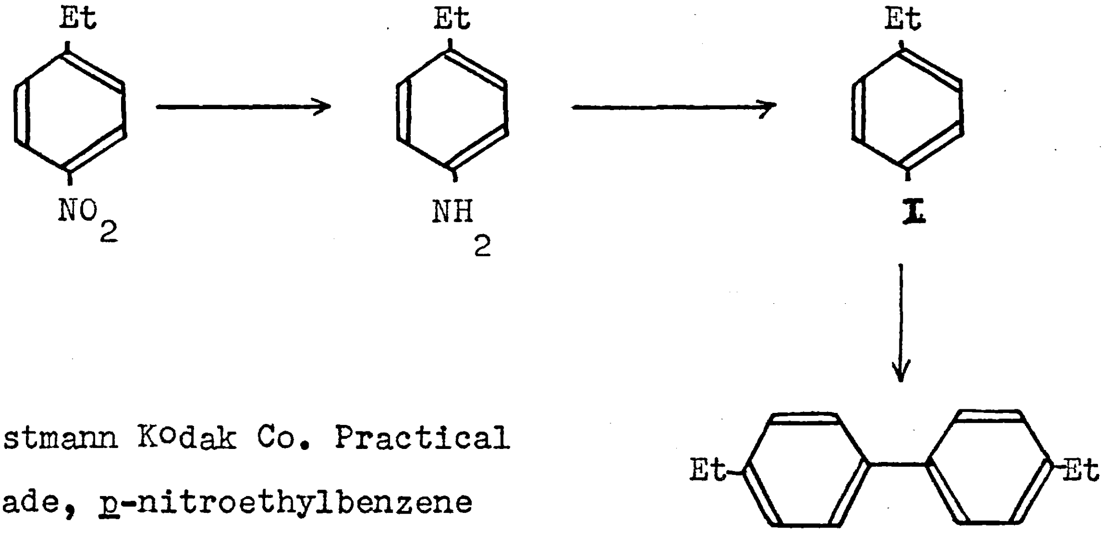
The interaction of *cyclo*hexanone with a Grignard reagent prepared from *o*-bromoethylbenzene gave 2-ethylphenyl*cyclo*hexan-1-ol. This carbinol dehydrated readily and was therefore not purified but converted directly into 2:3:4:5-tetrahydro-2'-ethyldiphenyl by boiling with anhydrous formic acid. (cf. Sherwood,Short and Stansfield,*J.Chem.Soc.*,1932, 1832). The yield based on *o*-bromoethylbenzene was 36%. Dehydrogenation to 2-ethyldiphenyl was effected by heating with the theoretical quantity of sulphur until the product no longer decolorised bromine in carbon tetrachloride.

2:2'-Diethyldiphenyl was then prepared by a similar set of reactions. This method was not suitable for preparing large quantities of material as the overall yield was only 1-2%. However 2g. were prepared by this method and the spectrum was found to agree well with that of 2:2'-diethyldiphenyl prepared via the Ullmann reaction.

Bromination of 2:2'-diethyldiphenyl with N-bromosuccinimide gave a 70% yield of α:α'-dibromo-2:2'-diethyldiphenyl. The melting point was not sharp and the substance is presumably a mixture of stereoisomers. A mixed melting point with the same substance prepared from the corresponding diol (Hall,Ladbury,Lesslie and Turner,*J.Chem.Soc.*,1956,3475) gave no depression. 2:2'-Divinyldiphenyl was obtained by dehydrobromination in boiling quinoline. Catalytic reduction of the divinyl compound gave 2:2'-diethyldiphenyl, showing that no cyclisation had taken place.



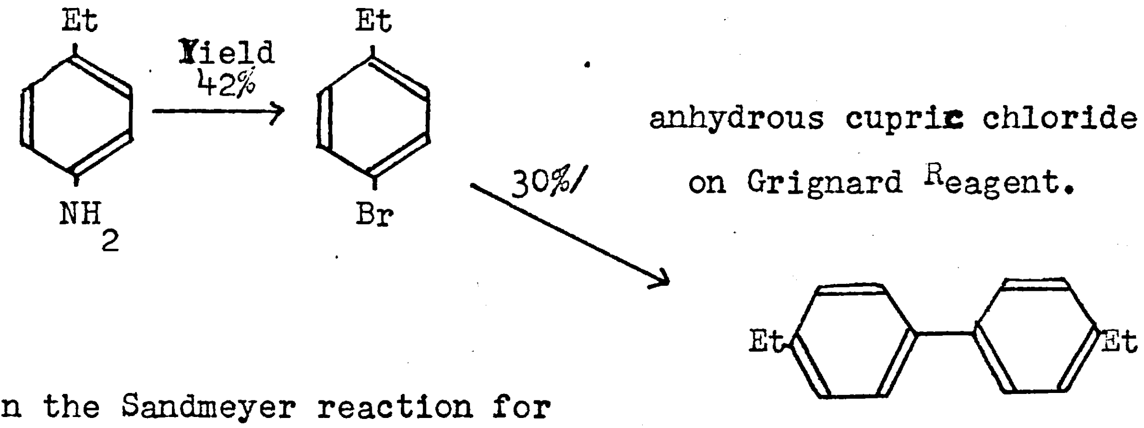
The method of Schultz and Flaschlander, (*J.prakt.Chem.*, 1902,*66*,163) for preparing 3:3'-diethylbenzidine was modified, a greater excess of reagent was used and the intermediary hydrazo compound was not isolated but converted directly into the benzidine. During the reduction step a bright red colour due to the azo compound developed rapidly and heating was continued until this disappeared. The length of time taken on different occasions varied considerably and the efficiency of the stirring appeared to be the determining factor. In each case some azo compound was isolated and this was reduced further and then converted into the benzidine. The free base was a hard solid m.p.71° which could not be crystallised. 3:3'-Diethylbenzidine hydrochloride was used directly in the next stage. Diazotisation followed by deamination using hypophosphorous acid gave pure 3:3'-diethyldiphenyl after repeated distillations from sodium to remove traces of phenolic impurities. The overall yield was 28%.



Eastmann Kodak Co. Practical Grade, *p*-nitroethylbenzene was used as starting material and purified by steam distillation. It was reduced with zinc and hydrochloric acid,(Cline and Reid,*J.Amer.Chem.Soc.*,1927,*49*,3150) this giving better yields than the West method (*loc. cit.*), used for *o*-nitroethylbenzene. The iodo compound was prepared in the usual way by diazotisation in sulphuric acid followed by treatment with aqueous potassium iodide.

Willgerodt and Bergdolt,(Annalen,1903,327,286) used the amine sulphate and diazotised in hydrochloric acid,the yield however was the same. Heating with an equal weight of copper powder finally gave 4:4'-diethyldiphenyl in 40% overall yield.

The following alternative route, as used for 2:2'-diethyldiphenyl, was also tried.



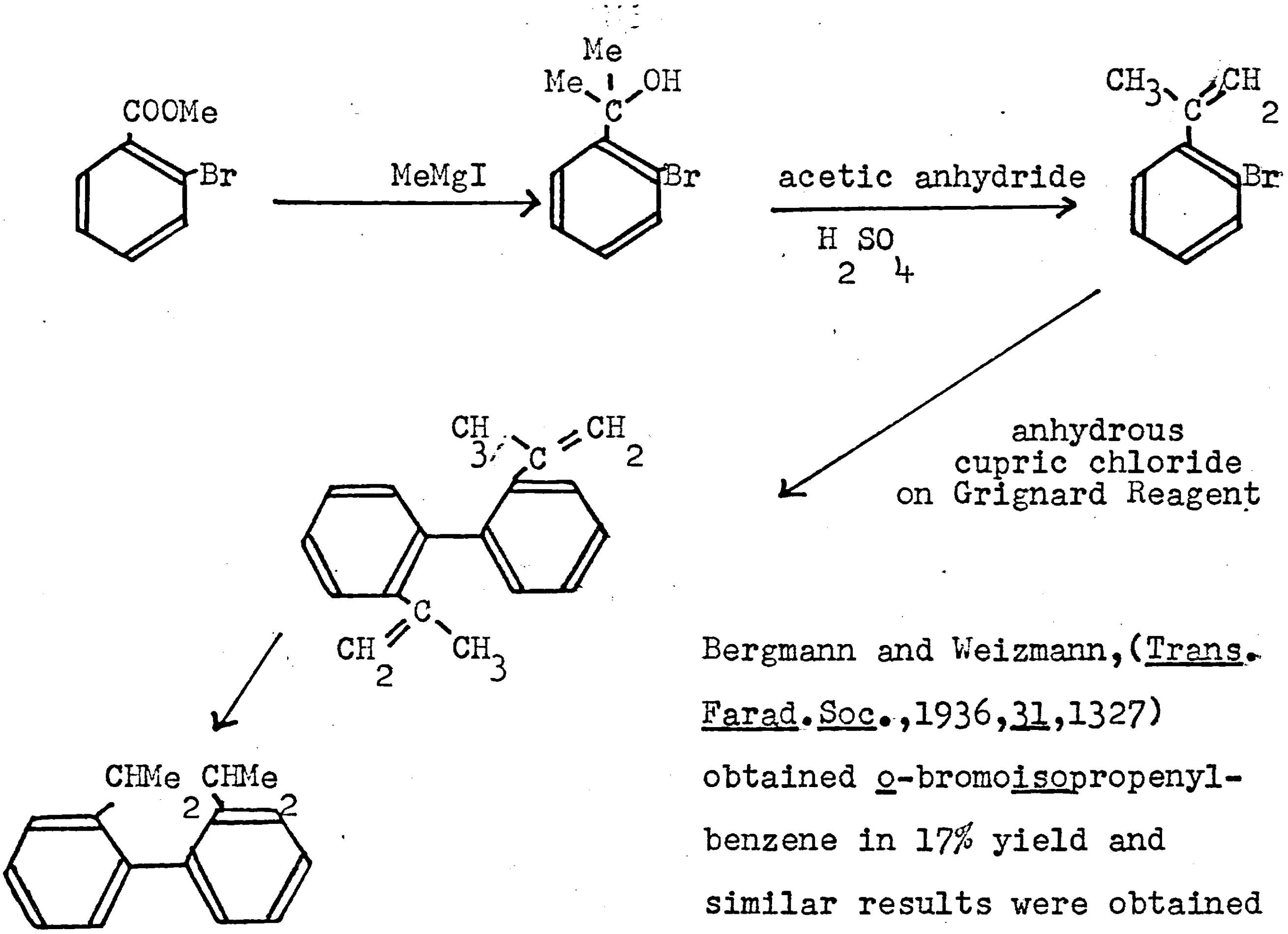
anhydrous cupric chloride on Grignard Reagent.

Again the Sandmeyer reaction for preparing the bromo compound gave the best yields. By this route the overall yield of 4:4'-diethyldiphenyl was 9%.

Bromination of 4:4'-diethyldiphenyl with N-bromosuccinimide gave α:α'-dibromo-4:4'-diethyldiphenyl. However dehydrobromination using the same conditions as used for the 2:2' compound gave a tarry product from which, although some solid was isolated, it could not be purified and was sparingly soluble in all solvents tried for crystallisation. Presumably polymerisation took place.

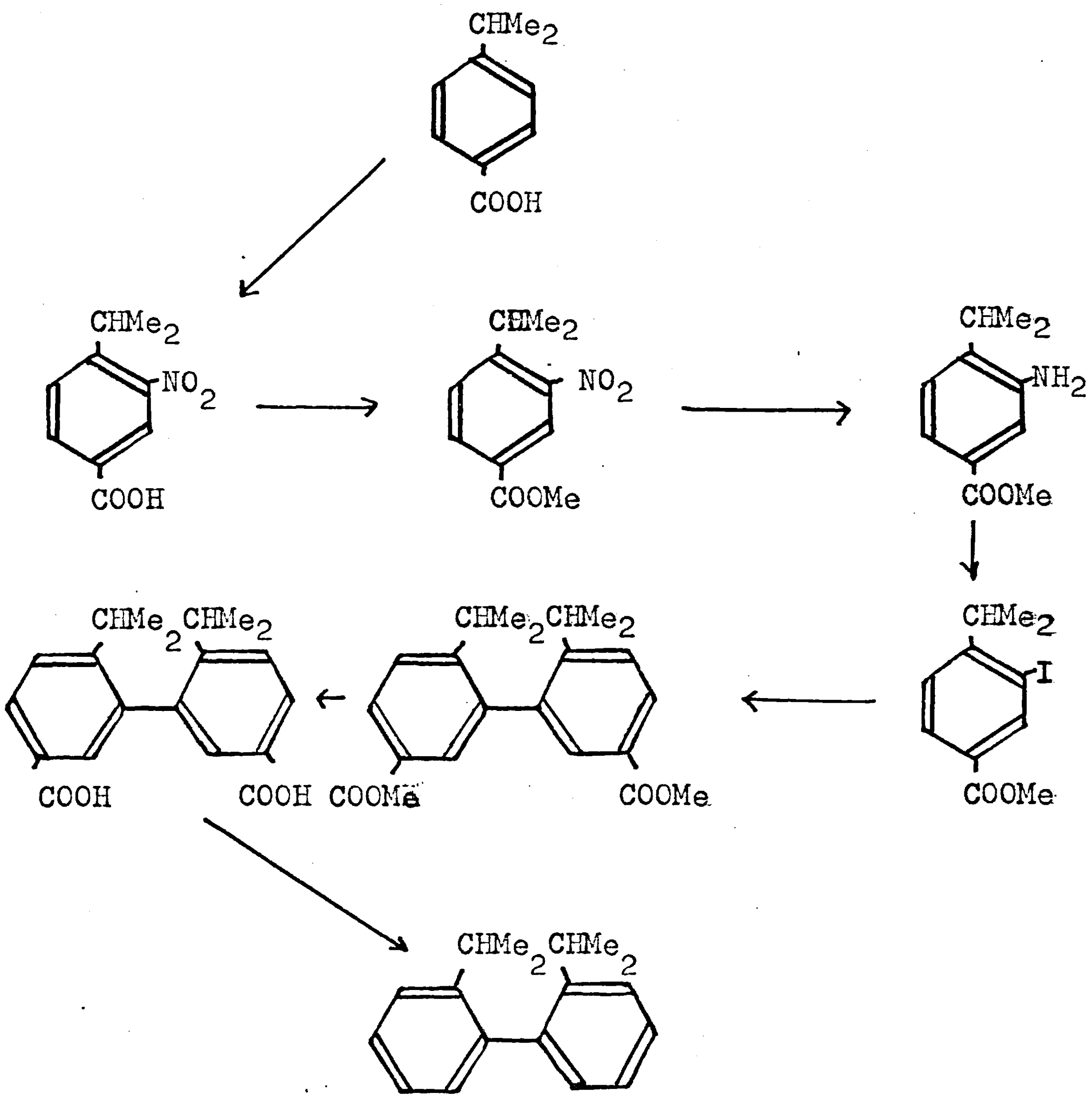
Di- and Tetra*iso*propyldiphenyl Series.

Two different routes to 2:2'-di-*iso*propyldiphenyl were considered.



Bergmann and Weizmann, (*Trans. Farad. Soc.*, 1936, *31*, 1327) obtained *o*-bromo*iso*propenylbenzene in 17% yield and similar results were obtained by repetition of their work. Attempts to prepare a Grignard reagent from *o*-bromo*iso*propenylbenzene were however unsuccessful and since in any case a reaction of this type with anhydrous cupric chloride does not give very high yields, this method was not developed further.

A more convenient route, which eventually gave good yields of 2:2'-di-*iso*propyldiphenyl is as follows:-



Moreover, the intermediary 6:6'-di-*iso*propyldiphenyl-3:3'-dicarboxylic acid was interesting to study optically.

Before carrying out the Ullmann reaction it was necessary to esterify the carboxyl groups to prevent excessive decarboxylation. It was found most convenient to esterify at the nitro-acid stage since this acid was difficult to reduce and the resulting amino acid difficult to isolate.

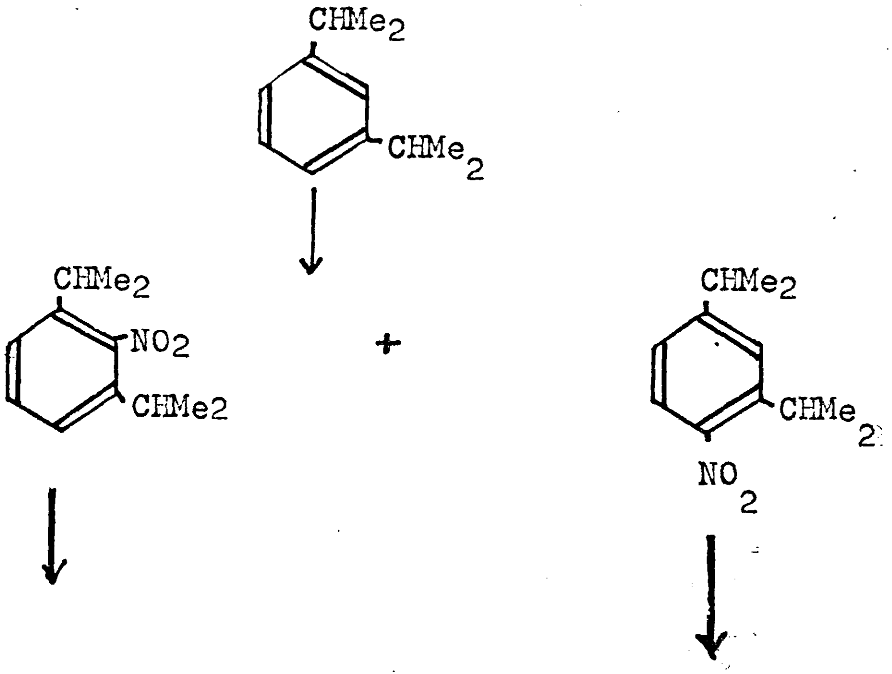
Nitration of cumic acid (Bryan and Foote,J.Amer.Pharm.Soc., 1949,38,572,and 1950,39,644) gave a 87% yield of 3-nitrocumic acid. Attempted reduction with iron filings and acetic acid,(Fileti,Gazzetta,1880,10,12) , ammonium sulphide,(Lippmann and Lange,Ber.,1889,13,1660) or ammoniacal ferrous sulphate was unsuccessful. In the first method a trace of the amino acid was isolated together with a substance identified as the acetyl derivative.

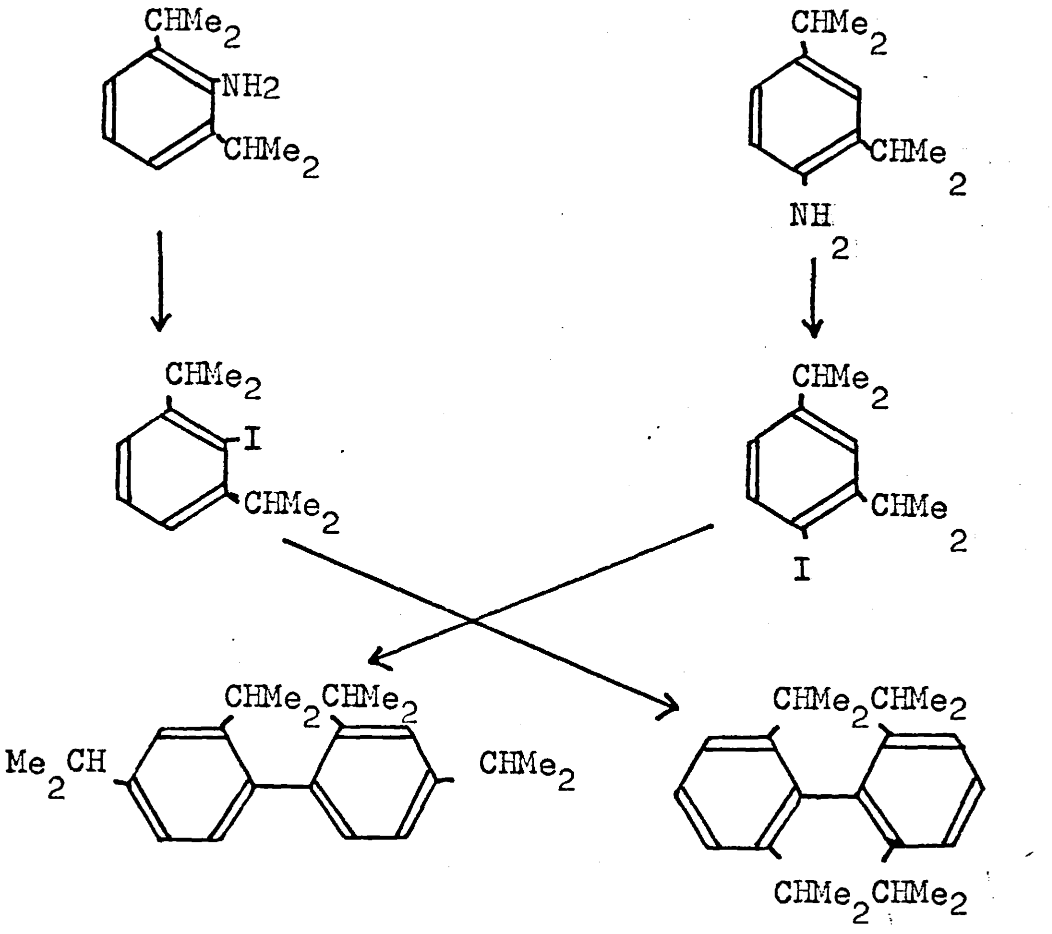
Treatment of the nitro acid with thionyl chloride, followed by methanol gave a 94% yield of the ester. (Bryan and Foote,loc.cit.). The ester was largely unchanged by shaking with hydrogen in the presence of platinum or palladium catalysts. Abenius (J.prakt. Chem.,18~~9~~89,40,439) reduced the ester using tin and hydrochloric acid and owing to hydrolysis isolated some amino acid in addition to the ester. In our case reduction in 88% yield was however finally achieved by reducing the nitro ester with tin and dry hydrogen chloride gas in methanolic solution. In this way hydrolysis was prevented.

The corresponding iodo compound was prepared in the usual manner using a very dilute solution to decrease any possibility of the ester being hydrolysed. Some of the ester was converted into the iodo acid since this compound had not previously been reported in the literature. An Ullmann reaction followed by hydrolysis of the corresponding ester in ethanolic sodium ethoxide gave 6:6'-di-*iso*propyldiphenyl-3:3'-dicarboxylic acid. Finally 2:2'-di-*iso*propyldiphenyl was obtained by decarboxylation, by boiling in quinoline in the presence of copper powder. This was a very satisfactory route to 2:2'-di-*iso*propyldiphenyl the overall yield being 25%.

Attempted bromination of 2:2'-di-*iso*propyldiphenyl with N-bromosuccinimide gave a bromo compound in poor yield. This analysed for a tribromo compound, $C_{18}H_{19}Br_3$, but could not be identified. Determination of the ultra-violet absorption spectrum gave no clue to its structure.

B.D.H., m-di-*iso*propylbenzene was available (100g.) and with this as starting material it was hoped to synthesise 2:2':4:4'-tetra-*iso*propyldiphenyl and 2:2':6:6'-tetra-*iso*propyl diphenyl.





m-Di-*iso*proplybenzene was distilled from sodium, and although there was no rise in boiling point, (b.p.200-203°)(literature, b.p.203°) it was later shown to have been contaminated with appreciable impurities, chiefly momo-*iso*propylbenzene. It had $n_D^{20°}$ 1.4909 which is in poor agreement with the literature value of $n_D^{20°}$ 1.4884.

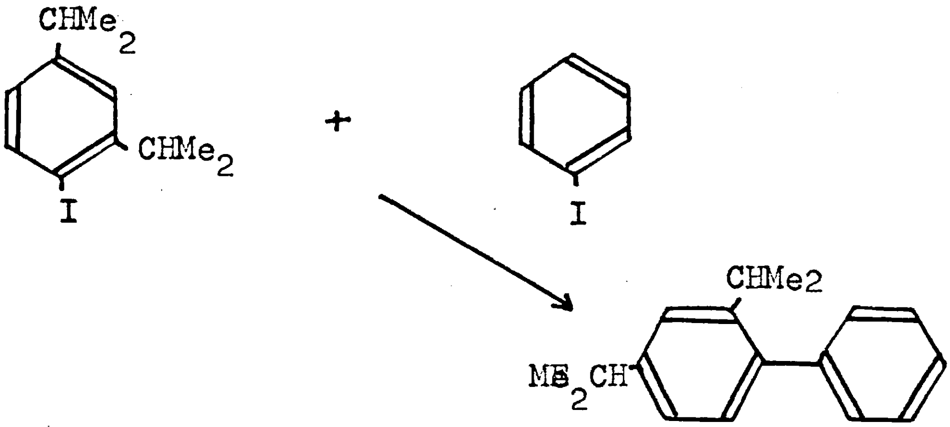
Nitration was carried out according to Newton, (*J. Amer. Chem. Soc.*, 1943, *65*, 2434) who obtained a low boiling fraction of 4-nitro-1:3-di-*iso*propylbenzene and a higher boiling fraction of 2-nitro-1:3-di-*iso*propylbenzene, in the ratio 3:1.

After repeated fractional distillations of the nitration product, two fractions were obtained which could not be purified by further distillation. The values of the refractive index of these products did not agree with those of Newton. Eventually the lower boiling fraction was shown to be an impure specimen of 4-nitro-isopropylbenzene, since this eventually gave 4:4'-di-isopropyldiphenyl which was identified by means of its spectrum, analysis and properties of its precursors. The larger, higher boiling fraction corresponded with Newtons low boiling fraction being an impure specimen of 4-nitro-1:3-di-isopropylbenzene. No 2-nitro-1:3-di-isopropylbenzene corresponding to Newtons higher boiling fraction was obtained which is hardly surprising considering the complex mixture of nitro compounds which was present in the nitration product.

Reduction of both nitro compounds was carried out catalytically using platinum oxide as catalyst. In each case the amines were identified by means of their acetyl and benzoyl derivatives.

4-Amino-1:3-di-isopropylbenzene diazotised in sulphuric acid gave an unusually stable diazo solution which did not decompose even at 15°. Treatment with aqueous potassium iodide gave the iodo compound, which was converted into 2:2':4:4'-tetra-isopropyldiphenyl. The product was a liquid and although it analysed satisfactorily, vapour phase chromatography showed it to be only c.a.80% pure containig c.a.1% of a compound which was probably a di-*iso*propyldiphenyl and less than 10% each of two other compounds which were probably position isomers resulting from some 2-nitro-1:3-di-*iso*propylbenzene or from other di-*iso*propylbenzenes present in the starting material.Further purification was not possible with the amount of material available.

The following synthesis of 2:4-di-*iso*propyldiphenyl by an unsymmetrical Ullmann was attempted.

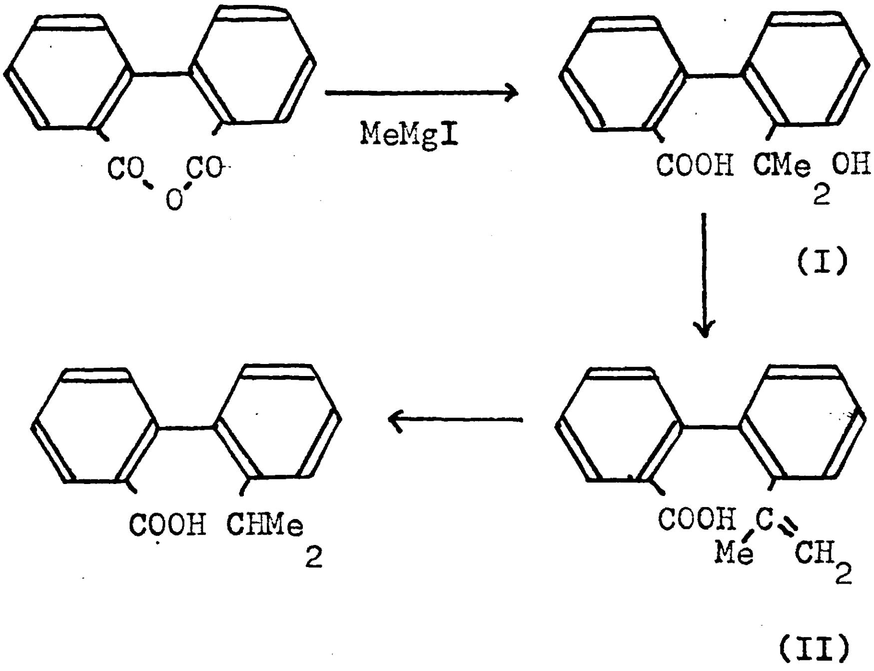


Any diphenyl formed in the reaction was removed as far as possible by steam distillation. After repeated fractional distillations , 2:4-di-*iso*propyldiphenyl was obtained as a colorless oil.It analysed for the expected product but vapour phase chromatography showed it to be a complex mixture, containing 2:2':4:4'-tetra-*iso*propyldiphenyl and traces of 5 to 6 other components. This is only to be expected, considering the doubtful purity of the starting material.

4:4'-Di-*iso*propyldiphenyl was prepared via the iodo compound in the usual way. After distillation the product solidified and hence purification was easier. After crystallisation from ethanol, m.p. 65-66°. Previously 4:4'-di-*iso*propyl-diphenyl had been described as existing in two forms. m.p. 49° and 65°. (Schreiner, *J. prakt. Chem.*, 1910, *81*, 424, Bert and Dorier, *Bull. soc. chim.*, 1925, *37*, 1398, Boedtker, *ibid.*, 1929, *45*, 645).

2-*iso*Propyldiphenyl and 2'-*iso*propyldiphenyl-2-carboxylic acid.

The following route was first attempted:-



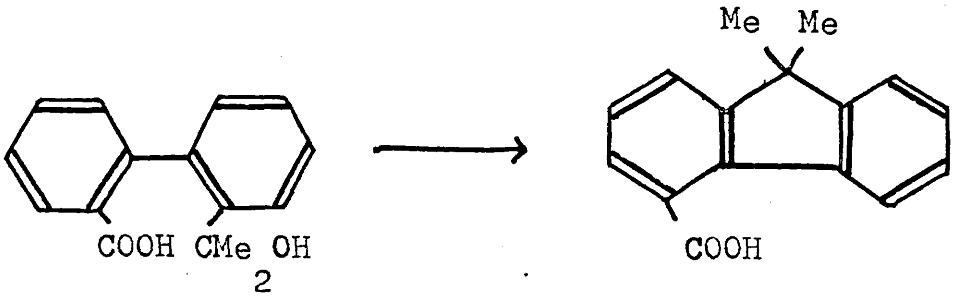
(I) was synthesised according to Jamison and Turner (J.Chem. Soc.,1942,437). The reaction was scaled up and in practise the lactone or a mixture of acid and lactone were obtained. Treatment of either the acid or the lactone with a) 50% sulphuric acid, or b) anhydrous formic acid gave the same product an acid (A). m.p.195-196° . Ridgwell (unpublished) had obtained a substance which was presumably the same compound by heating (I) with 48% hydrobromic acid in a sealed tube for 1 hour. This had m.p.195-197.5° and this was considered to be (II) since it analysed for $C_{16}H_{14}O_2$.

Acid (A) however did not decolorise bromine in carbon tetrachloride and could not be reduced catalytically. The methyl ester (B) was prepared and again gave no test for unsaturation. In fact it was unchanged after shaking in a hydrogenator with platinum oxide as catalyst for 20 hours, at a hydrogen pressure of 100lbs/sq". Finally (A) was decarboxylated by boiling quinoline in the presence of copper powder to give a neutral substance (C). This substance gave no tests for unsaturation and was a solid m.p.95-96° . This step gave
The final proof that (A) was not 2'-isopropenyl-2-carboxylic acid (II), since decarboxylation should in this case give 2-isopropenyldiphenyl, a liquid b.p.107/ 2 mm. (Mowry, Dazzi, Renoll and Shortridge,J.Amer.Chem.Soc.,1948,70,1916). (C) analysed however for $C_{15}H_{14}$.

The most likely alternative dehydration of 2'-(α-hydroxy-

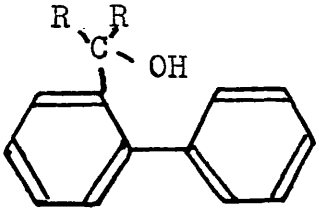
-isopropyl)-diphenyl-2-carboxylic acid (I) is a cyclic dehydration as follows:-

(I)

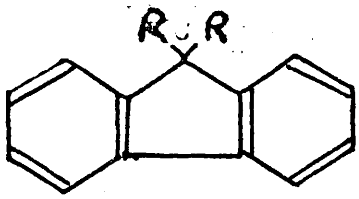


Decarboxylation should then give 9:9-dimethylfluorene.

Strong evidence in favour of this was available. Anchel and Blatt,(J.Amer.Chem.Soc.,1949,63,1948) had shown that carbinols of the general formula,



could be readily dehydrated using acetic acid-hydrochloric acid mixtures to give 9:9-dialkylfluorenes. In particular, 9:9-dimethylfluorene could be obtained in quantitative yield from 2-α-hydroxyisopropyldiphenyl by simply dissolving it in concentrated sulphuric acid. On dilution a solid was obtained which after crystallisation gave pure 9:9-dimethylfluorene,m.p.95-96°.

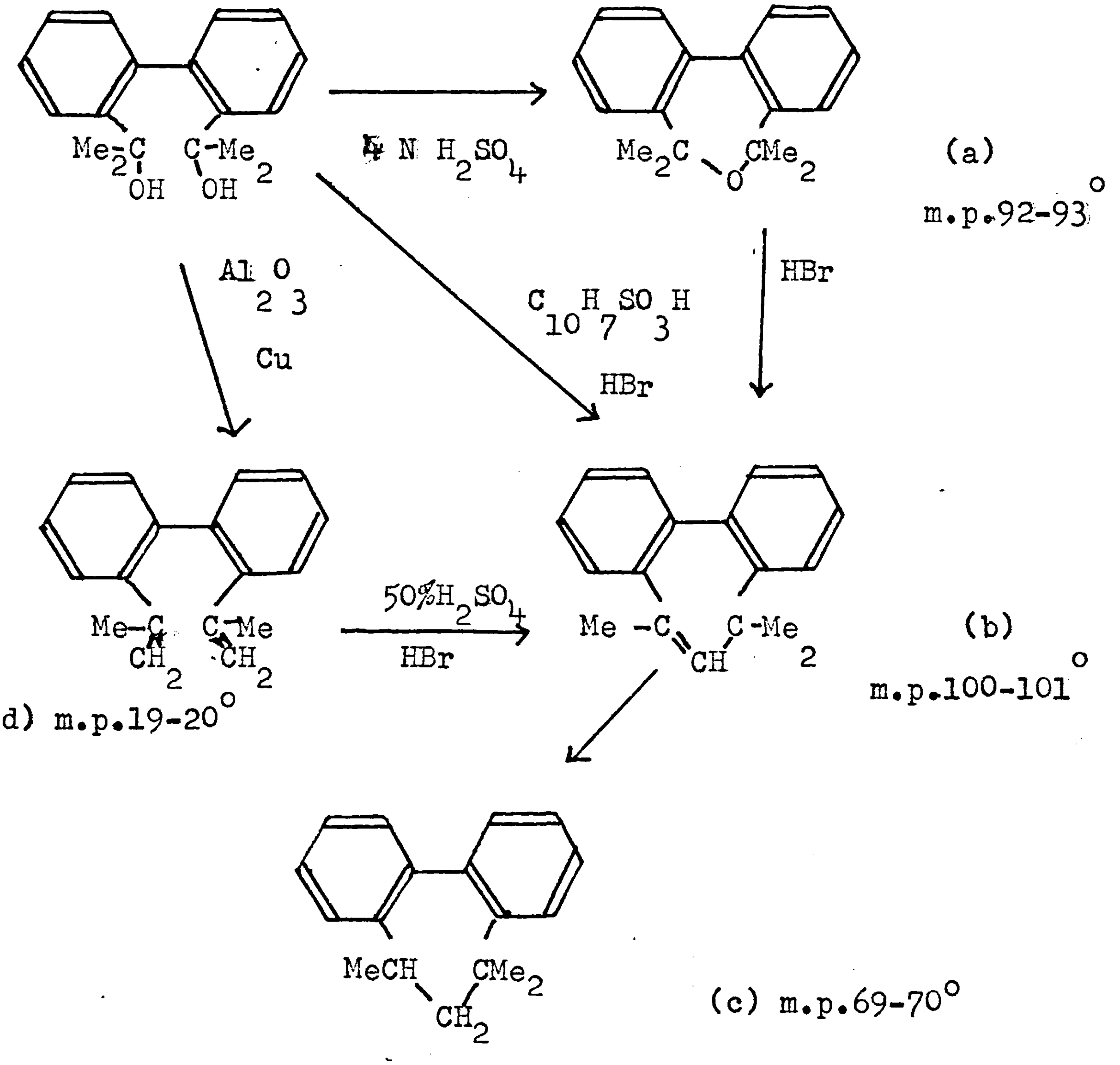


A similar reaction to the one here is the preparation of 9:9-diphenylfluorene-4-carboxylic acid from 2'-(α-hydroxybenzhydryl)-diphenyl-2-carboxylic acid or its lactone,

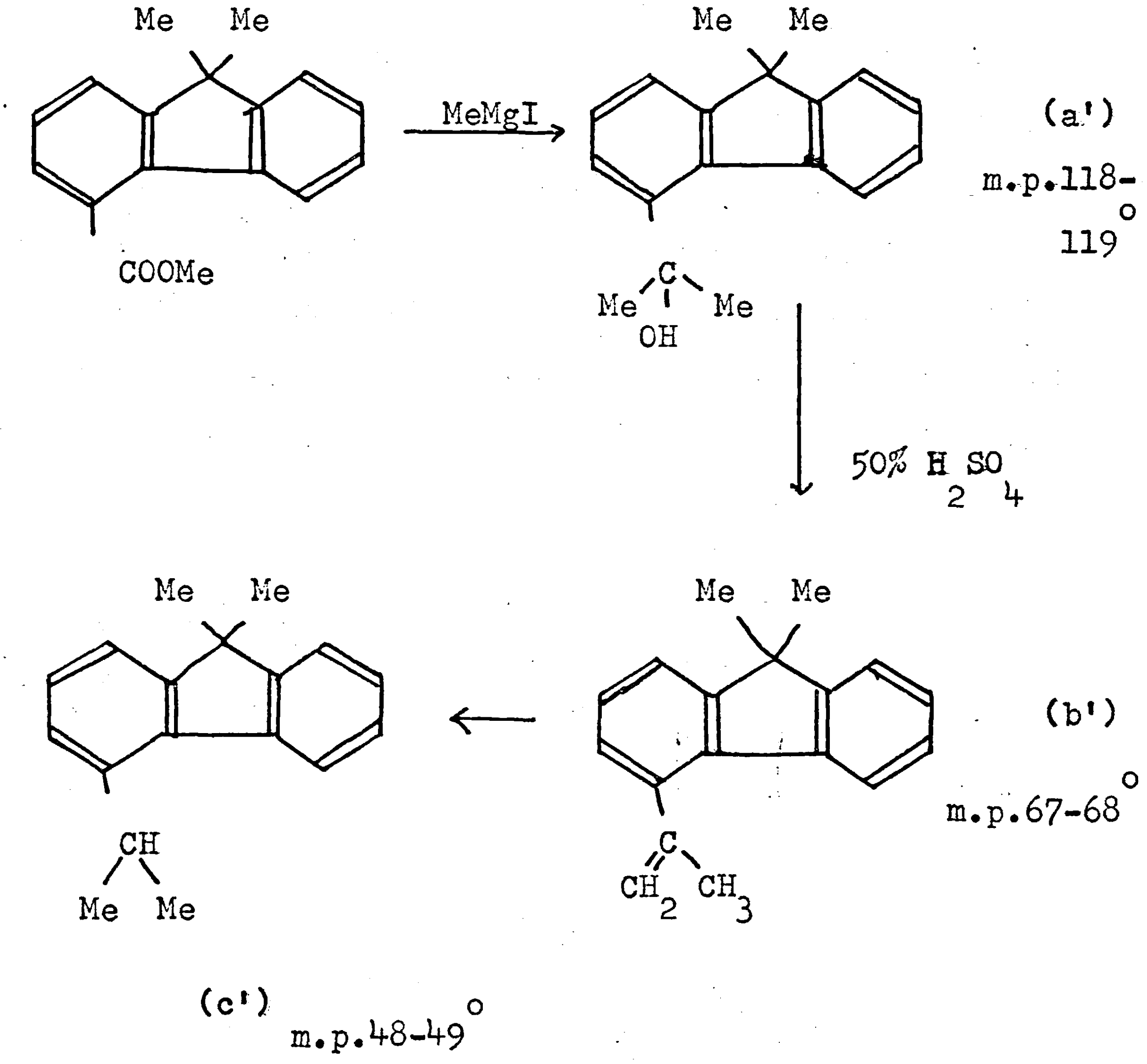
(Sergeev,*J.Russ.Phys.Chem.Soc.*,1929,*61*,1421)

Final identification of (C) as 9:9-dimethylfluorene was obtained from spectroscopic evidence. (A) is then 9:9-dimethylfluorene-4-carboxylic acid and (B) its methyl ester.

Hall,Ladbury,Lesslie and Turner,(*J.Chem.Soc.*,1956,3475) studied the dehydration of 2:2'-di-(α-hydroxy*iso*propyl)-diphenyl under different conditions. Their results are summarised below.



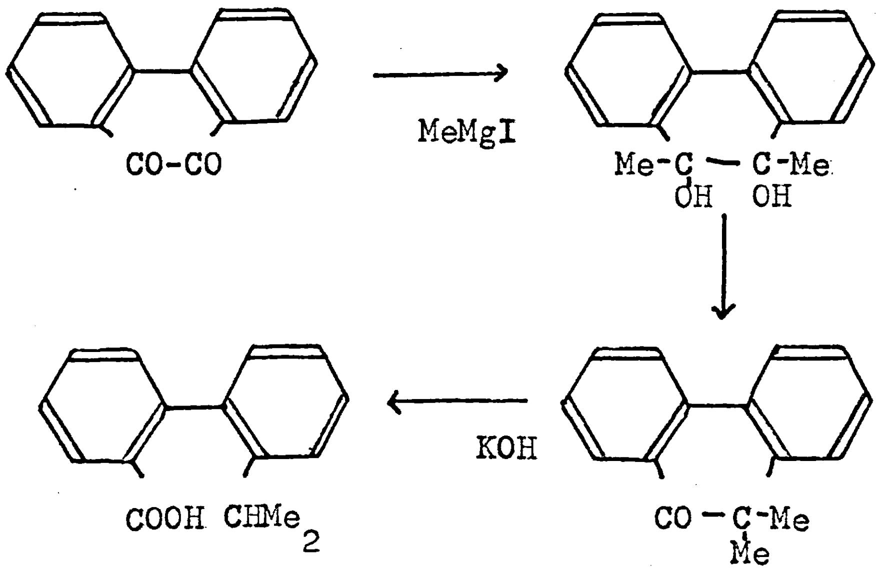
(a),(b) and (c) were identified by means of their spectra. The possibility of cyclic dehydration to give a fluorene derivative could not however be overlooked. The following series of reactions were therefore carried out on 9:9-dimethylfluorene-4-carboxylic acid. (a) and (a'), (b) and (b') etc. are then isomeric.



From the physical properties and the ultra_violet absorption

absorption spectra, (a) and (a') etc. are not identical thus confirming the views of Hall et.al.(loc.cit.).

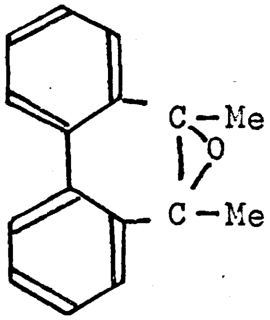
Dehydration of 2:2'-di-(α-hydroxy*isopropyl*)-diphenyl with alumina gave the normal product, 2:2'-di-*iso*propenyl-diphenyl.Also dehydration of 2-(α-hydroxy*iso*propyl)-diphenyl in the vapour phase over alumina gives an 83% yield of 2-*iso*propenyldiphenyl, no 9;9-dimethylfluorene being formed. (Mowry,Dazzi,Renoll and Shortridge,*loc.cit.*) Alumina dehydration was therefore tried in the case of 2'-(α-hydroxy-*iso*propyl)-diphenyl-2-carboxylic acid. (I). The product obtained was an olefinic acid, m.p.122°. This analysed correctly for 2'-*iso*propenyldiphenyl-2-carboxylic acid. Finally, catalytic reduction gave 2'-*iso*propyldiphenyl-2-carboxylic acid, having m.p. and mixed m.p. with a specimen of the same acid prepared by the following route, identical.



(III)

This alternative route for the preparation of 2'-*iso*propyldiphenyl-2-carboxylic acid had beem used by Meerwein,(*Annalen*,1913,*396*,225). Meerwein prepared 9:10-dimethyl-9:10-dihydroxyphenanthrene by reacting phenanthraquinone with methylmagnesium iodide.(Method of Zincke and Tropp,*Annalen*,1908,*362*,242). By using the improved method of Hall et.al.(*loc*.*cit*.) a 67% yield of 9:10-dimethyl-9:10-dihydroxyphenanthrene was obtained.

Zincke and Tropp (*loc*.*cit*.) dehydrated the diol(III) using several reagents to obtain a compound $C_{16}H_{14}O$. This they said was,

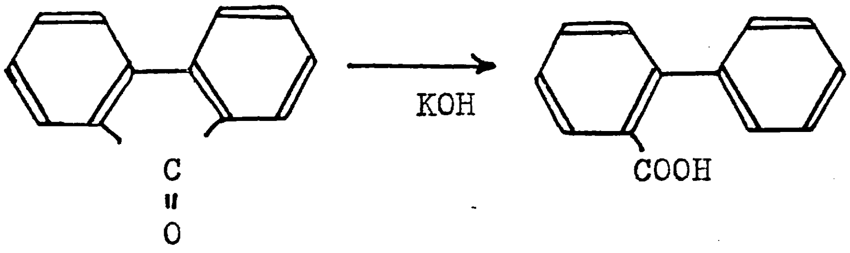


Meerwein however studied several reactions of this type and showed that the product was realy 9:9-dimethylphenanthrone, this being produced as a result of a pinacol-pinacolone rearrangement of the diol.

The diol was most conveniently dehydrated by simply dissolving in hot glacial acetic acid and then adding a few drops of concentrated sulphuric acid.

Meerwein fused 9:9-dimethylphenanthrone (1.3g.) with potassium hydroxide (5g.) at 220-240° for 30 mins. and obtained an acid which analysed correctly for 2'-*iso*propyldiphenyl-

-2-carboxylic acid.The following reaction was quoted in favour of this.(Fittig and Ostermayer,*Annalen*,1873,*166*,374).



The potassium hydroxide fusion was carried out a number of times. It was scaled up and proportionally less alkali was used.By carrying out the fusion at lower temperatures the yield was improved from 31 to 61%. The acid obtained analysed correctly for 2'-*iso*propyldiphenyl-2-carboxylic acid and had a higher melting point (110-111°) than that recorded by Meerwein (104-106°).

Finally 2'-*iso*propyldiphenyl-2-carboxylic acid was decarboxylated to give 2-*iso*propyldiphenyl.For spectral purposes this was purified by two crystallisations from ethanol at low temperatures,m.p.25-26°, and then redistilled.

Whenever a compound was to be used for spectral purposes it was obtained as pure as possible and the purity was then usually checked by examination by the method of gas phase chromatography. This part was carried out by Dr.G.H.Beaven and Dr.E.A.Johnson,whom I should like to thank and also Dr. A.T.James for the use of the gas chromatography apparatus.

It was found without exception that compounds which were solids and could be purified therefore by crystallisation were readily obtained pure. Repeated crystallisations gave

~~gave~~ specimens suitable for spectral purposes. In the case of most liquid specimens however ~~the~~ substance was not so readily freed from last traces of impurities. The formation of complexes between 2:4:7:-trinitrofluorenone and certain of the diphenyls prepared was therefore studied.(see Castro and Andrews,J.Amer.Chem.Soc.,1955,77,5189). After crystallisation these complexes can be decomposed to regenerate the diphenyl compound by passing through an alumina column (Orchin and Woolfolk,J.Amer.Chem.Soc.,1946,68,1727). Of the compounds studied only 4:4'-diethyldiphenyl formed a complex under the conditions used. None of the ortho substituted diphenyls studied were sufficiently planar to allow the 2:4:7-trinitrofluorenone to come close enough for complex formation.

Ultraviolet Absorption Spectra

The ultraviolet absorption spectra of the following compounds have been determined.

COMPOUND	TABLE	PAGE	FIG.
Ethylbenzene	1	49	1
Diphenyl	4	52	-
2:2'-Diethyldiphenyl	2&3	51	11
3:3'-Diethyldiphenyl	4	52	111
4:4'-Diethyldiphenyl	4	52	111
2-Ethyldiphenyl	5	53	V
2:2'-Di-*iso*propyldiphenyl	2	51	11
4:4'-Di-*iso*propyldiphenyl	4	52	1V
2-*iso*Propyldiphenyl	5	53	V
2:2':4:4'-Tetra-*iso*propyldiphenyl	2	51	11
α:α'-Dibromo-2:2'-diethyldiphenyl	-	-	V1
$C_{18}H_{19}Br_3$	-	-	V1
9:9-Dimethylfluorene	6	55	V11
4-*iso*Propenyl-9:9-dimethylfluorene	6	55	V111
4-*iso*Propyl-9:9-dimethylfluorene	6	55	V11

All the spectra were measured on a Unicam S.P. 500 spectrophotometer.

The intensity of absorption is related to the thickness of the absorbing layer (x) and the concentration of the absorbent (c). For dilute solutions the Beer-Lambert Law holds. This states that the fraction of light absorbed is proportional to the number of absorbing molecules (n).

$$\mathrm{Log.}_{10} \frac{I\lambda o}{I\lambda} = nk = D$$

$I\lambda o$ is the intensity of the incident light of wavelength λ

$I\lambda$ is the intensity of the transmitted light

D is termed the extinction or optical density

At constant temperature,

$$n \propto cx$$

Various proportionality constants may be used, but in the present work, ε, the molecular extinction coefficient was used.

Thus,

$$D = \varepsilon cx$$

where, c is the concentration in g.mols/litre

x is measured in cm.

In all cases the solvent used was 95% ethanol. Solutions of various concentrations were made up so that over the whole range of values studied, λ, 2,100-4,000 Å, each part of the spectrum was investigated at a suitable concentration of the absorbent, to give accurate readings of D on the spectrophotometer. (i.e. D, 0.2-0.7). In each case an independent check of points of interest on the spectra was made using a new set of solutions. The quartz cells used had $x = 1.0, 0.5, 0.2$ cm.

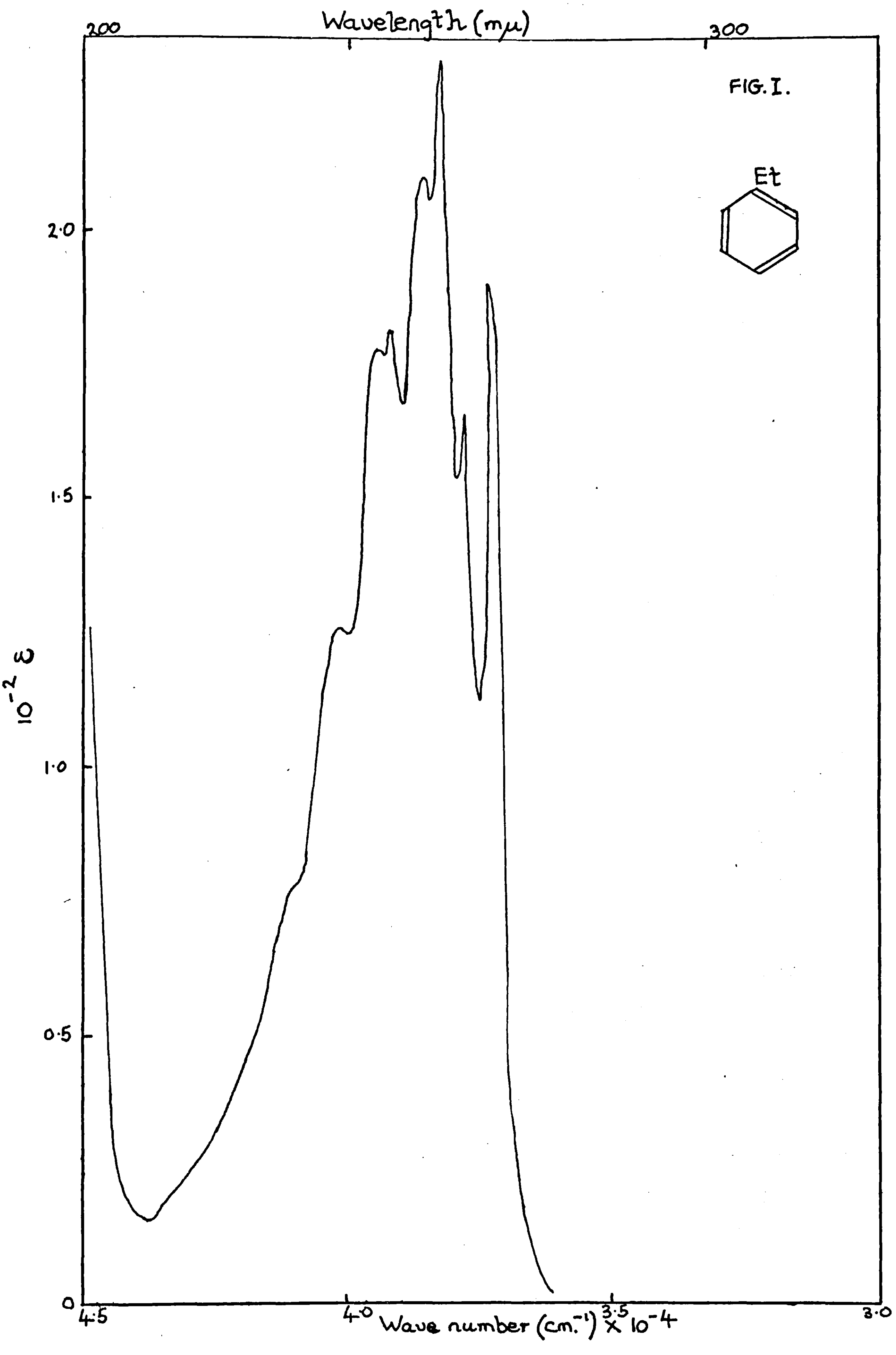
The light absorbing properties of each compound were best shown graphically by plotting ε against $\frac{1}{\lambda}$

Discussion of results.

i) Alkyldiphenyls.

Data for the alkylbenzenes were neccessary for comparison with the corresponding diphenyls. In the case of ethylbenzene suitable data in ethanol as solvent were not available and hence the ultra violet absorption spectrum was determined in this solvent. (see Fig. 1, Table 1). The data for *iso*-propylbenzene and di-*iso*propylbenzene were taken from the catalogue of Ultra violet Spectral Data of the American Petroleum Research Institute Project No.44

FIG. I.



Wavelength (mμ)
200
300
10^{-2} ε
2·0
1·5
1·0
0·5
0
4·5
4·0
3·5
3·0
Wave number (cm.$^{-1}$) x 10^{-4}
Et

TABLE 1.

Ethylbenzene	λ max. 268	εmax.190
	λ max. 261.5	εmax.230
	λ max. 255	εmax. 180

λ in mμ

In the spectra of both 2:2'-diethyldiphenyl and 2:2'-di-isopropyldiphenyl traces of a residual conjugation band still remain at λ c.a. 227 mμ (see Fig.2, Table 2). The finer details of these spectra are best discussed in relation to the spectra of 2:2'-dimethyldiphenyl and 2:2'-ditert.butyldiphenyl. (Everitt,Hall and Turner,*J.Chem. Soc.*,1956,2286).

It is seen that as the size of the ortho substituents is increased, there is a decrease in the extent of conjugation between the two benzene rings until in the case of 2:2'-ditert.butyldiphenyl no trace of a discrete conjugation band remains. The minimum between the short-wave band and the long-wave fine structure decreases from dimethyldiphenyl to ditert.butyldiphenyl, as the overlapping of the short-wave band by the residual conjugation band becomes less. This overlapping has obliterated one of the fine structure bands of the alkylbenzene partial chromophores in dimethyl- and diethyl-diphenyl. In the other two compounds this fine structure band is present as an inflection at 258 mμ. All four compounds show at least two bands of the alkylbenzene partial chromophores at 263.5 and 270-271 mμ . In diethyldiphenyl and di-*iso*propyldiphenyl the intensities of these bands are slightly reduced as compared with dimethyldiphenyl. In di*tert*,butyldiphenyl the intensities are much reduced but are still a little greater than twice those of *tert*.butylbenzene. In the corresponding series of alkylbenzenes there is also a slight reduction in the intensities in the series ethyl to *tert*.butyl, but this is of the order of 20%, whereas in the dialkyldiphenyls it is of the order of 50%.Thus except perhaps in the case of 2:2'-di*tert*.butyldiphenyl,the long-wave fine structure band is overlapped by the residual conjugation band,

Because of the doubtful purity of the specimen of 2:2'-4:4'-tetra-*iso*propyldiphenyl obtained, conclusions about its spectrum must be treated with reserve. However it appears that in this compound the steric effect of the *ortho* substituents is partly compensated by the increased absorption resulting from the *para* substituents. This increased absorption is apparent in the long wave region where the bands are present only as inflections with large increases in intensities, and also in the 260-225 mμ region where there is a long-wave shift of the residual conjugation band. In addition there is no longer a distinct minimum between the residual conjugation band and the long-wave band.

TABLE 2.

DIPHENYL COMPOUND					Long-wave fine structure							
x	$\lambda_{inf.}$	$\varepsilon_{inf.}$	λ_{min}	ε_{min}	$\lambda_{inf.}$	$\varepsilon_{inf.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
2:2'-Diethyl	(ca.227)	6,000	258.5	685			263.5	730	269.5	530	271	560
2:2'-Di-isopropyl	(ca.227)	5,500	254	630	(258)	640	263.5	720	269	500	271	560
2:2'-4:4'-tetra-isopropyl	(ca.234)	8,800					(ca.265)	2,750			(ca.273.5)	1,900

N.B. The data given for 2:2'-diethyldiphenyl were measured with a specimen which had been purified by crystallisation. Table 3 gives the data obtained with different specimens before crystallisation. p.73

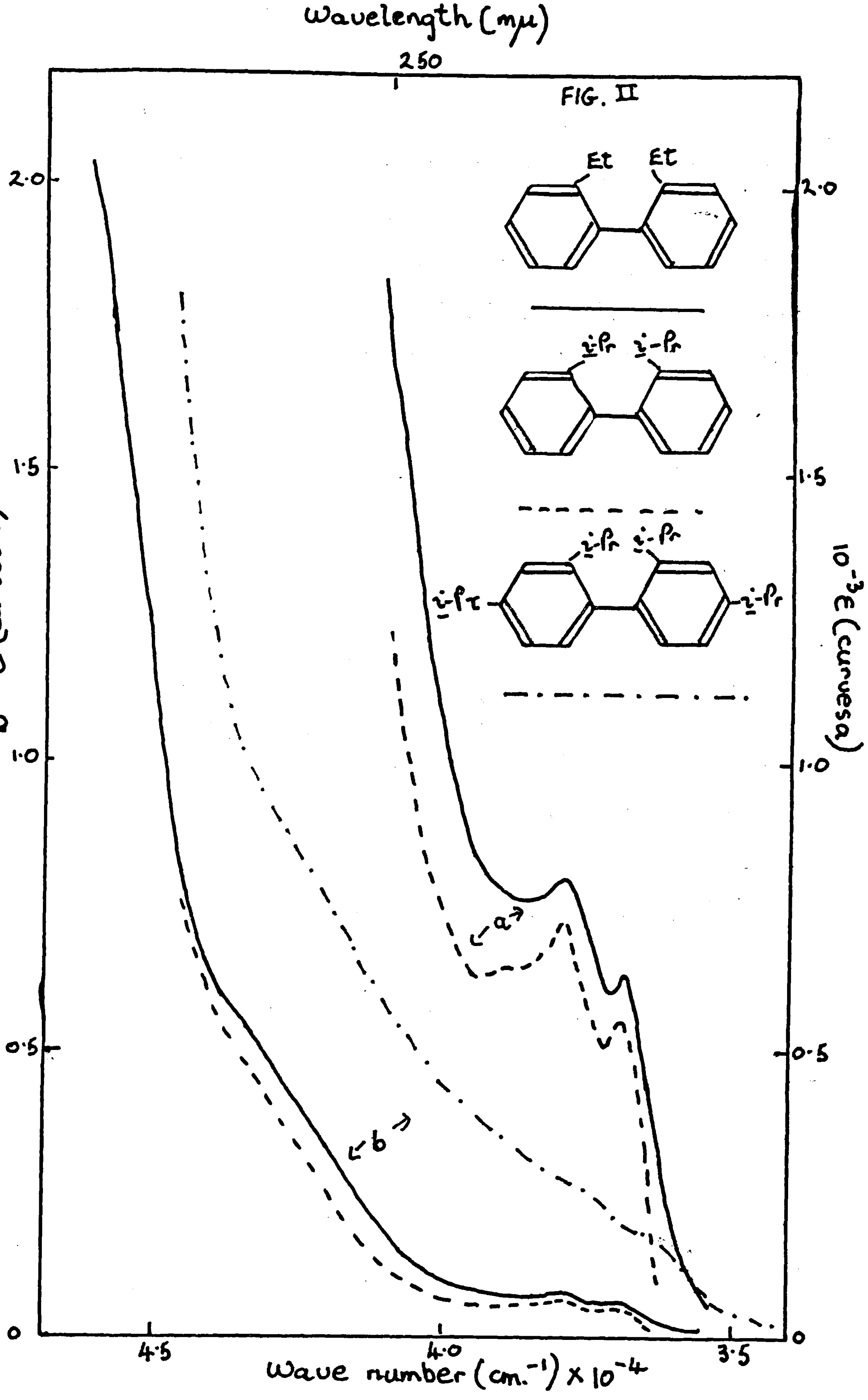
TABLE 3.

Source of 2:2'-diethyl-diphenyl					Long-wave fine structure					
	$\lambda_{inf.}$	$\varepsilon_{inf.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$	$\lambda_{min.}$	$\varepsilon_{min.}$	$\lambda_{max.}$	$\varepsilon_{max.}$
Ullmann Reaction,p.72	(ca.227)	6,000	258.5	760	263.5	810	269	600	271	640
2-Ethylcyclo-hexanone p.83	(ca2227)	6,000	261.5	780	263.5	790	269	590	271	620

Wavelength in mμ

x I am indebted to Dr E.A. Johnson who carried out this part of the work

FIG. II


Wavelength (mμ)
250
Et
Et
i-Pr
i-Pr
i-Pr
i-Pr
i-Pr
i-Pr
2·0
1·5
1·0
0·5
0
10^{-4} ε (curves b)
10^{-3} ε (curves a)
a
b
4·5
4·0
3·5
Wave number (cm.$^{-1}$) × 10^{-4}

3:3'-Diethyldiphenyl, 4:4'-diethyldiphenyl and 4:4'-di-isopropyldiphenyl are all typical conjugated diphenyls with a distinct conjugation band in the 250 mμ region, and having no long-wave fine structure. In the p:p'compounds there is a marked long-wave shift of the absorption band accompanied by an increase in the intensity of absorption. (Bathochromic Effect)

TABLE 4

Diphenyl Compound	Minimum		Conjugation Band	
	λ min.	ε min.	λ max.	ε max.
Diphenyl	222	4300	249	17300
3:3'-Diethyl	228.5	6200	251	16,500
4:4'-Diethyl	226.5	4500	256.5	22,500
4:4'-Di-isopropyl	226	4600	256.5	23,500

λ in mμ

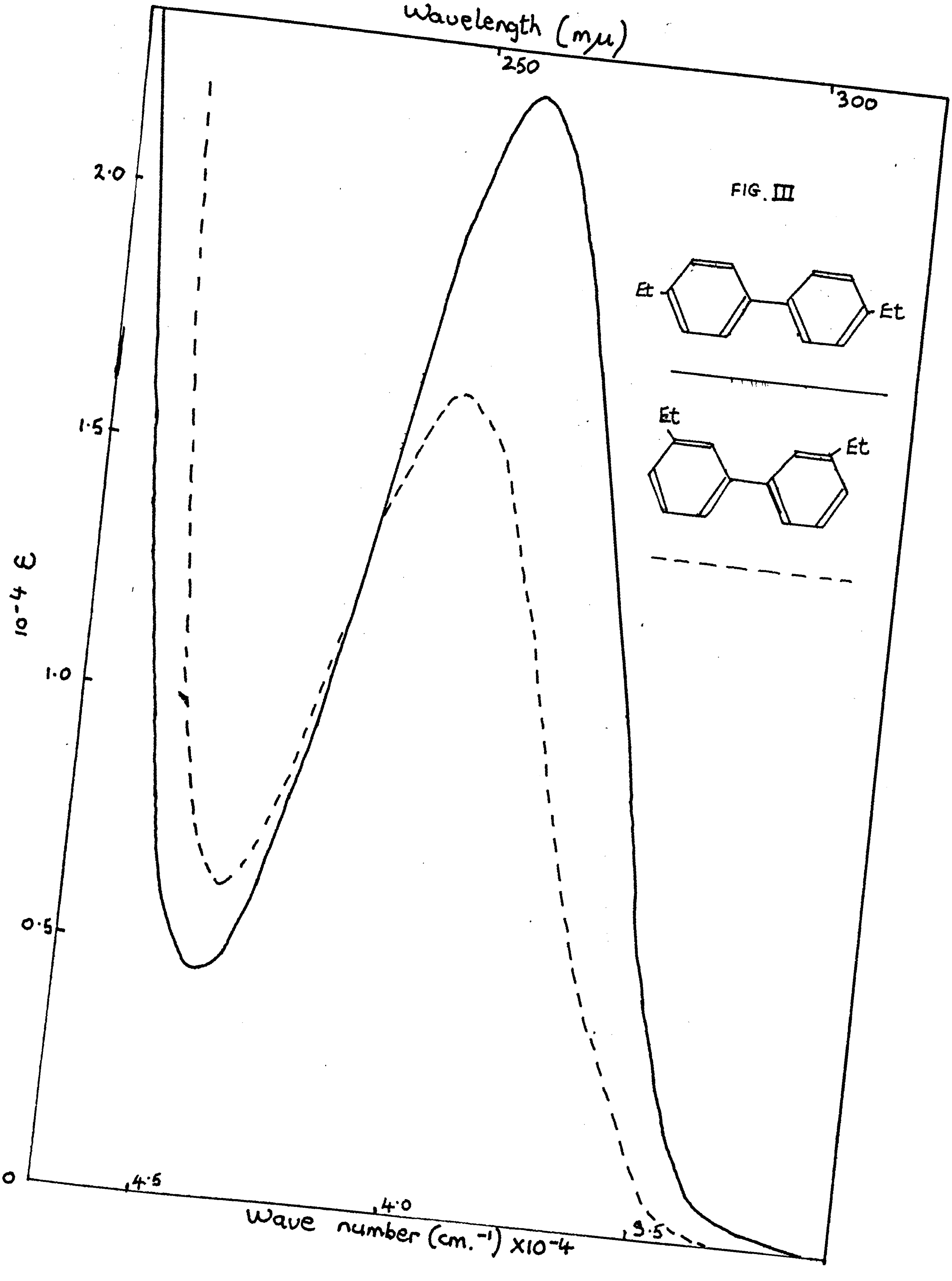

Wavelength (mμ)
250
300
2·0
1·5
1·0
0·5
0
10⁻⁴ ε
4·5
4·0
3·5
Wave number (cm.⁻¹) x10⁻⁴
Et
Et
Et
Et

FIG. III

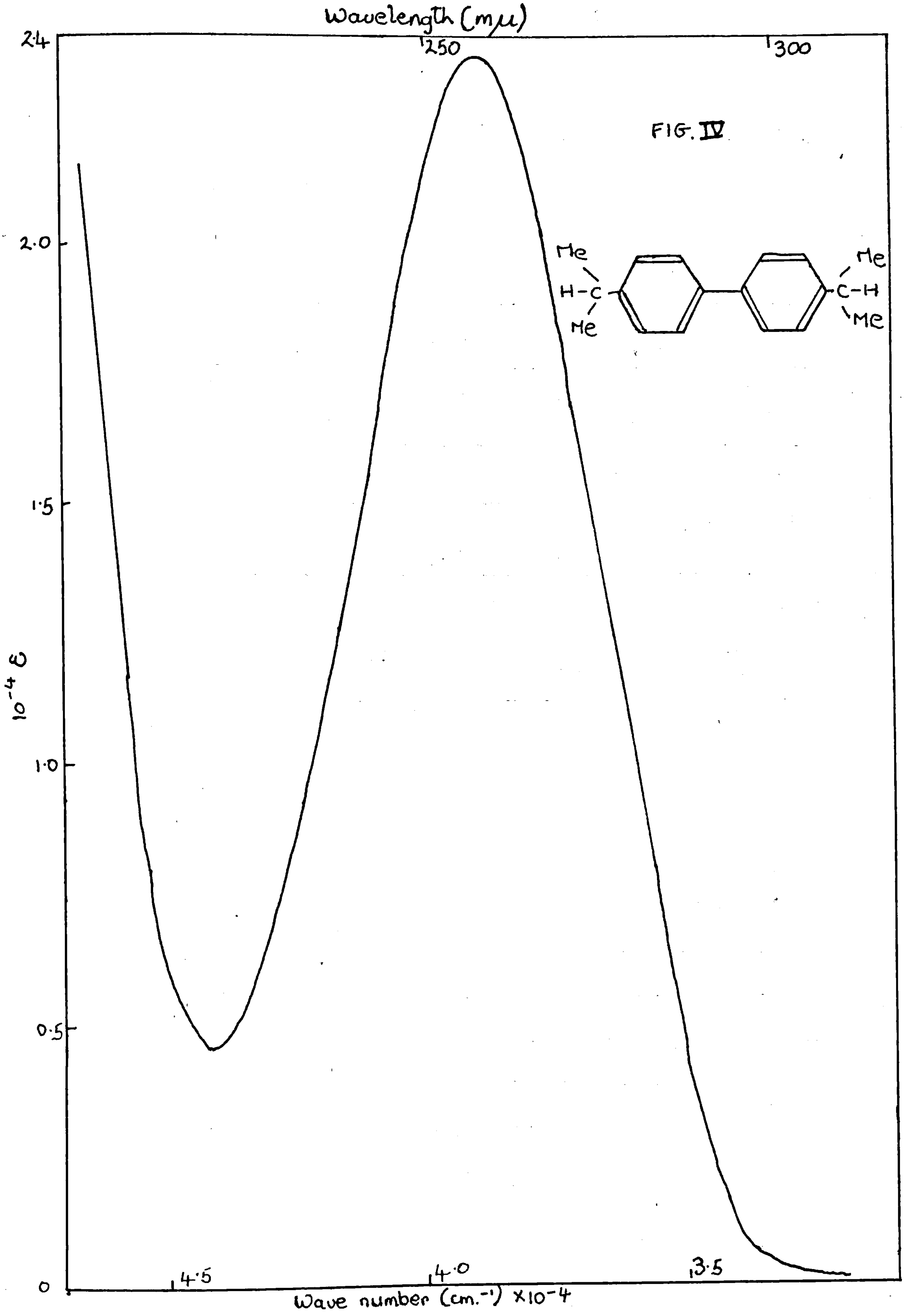


FIG. IV

Wavelength (mμ)
250
300
2·4
2·0
1·5
1·0
0·5
0
$10^{-4}\,\varepsilon$
4·5
4·0
3·5
Wave number (cm.⁻¹) ×10⁻⁴
Me
H–C
Me
Me
C–H
Me

Recent data for various 2-alkyldiphenyls are given below.

TABLE 5

2-Alkyldiphenyl	λ max.	ε max.	Reference
2-Methyl	235	10,500	Braude and Forbes, *J.Chem. Soc.*, 1955, 3776.
2-Ethyl	233 233 234.5	10,500 9,000 9,100	Braude and Forbes, *loc.cit.* Braude, Sondheimer and Forbes, *Nature*, 1954, 173, 117. Own work
2-*iso*Propyl	233 233 233	11,000 8,800 8,600	Braude and Forbes, *loc.cit.* Own work Beaven, (private communication,) source as Braude and Forbes.

Solvent 95% Ethanol λ in mμ

The values obtained for $\varepsilon_{max.}$ in the present work are thus similar to the values given by other workers, however in the case of 2-ethyldiphenyl the values given even by the same wofkers on different occasions vary outside the limits of experimental error. In our case the absorption maximum was at longer wavelengths. Ultra violet absorption spectra are very sensitive to small amounts of impurities and this probably explains the discrepencies in the above results.

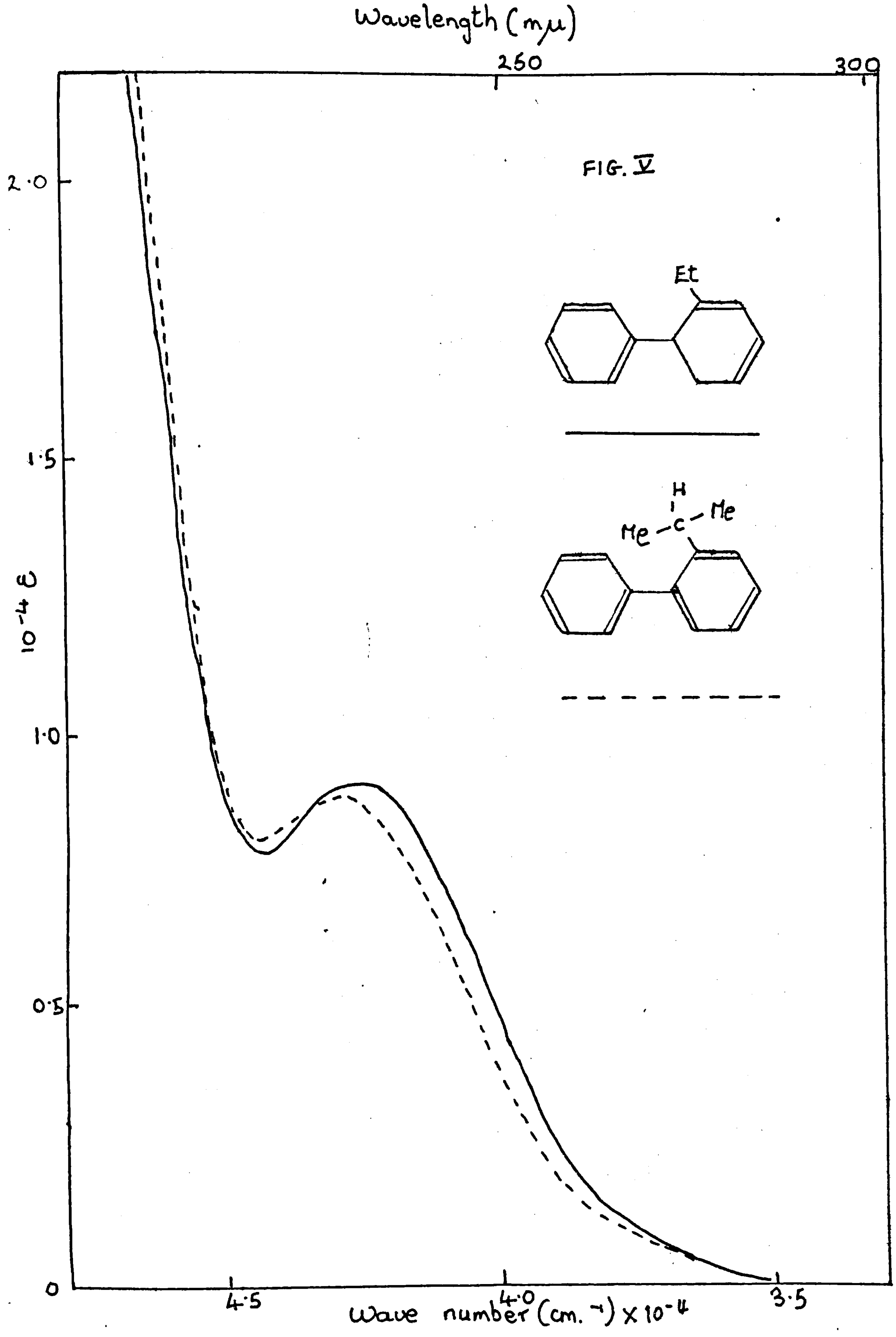

Wavelength (mμ)
250
300
2·0
1·5
1·0
0·5
0
10⁻⁴ ε
4·5
4·0
3·5
Wave number (cm.⁻¹) × 10⁻⁴
Et
H
Me
C
Me

FIG. V

In our own results there is a slight decrease in $\varepsilon_{max.}$ as the size of the *ortho* substituent is increased. The same conclusions as Braude and Forbes(*loc.cit*) may be drawn however:- 'all but the methylene group attached directly to the phenyl ring can adopt conformations such that they cause little or no additional interference.'

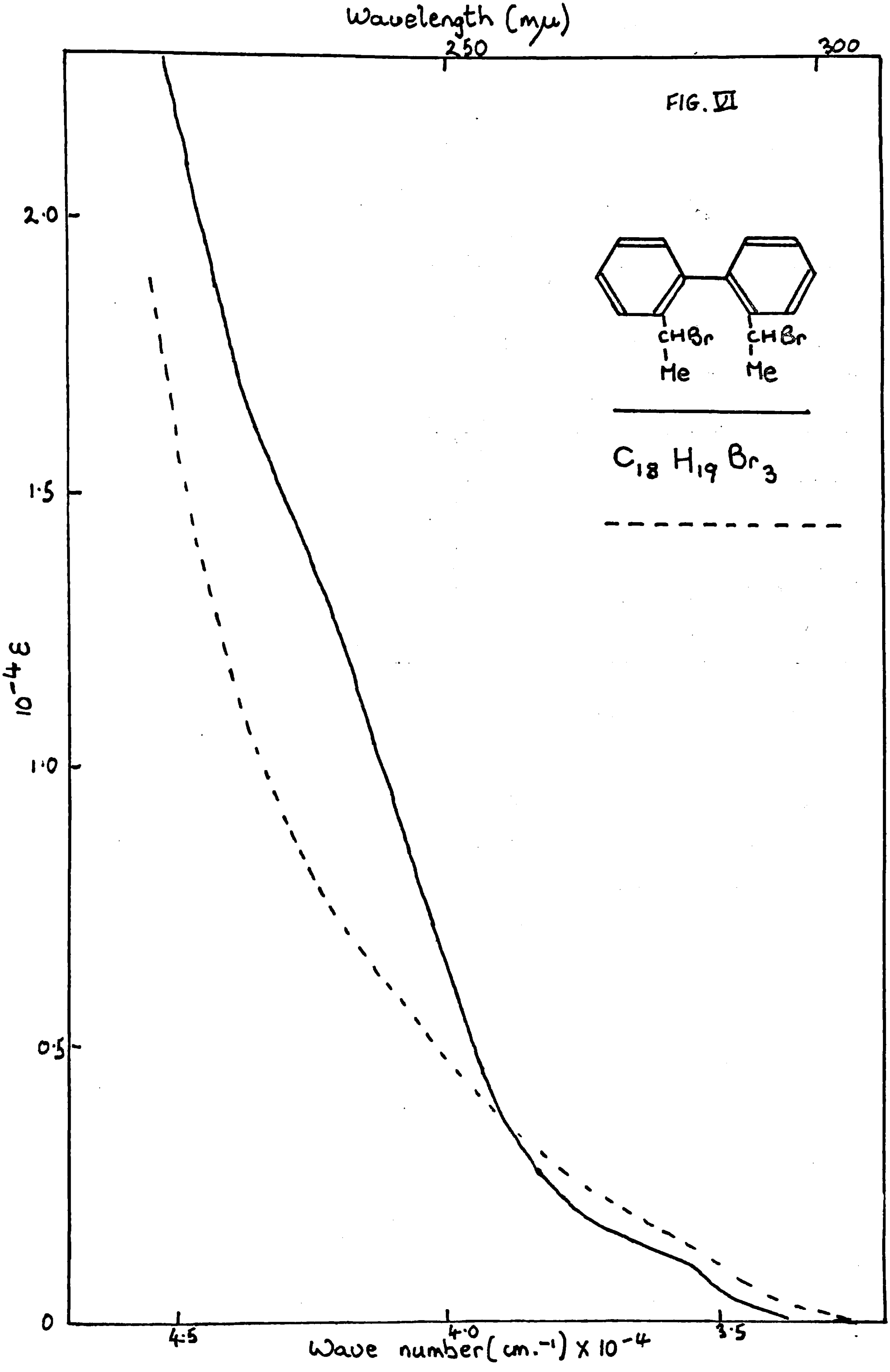
ii) *Bromo compounds*.

The spectrum of the unidentified $C_{18}H_{19}Br_3$ obtained by the action of N-bromosuccinimide on 2:2'-di-*iso*propyl-diphenyl was determined in the hope that it would through some light on its structure. The spectrum of $\alpha:\alpha'$-dibromo-2:2'-diethyldiphenyl was determined to act as a reference compound since the spectra of similar compounds to these have not previously been studied. These spectra are given for comparison in Fig.V1. The spectrum of $C_{18}H_{19}Br_3$ is featureless and no conclusions may be drawn.

iii) *Fluorene Compounds*.

All three fluorene compounds show typical fluorene type spectra having much fine structure. Interpretation of the small wavelength shifts and intensity changes must await however the correct assignment of the bands in fluorene itself. The spectrum of 4-*iso*propenyl-9:9-dimethylfluorene shows less fine structure than that of either 4-*iso*propyl-

FIG. VI



Wavelength (mμ)
250
300
2·0
1·5
1·0
0·5
0
$10^{-4}\varepsilon$
4·5
4·0
3·5
Wave number (cm.⁻¹) X 10⁻⁴
CHBr
Me
CHBr
Me
$C_{18}H_{19}Br_3$

9:9-dimethylfluorene or 9:9-dimethylfluorene.

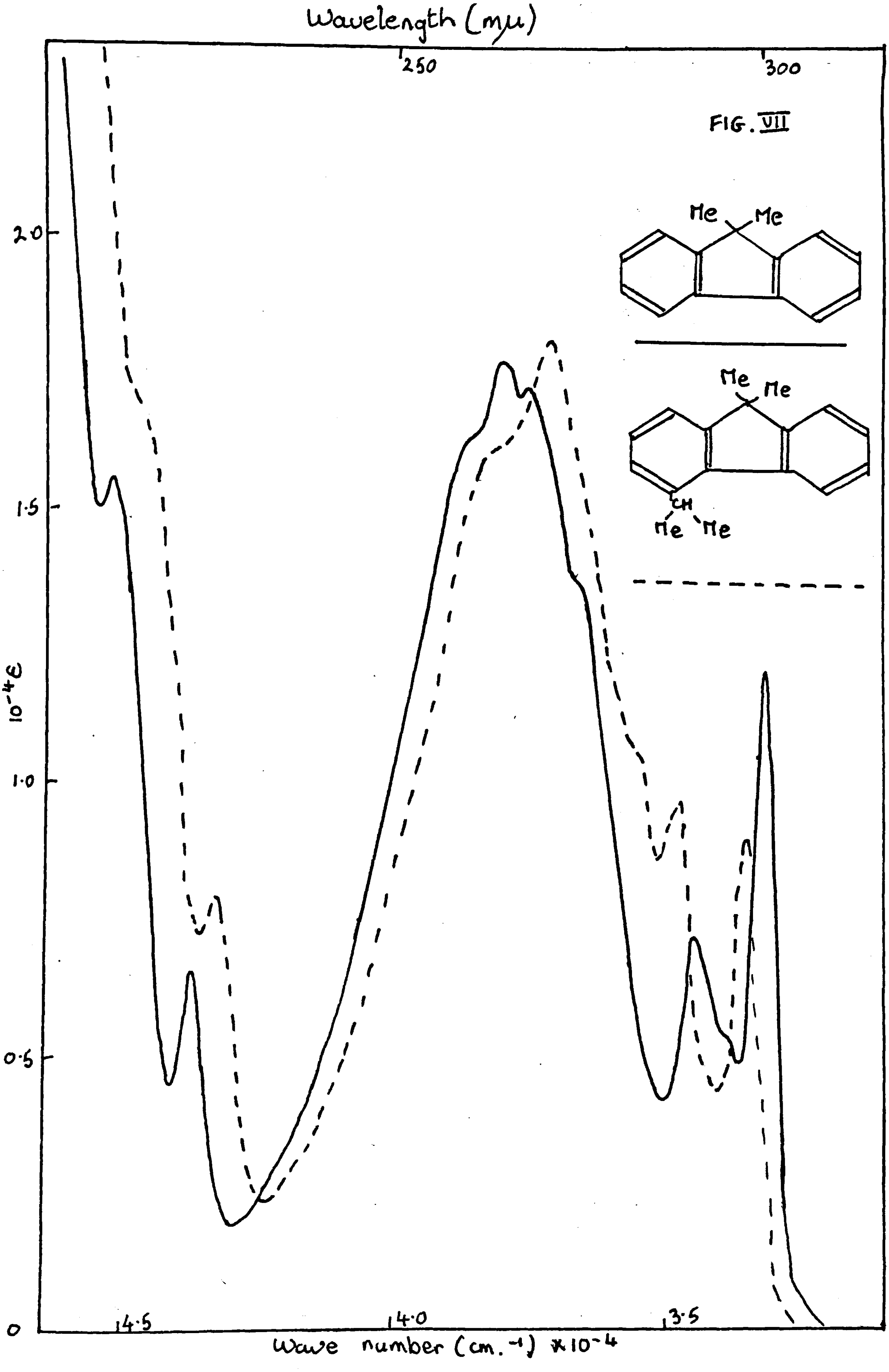
Table 6

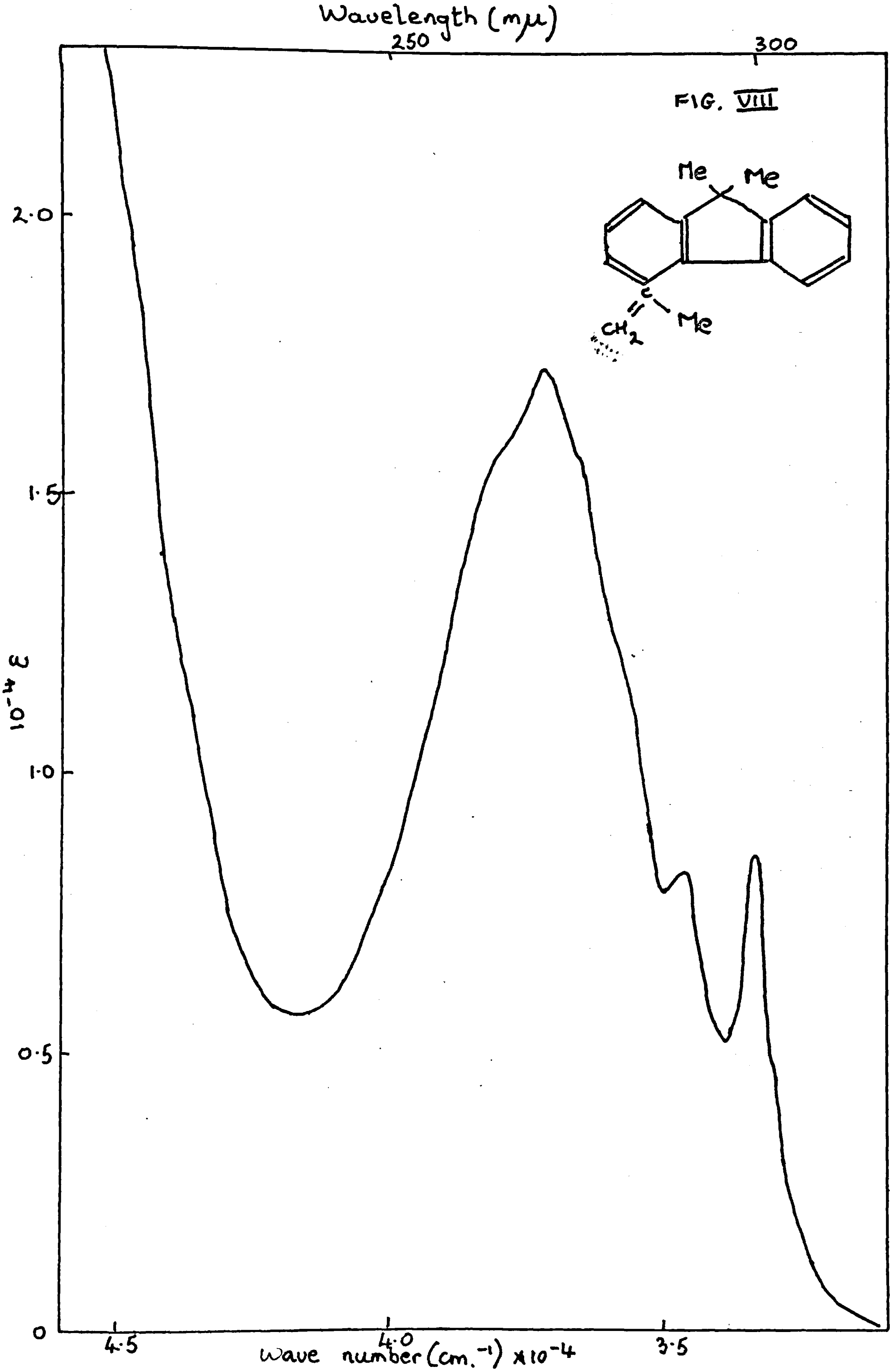
Substance	Diphenyl Band		Long-wave Band	
	λ max.	ε max.	λmax.	εmax.
Fluorene[x]	2600	19,000	3000	10,000
9:9-Dimethylfluorene	2630	17,500	3020	12,000
4-*iso*Propyl-9:9-dimethylfluorene	2690	18,000	2985	9,000
4-*iso*Propenyl-9:9-dimethylfluorene	2685	17,000	2995	8,500

[x] Mayneord and Roe (*Proc.Roy.Soc.*,1937,A,*158*,634.) λ in Å

In the spectra of the different compounds studied in this work all four effects which may be produced by the introduction of substituents in aromatic compounds have been illustrated.

FIG. VII


Wavelength (mμ)
250
300
2·0
1·5
1·0
0·5
0
$10^{-4}\varepsilon$
4·5
4·0
3·5
Wave number (cm.$^{-1}$) × 10^{-4}
Me
Me
Me
Me
CH
Me
Me


Wavelength (mμ)
250
300
FIG. VIII
Me
Me
Me
CH2
C
2.0
1.5
1.0
0.5
0
10⁻⁴ ε
4.5
4.0
3.5
wave number (cm.⁻¹) x10⁻⁴

Optical Work.

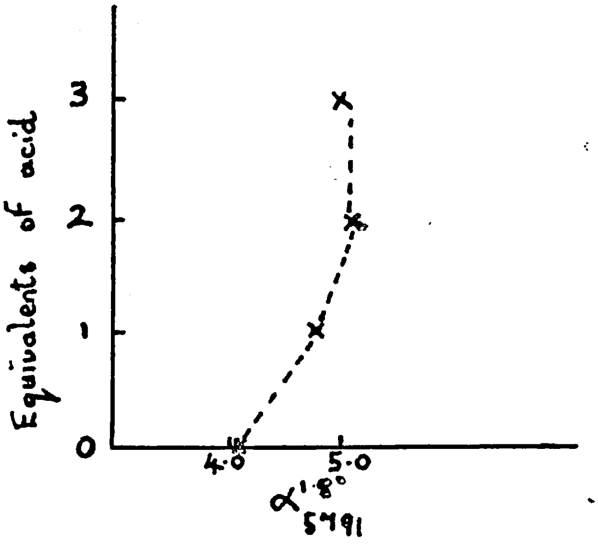
In the case of 2:2'-di-isopropyldiphenyl, spectroscopic evidence shows a discrete conjugation band and all attempts to demonstrate optical activity in 6:6'-di-isopropyldiphenyl-3:3'-dicarboxylic acid have been unsuccessful. Activations with brucine, quinidine, and cinchonidine were attempted without success. Difficulties were encountered since the acid was sparingly soluble in most solvents. In an attempt to overcome this difficulty the dimethyl ester was prepared since this should have greater solubility. This ester was dissolved in ethyl (+)-tartrate and left for 3 days.

Glazer, Harris and Turner, (J. Chem. Soc., 1950, 1753) showed that optical activation of a racemic compound e.g. N-benzoyl-2'-chloro-6-methyldiphenylamine-2-carboxylate, by an optically active solvent, ethyl (+)-tartrate, was possible. In the case of **methyl** 6:6'-di-isopropyldiphenyl -3:3'-dicarboxylate however, after removal of the optically active solvent the ester was found to be inactive.

2'-isoPropyldiphenyl-2-carboxylic acid was then studied. Again no mutarotations were observed with this acid in the presence of the above alkaloids even at low temperatures. This acid was more soluble in organic solvents and it was therefore possible to study the effect of the addition of excess acid. Jamison and Turner, (J. Chem. Soc., 1938, 1646) showed that the optical rotation at equilibrium of a solution containing 1 equivalent of a labile acid and 1 equivalent of an alkaloid was very sensitive to the addition of excess acid. Only compounds in which optical activity might be expected from structural considerations showed a change in the rotation at equilibrium on the addition of excess acid. It was suggested that this phenomenon might be used as an indication of potential optical activity in compounds which otherwise appeared inactive.

A solution containing 1 equivalent of 2'-*iso*propyldiphenyl-2-carboxylic acid and 1 equivalent of quinidine was found to be sensitive to the addition of excess acid (1 equivalent). The addition of still more acid, however caused no further change in rotation. In the case of 2'-*iso*propenyldiphenyl-2-carboxylic acid no change in the optical rotation was observed when excess acid was added to a solution of 1 equivalent of acid and 1 equivalent of quinidine.

Addition curve for 2'-isopropyldiphenyl-2-carboxylic acid with quinidine.



Although this gives possible evidence of potential optical activity it has not been possible to demonstrate any optical activity.

Recently, Harris (J.Chem.Soc.,1955,4152) studied the effect of temperature on the equilibrium between partially labile diastereoisomers. The acids studied were chiefly in the N-benzoyldiphenylaminecarboxylic acid series. The alkaloid used was quinidine. The acids fell roughly into two classes.

a) Optically inactive acids in which the rotation of the equilibrium mixture altered only slightly with temperature.

b) Optically active acids of low optical stability in which the rotation of the equilibrium mixture altered substantially with temperature. The alteration in rotation was shown to be due to the variation in the position of the equilibrium

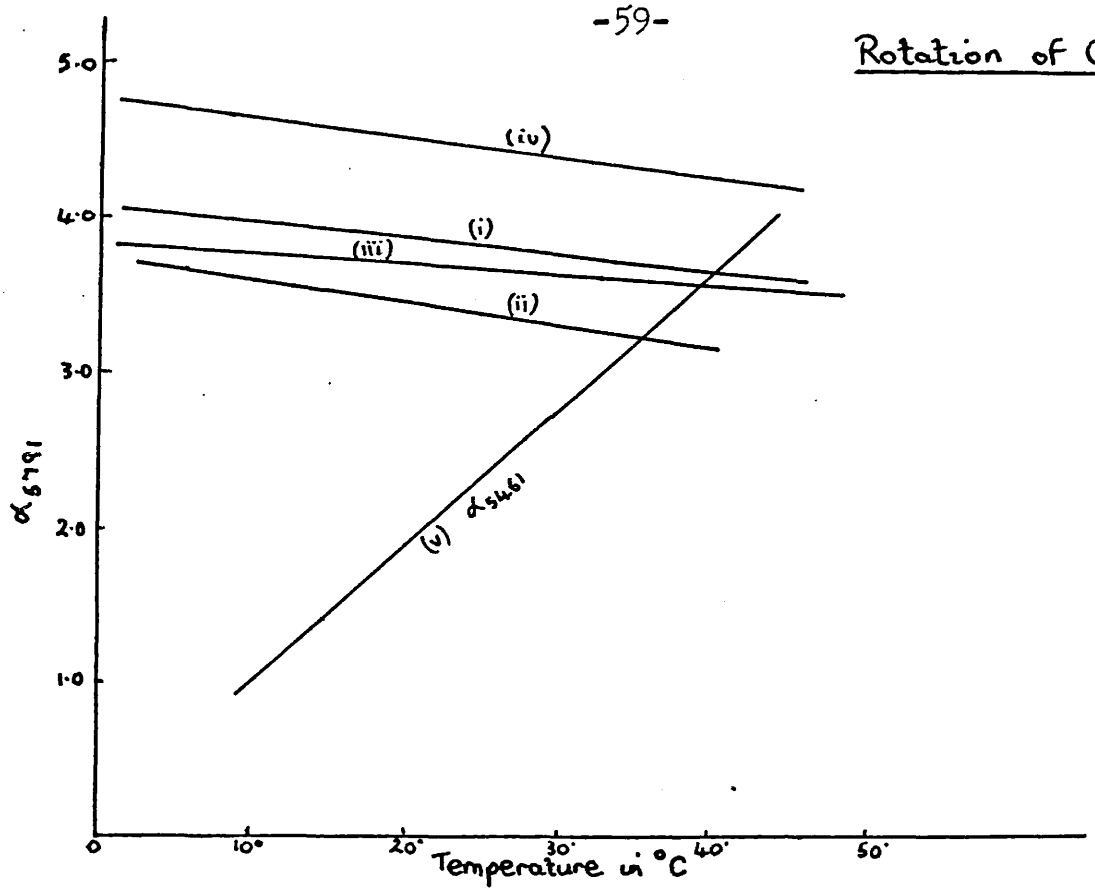
$$(+)\text{-acid,quinidine} \rightleftharpoons (-)\text{-acid,quinidine},$$

with temperature.

It was concluded that if this phenomenon was general and was capable of being distinguished from other temperature dependent influences on rotation, it should be of value in the diagnosis of optical activity in highly labile compounds.

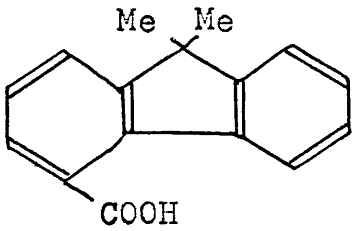
In order to study this phenomenon further the following series of compounds have been compared.

Rotation of Quinidine Salts



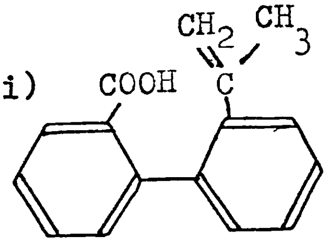
(i) Quinidine, Present work

(ii)



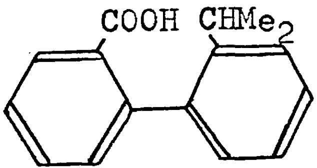
Present work

(iii)



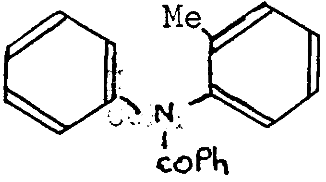
Present work

(iv)



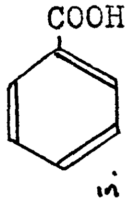
Present work

(v)



Harris (loc.cit.) in $CHCl_3$

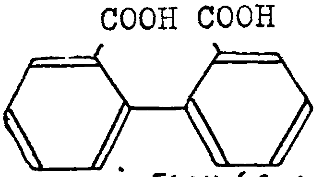
(vi)



see, Harris (loc.cit.)

in $CHCl_3$

(vii)



in EtOH (2vol.) $CHCl_3$ (1vol.)

Lesslie, Turner and Winton, J.Chem.Soc., 1941, 257.
values range from $\alpha^{0.8^\circ}_{5791}$ + 9.14° → $\alpha^{45.5^\circ}_{5791}$ + 5.23°

Compound (v) was added for comparison so that the order of the effect observed by Harris (loc.cit.) could be seen. Compounds (ii),(iii) and (iv) show approximately the same variation of rotation with temperature as quinidine itself, this being of the same order as that shown by benzoic acid. From structural considerations (iii) and (iv) might be expected to show appreciable variation of rotation with temperature as in the case of diphenic acid. The present work thus does not give evidence for this phenomenon being general but no more can be said in the present incomplete state of our knowledge of this behaviour.

Experimental

For all rotation measurements a 2 dcm. polarimeter tube was used. The tube was jacketed and a steady temperature was maintained by rapidly pumping water from an electrically heated thermostat through the jacket.

Solvent

Commercial B.P. chloroform was washed 5 times with water and a preliminary drying carried out by shaking with calcium chloride. It was finally dried over anhydrous sodium sulphate. 2.5% Ethanol was then added to give solvent X in which the acids used were more soluble than in chloroform.

Quinidine.

This was purified by the method of Harris, (J.Chem. Soc., 1955,4152). Commercial quinidine was first crystallised from benzene using charcoal. It was then dissolved in the minimum quantity of washed chloroform and the solution dried over anhydrous sodium sulphate. After filtration, dry light petroleum (40-60°) was added. The first two crops which precipitated were oily and these were filtered off and discarded. The third crop gave a finely divided specimen which was filtered off and dried.

$$[\alpha]^{9^\circ}_{5461} = +306.8$$

c = 1.620

$$[\alpha]^{9^\circ}_{5791} = +246.3$$

Method

In attempts to observe a first order asymmetric transformation the following technique was adopted. The acid (1 equivalent) and the alkaloid (1 equivalent) were weighed into a 20 ml. volumetric flask and then dissolved in solvent X which had stood in the thermostat at the desired temperature for some time. The solution was made up to the mark, shaken thoroughly and then filtered into the polarimeter tube which was in position ready to take readings with water circulating through the jacket, from the thermostat. In this way the sparingly soluble acids could be dissolved more rapidly. The stop clock was started at the time of wetting and by this method readings could be taken within 1-2 mins.

In the study of the variation of equilibrium rotation with temperature, quinidine (1 equivalent) and acid (1 equivalent) were dissolved in 20 ml solvent X and examined polarimetrically over a range of temperatures. Measurements were made at each temperature ascending gradually from one temperature to the next and then further measurements were taken as the temperature was lowered from point to point. In all the acids studied the variation of rotation with temperature was small. The results are shown graphically on p.59.

Attempted activation of methyl 6:6'-di-*iso*propyldiphenyl-3:3'-dicarboxylate.

Methyl 6:6'-di-*iso*propyldiphenyl-3:3'-dicarboxylate (1g.) was dissolved in 100 ml. ethyl (+)-tartrate by warming to 80-90°. After cooling it was left at room temperature for 3 days. The solution was cooled in ice and poured into ice-water. After rapid filtration, the ester was washed well with ice-water and then dried. 0.2g. Were dissolved in 20ml. solvent X and examined polarimetrically. The solution was inactive.

Addition curve of 2'-isopropyldiphenyl-2-carboxylic acid with quinidine (see p.57)

Quinidine

0.162 g. quinidine in 20ml solvent X had

$\alpha_{5791}^{1.8^\circ}$ 4.06

Acid (1 equivalent) and base (1 equivalent).

0.12g. acid and 0.162 g. quinidine were dissolved in 20 ml. solvent X and examined polarimetrically at 1.8°.

Time after wetting in mins.	$\alpha_{5791}^{1.8^\circ}$
1.5	4.73
2.8	4.74
4.2	4.74
	4.74

Acid (2 equivalents) and Base (1 equivalent).

An additional 0.12 g. acid were added

$\alpha_{5791}^{1.8^\circ}$ 5.08

Acid (3 equivalents) and Base (1 equivalent).

A further 0.12g. were added.

$\alpha_{5791}^{1.8^\circ}$ 5.03

EXPERIMENTAL.

2-Ethyldiphenyl and 2:2'-diethyldiphenyl.

Ethylbenzene.

Ethylbenzene was purified by shaking with cold saturated ferrous sulphate solution to remove peroxide impurities, washed with water, dried over calcium chloride and then distilled. b.p. 137°. For spectral purposes it was fractionated using a 40 cm. Vigreux Column and had b.p. 135° / 760 mm. $n_D^{25^\circ}$ 1.4942. (Literature value, $n_D^{20^\circ}$ 1.4958.)

Mononitration of ethylbenzene.

Cline and Reid, J. Amer. Chem. Soc., 1927, 49, 3150.
Ford-Moore and Rydon, J. Chem. Soc., 1946, 679.
Brown and Bonner, J. Amer. Chem. Soc., 1954, 76, 6505.

To ethylbenzene (212g.) a mixture of nitric acid (110ml., d 1.42) and sulphuric acid (110ml., d 1.84) was added during 2 hours. The reaction mixture was stirred mechanically and cooled externally to keep the temperature betweem 20-30°. After the addition of the acid mixture stirring was continued for another hour. The oily layer was then separated from the acid and washed with water and sodium carbonate solution. It was purified by steam distillation, dried over calcium chloride and finally fractionated using a vacuum jacketed column. From 209g. of mixture to be fractionated, 40g. ethylbenzene were recovered. Three fractionations gave :-

o-nitroethylbenzene, b.p. 139-143° / 43mm. (93.5g.)
$n_D^{25°}$ 1.5329 32%

intermediary fraction, b.p.143-149° / 43mm. (22g.)

p-nitroethylbenzene, b.p.149-151° / 42mm. (33g.)
$n_D^{25°}$ 1.5428 11%

2:4-Dinitroethylbenzene.

A modified method of Weisweiller, (Monatsh., 1900, 21, 39) was used. Concentrated nitric acid (304ml., 2.4mol., d.1.42) and concentrated sulphuric acid (469ml., 4.4mol., d. 1.84) were mixed together and cooled to 28-30° in an ice bath. Ethylbenzene (246g., 1 mol.) was then added to the acid mixture which was stirred mechanically. The temperature rose on addition of ethylbenzene and the rate of addition was controlled to keep the temperature at 45-50°. Addition took 2 hours and stirring was continued fot a further 30 mins. Finally the mixture was warmed up on a boiling water bath during 30 mins. to complete the reaction, cooled and the top oily layer separated off. This was washed with water, sodium carbonate solution, water, dried over calcium chloride and distilled under reduced pressure. After two distillations, 2:4-dinitroethylbenzene was obtained in 81% yield. b.p. 174°/ 15-16 mm. $n_D^{25°}$ 1.5635.

2-Nitro-4-aminoethylbenzene.

Method 1.

Sodium sulphide (58g.,1.2 mol.), sulphur (15g.,2.4mol.) and water (400ml.) were boiled gently to obtain a clear solution. This was transferred to a 3l., 3-necked flask, fitted with a stirrer and reflux condenser. 2:4-Dinitroethylbenzene (39g., 1 mol.) was added during 30 mins. and the mixture boiled under reflux for a total of 2½ hrs. The mixture was then cooled in an ice-salt bath and filtered through a cold Buchner funnel. The semi-solid obtained was extracted twice with 1:1 hydrochloric acid and the solution boiled with charcoal and filtered. The solid hydrochloride which crystallised on cooling was filtered, washed and crystallised from dilute hydrochloric acid. The base was liberated with ammonium hydroxide solution and crystallised from light petroleum (b.p. 80-100°), or more conveniently because of higher solubility, from aqueous ethanol. 2-Nitro-4-aminoethylbenzene was obtained as orange flakes, m.p.45-46°. Yield 41-47%.

Method 2.

Schultz, *Ber.*,1909,*42*,2633)

Cline and Reid, *loc.cit.*

2:4-Dinitroethylbenzene (50g.,1 mol.) was dissolved in ethanol (150g.) and ammonia (150g.,*d*.0.88) was added. The solution was saturated with hydrogen sulphide and boiled on a warm water bath. This proceedure was repeated until an increase in weight of 30 g. was obtained. The product was filtered hot to remove sulphur and poured onto ice. The solid was filtered off and dissolved in 1:1 hydrochloric acid, boiled with charcoal and filtered. The hydrochloride which crystallised out was filtered, washed with ether and recrystallised from dilute hydrochloric acid four times. The base was liberated with ammonia and crystallised from dilute ethanol. m.p. 45-46°. Yield 32%. Schultz , loc.cit. mp. 43° Cline and Reid, loc.cit. m.p. 45° .

The acetyl derivative was prepared and had m.p. 110° . Schultz, m.p. 101° , and Cline and Reid, m.p. 110° .

Deamination of 2-nitro-4-aminoethylbenzene.

2-Nitro-4-aminoethylbenzene (33g., 1 mol.) was dissolved in water (200ml.) and concentrated hydrochloric acid (50ml. 36%) by warming and then cooled to -4° . An additional 45ml. hydrochloric acid was then added. Sodium nitrite (14.5g., 1.1 mol.) dissolved in water (50ml.) was added keeping the temperature between 0° and -4° throughout the addition. After the addition the diazo solution was stirred at 0° - -4° for another 30 mins. 50% Hypophosphorous acid (313ml., 3 mol.) at 0° was added to the solution during 40 mins. and the mixture stirred at 0° for another hour. After standing overnight in a refrigerator (5°) the product was steam distilled, the oily layer separated and the aqueous layer extracted with ether. The ethereal solution was washed once with 10% sodium hydroxide solution, then with water, dried over calcium chloride and the ether distilled. Two distillations under reduced pressure using a small fractionating column gave a 62% yield of o-nitroethylbenzene as a pale yellow oil, b.p. 110-112° /17 mm., 224° / 760 mm. $n_D^{25°}$ 1.5339.

Purification of commercial o-nitroethylbenzene.

Eastmann Kodak, practical grade o-nitroethylbenzene was used and purified by steam distillation. b.p. 227° / 760mm. $n_D^{25°}$ 1.5340

o-Aminoethylbenzene.

Method 1.

Platinum Oxide Catalyst.

The platinum oxide used in this and all subsequent catalytic reductions was prepared according to Adams, Voorhees and Shriner, Organic Syntheses, Collective Volume I, 463.

Chloroplatinic acid (3g.) in water (10ml.) was added to potassium nitrate (30g.). The mixture was heated gently over a ring burner with shaking until it had evaporated to dryness. The temperature was then gradually increased and the mixture heated very fiercely for 30 mins. After cooling the product was treated with 50 ml. water, filtered and washed free from nitrate. It was dried in a vacuum dessicator. Yield, PtO_2,H_2O (1.4g.) 100%.

o-Nitroethylbenzene (13.4g.) was dissolved in absolute ethanol (100ml.) and platinum oxide (o.15g.) added. The mixture was then shaken in a hydrogenator for 1 hour, the pressure of hydrogen being 52lbs/sq.". After filtration from the catalyst the ethanol was distilled and the acetyl derivative of the residue was prepared. Yield 8.5g after crystallisation from dilute ethanol. m.p. 112-113°. Yield 57%. Although catalytic reduction gave satisfactory yields it was not a suitable method for large scale work.

Method 2.

Reduction with iron and hydrochloric acid by the method of Cline and Reid, J.Amer.Chem.Soc.,1927,49,3150 gave a 50% yield of o-aminoethylbenzene.. The yield was finally improved to 69-70% by carrying out the reduction in ethanol. (cf. West,J.Chem.Soc.,1925,127,494)

o-Nitroethylbenzene (151g.,1 mol.) was dissolved in industrial spirit (450ml.) and water (50 ml.) in a 4l. flask fitted with a wide reflux condenser. Concentrated hydrochloric acid (10ml.,36%) was added and the mixture heated to boiling on a water bath. Iron powder (50g.) was then added and after a few minutes the reaction became vigorous and in some cases cooling under a tap was neccesary. A further quantity of iron powder (150g.) was added in three portions during 30 mins. From time to time the reaction flask was shaken well and heating continued for a total of 3½ hrs.

The mixture was neutralised with 10% sodium hydroxide solution and then steam distilled. The alcohol distilled first and the receiver was changed when the amino compound started to distill. The acetyl derivative was prepared directly by adding acetic anhydride (102g.,1 mol.) to the steam distillate. The mixture was stirred and the acetyl derivative separated out almost directly as a white solid. When cool the solid was filtered, washed and dried m.p.112-113°. Crystallisation fron dilute ethanol did not change the melting point. Yield 126g.

The acetyl derivative (126g.) was hydrolysed by boiling with 5 times its weight of 20% hydrochloric acid. After cooling, the mixture was neutralised , extracted with ether and dried. The ether was distilled and the o-aminoethylbenzene distilled from zinc dust. In this way it was obtained as a colourless oil, b.p.210-211°. $n_D^{22.5^\circ}$ 1.5598. Yield 85g. This represents a yield of 70% based on o-nitroethylbenzene.

Later, practical grade o-aminoethylbenzene was obtained from Eastmann Kodak. In the first place the base was purified as the hydrochloride but it was later found to be sufficient to dry over potassium hydroxide pellets and then distill from zinc dust. It had b.p. 210-211°. $n_D^{25^\circ}$ 1.5579. Wepster, (private communication) $n_D^{25^\circ}$ 1.5578.

o-Iodoethylbenzene.

A modified method of Mascarelli and Longo, (Gazzetta, 1941,71,397) was used.

o-Aminoethylbenzene (30g.,1 mol.) was dissolved in concentrated sulphuric acid (20ml., 1.3 mol., d. 1.84) and water (700ml.) by warming and then cooled to -1° in an ice-salt mixture. Sodium nitrite (20g., 1.2 mol.) in water (90ml.) was then added, the temperature being maintained at 0- -2° throughout the diazotisation. Potassium iodide (62g., 1.5 mol.) dissolved in water (100ml.) was then added slowly with stirring. A vigorous reaction set in and after standing at room temperature for 1 hr. the mixture was warmed on a water bath until no more nitrogen was evolved. A heavy brown oil separated out. The mixture was saturated with sulphur dioxide, made alkaline and then steam distilled. The oily layer was separated, dried and distilled. o-iodoethylbenzene distilled as a pale yellow oil, b.p. 90° / 12mm. Yield 80%. Mascarelli and Longo, loc.cit., b.p. 96-96.5° / 14-15 mm.

This reaction was carried out a number of times and eventually scaled up to 240g. of o-aminoethylbenzene. In each case yields between 75 and 82% were obtained. Care must be taken on addition of the potassium iodide as the reaction is very vigorous.

2:2'-Diethyldiphenyl

Mascarelli and Longo, (loc.cit.)

o-Iodoethylbenzene (50g.) was heated with copper bronze (10g.) in a boiling tube in a metal bath at 232-242°. A further quantity of copper powder (40g.) was added in portions during 1½ hrs. and the mixture heated for a total of 3 hrs. As far as possible the mixture was kept stirred but as the reaction proceeded it became very pasty and stirring was difficult. The product was extracted with boiling monochlorobenzene and filtered from the copper through a pad of filter papers. The chlorobenzene was distilled and the residue fractionated under reduced pressure using a Claisen flask with a small fractionating column. After two distillations the second from sodium metal, 14g., 31% of a colourless liquid was obtained. b.p. 140-143°/14-15 mm. This was combined with the product from two similar reactions and the whole redistilled from sodium to give a product free from iodine. b.p. 142-143°/ 14-15 mm. $n_D^{25^\circ}$ 1.5624. Mascarelli and Longo, (loc.cit.) give b.p. 147°/ 14-15mm.

(Found: C, 91.4; H, 8.5, Calculated for $C_{16}H_{18}$ C, 91.4; H, 8.6%).

This reaction was later repeated on a larger scale with increased yields. Two batches of 150g. o-iodoethylbenzene were heated with an equal weight of copper powder. The combined yield of 2:2'-diethyldiphenyl was 85g., 60% yield.

For spectral purposes it was found to be necessary to purify a specimen further by crystallisation.(see p.24). This was carried out by dissolving 2:2'-diethyldiphenyl in ethanol at room temperature and then cooling to *c.a.* -35° in an acetone-drycold mixture. It crystallised in flakes which were filtered off on a precooled sintered glass funnel and crystallised twice more in this way. The specimen was finally redistilled. $n_D^{25°}$ 1.5602.

o-*Bromoethylbenzene*.

Method 1.

cf. Gattermann, *Ber*.,1890,*23*,1218.

Organic Syntheses, 1929,*9*,22.

o-Aminoethylbenzene (30g.,1 mol.) was dissolved in hydrobromic acid (170ml., 4 mol., 48-50%) in a flask by warming and then cooled in a freezing mixture to -2°. Sodium nitrite (19g., 1.1 mol.) dissolved in water (20ml.) was added slowly. After each addition of nitrite the flask was stoppered and shaken until all the brown fumes were absorbed. When the diazotisation was complete copper powder (2g.) was added, the flask was fitted with a reflux condenser and then warmed gently on a water bath. After a few minutes the mixture began to effervesce and the flask was cooled in ice until the reaction was less vigorous. Finally the mixture was heated on a water bath until no more nitrogen was evolved. After dilution with water (200ml.) the mixture was steam distilled. The distillate was made alkaline and the oily layer separated, washed with water, concentrated sulphuric acid, alkali and water again. It was dried and distilled. o-Bromoethylbenzene was obtained in 34% yield as a colourless liquid, b.p. 66-68° / 9-10mm.

Method 2.

cf. Sandmeyer, Ber., 1884, 17, 2650.

When diazotisation was carried out in sulphuric acid the yield was only 17%. The yield was improved considerably by carrying out the diazotisation in hydrobromic acid as follows:-

o-Aminoethylbenzene (121g., 1 mol.) was dissolved in 48-50% hydrobromic acid (506ml., 3 mol.) and cooled to -2°. It was diazotised at -1 - -3° by the addition of sodium nitrite (83g., 1.2 mol.) in water (150ml.) The diazo solution was then poured into a solution of cuprous bromide (143.5g.) in 48-50% hydrobromic acid (200ml.) when a thick brown sludge was formed. It was warmed on a water bath and when the reaction became vigorous the flask was removed from the heat and shaken well. When the vigorous reaction had subsided the mixture was heated on a steam bath until no more nitrogen was evolved. It was then steam distilled. The distillate was made alkaline and the oily layer separated. Extraction of the aqueous layer with ether did not improve the yield. The oil was washed with concentrated sulphuric acid, 30% sodium hydroxide solution and water. It was dried over calcium chloride and distilled. o-Bromoethylbenzene was obtained as a colourless oil b.p. 63-64° / 8-9 mm. n_D^{25} 1.5476. Yield, 92.5g., 50%.

2:2'-Diethyldiphenyl

cf. Krizewsky and Turner, *J.Chem.Soc.*,1919,**115**,559.

Magnesium (10.4g., 1.3 atoms) in a 2l. flask, fitted with reflux condenser, dropping funnel and stirrer was covered with ether (200ml.). O-Bromoethylbenzene (66g.,1 mol.) was then added slowly from a dropping funnel. In the first place about ¼ of the bromo compound was added and once the reaction started the stirrer was set in motion and the rest of the bromo compound added. The mixture was warmed on a water bath for 30 mins. to complete the reaction and then decanted from the unreacted magnesium into another flask.

Anhydrous cupric chloride was then added in small portions. A vigorous reaction started and when it had subsided more cupric chloride was added from time to time until there was no further reaction. A total of 72g., of cupric chloride was added. Finally the reaction was heated under reflux for 1 hr. The semi-solid mass obtained was decomposed with ice and the cuprous chloride dissolved by the addition of concentrated hydrochloric acid. The ethereal layer was separated and the aqueous layer extracted with ether. The combined ether solutions were washed, dried over calcium chloride and the ether distilled. The residue was then distilled under reduced pressure.

The first fraction, 25 g. had b.p. 53-120° / 9-10 mm. , a large portion of this having b.p. 53-55° / 10 mm.

The second fraction had b.p. 141-147/ 14-15 mm. Redistillation of this fraction gave pure 2:2'-diethyldiphenyl, (10g.), b.p. 142-143° / 14-15 mm. $n_D^{25°}$ 1.5619. Yield 28%.

2-Ethyldiphenyl.

cf. Orchin , J.Amer.Chem.Soc.,1946,68,571.

Magnesium (14.5g.,1.2 atoms) was covered with dry ether (200ml.) and o-bromoethylbenzene (92.5g., 1 mol.) was added slowly from a dropping funnel. About ¼ of the bromo compound was added at the beginning and once the reaction had started the mixture was stirred mechanically and the rest of the bromo compound added. When all the bromo compound was added the mixture was heated gently under reflux for 1 hour. The flask was then removed from the water bath and cyclohexanone (49g., 1 mol.) dissolved in ether (50 ml.) was added slowly to the stirred mixture. After the addition of ketone the mixture was heated under reflux for 20 hrs. The product was decomposed with ice and the basic magnesium salt dissolved by adding concentrated hydrochloric acid. The ether layer was separated and the aqueous layer extracted with ether. After washing with dilute hydrochloric acid, water, 10% sodium hydroxide solution and water, the ethereal solution was dried over anhydrous sodium sulphate. The carbinol readily dehydrated and therefore no attempt was made to isolate the carbinol pure. The ether was distilled and the residue then distilled rapidly under reduced pressure. A small fraction (7g.) b.p. 45° / 10mm was obtained. The bulk however had b.p. 117-121/ 10 mm. and the fraction boiling up to 150° at this pressure was collected. The boiling point indicated that some dehydration had already taken place. Yield 48 g.

Dehydration of carbinol.

The carbinol (48g.) was dehydrated by boiling gently under reflux with 98-100% formic acid.(150ml.) After cooling the top oily layer was separated and the lower layer extracted three times with benzene. The combined benzene washings and oily layer were washed with water, 10% sodium hydroxide solution and water, dried over calcium chloride and the benzene distilled. The residue was distilled twice in vacuum and gave a 36% yield of 2:3:4:5-tetrahydro-2'-ethyldiphenyl. (33g.) (Yield based on bromo compound.) b.p. 117-119° / 10mm.

$n_D^{25^\circ}$ 1.5368

(Found: C, 90.1; H, 9.8. $C_{14}H_{18}$ requires, C, 90.3; H,9.7%).

2-Ethyldiphenyl.

2:3:4:5-Tetrahydro-2'-ethyldiphenyl (21.5g.) was heated at its boiling point with the theoretical amount of sulphur (6.25g.) in a metal bath at 220 ± 5° for 4½ hrs. The product was then distilled in vacuum, b.p. 117-120° / 9-10 mm. It was then fractionated (over sodium) using a small apparatus with a Vigreux type column.

First few drops, $n_D^{20^\circ}$ 1.5695

Main fraction, $n_D^{20^\circ}$ 1.5740 -12g. 12%

Last few drops, $n_D^{20^\circ}$ 1.5685

After 4 more distillations of the main fraction from sodium a specimen b.p. 109-110° / 8 mm. was obtained. $n_D^{20^\circ}$ 1.5730, $n_D^{25^\circ}$ 1.5711. In each case the refractive index of the first few drops, the main fraction and the last few drops was determined, but did not appear to follow any definite pattern. The presence of sulphur in the diphenyl probably accounts for this. The specimen obtained was sent for analysis. (Found: C,92.1, H,8.0, Calculated for $C_{14}H_{14}$ C,92.3, H,7.7%)

Although the analysis was satisfactory the sample gave a slight decolorisation of bromine in carbon tetrachloride. It was therefore again treated with sulphur for 4 hrs., initially at 260° and the temperature was later raised to keep the solution boiling. It was then distilled repeatedly with sodium until there was no further reaction. This specimen did not decolourise bromine. $n_D^{20^\circ}$ 1.5805, $n_D^{25^\circ}$ 1.5787. Orchin (loc.cit.) $n_D^{20^\circ}$ 1.5808, Goodman & Wise, (J. Amer. Chem. Soc., 1950, 72, 3076) n_D^{20} 1.5805, Braude & Forbes, (J. Chem. Soc., 1955, 3776) n_D^{20} 1.5783.

Attempted preparation of complex of 2-ethyldiphenyl with 2:4:7-trinitrofluorenone.

2-Ethyldiphenyl (0.2 g., 1 mol.) was dissolved in acetic acid (3ml.) and 2:4:7-trinitrofluorenone (0.35g., 1 mol.) dissolved in acetic acid (5ml.) was added. The yellow solution was concentrated to half its volume. On cooling yellow needles crystallised out. Yield 0.3g. m.p. and mixed m.p. with 2:4:7-trinitrofluorenone 174-175°.

2-Ethylcyclohexanone.

A mixture of sodamide (43g., 1.1 mol.) and benzene (800ml.) was boiled gently under reflux in a 3-necked flask fitted with dropping funnel and mechanical stirrer. Cyclohexanone (98g., 1 mol.) was then added gradually during 1 hr. When the ketone was added the solution became cloudy and as the reaction proceeded a heavy white sludge was formed.

After the addition of the ketone the mixture was heated for another 1½ hrs. Ethyl iodide (156g., 1 mol.) was then added from a dropping funnel, the addition taking 1 hr. When the ethyl iodide was first added the reaction mixture was yellow in colour but the colour gradually faded as the reaction proceeded. Heating under reflux was continued for a further 2½ hrs., then, after cooling, water was added to decompose any unchanged sodamide and to dissolve the sodium iodide formed. The benzene layer was separated off and the aqueous layer extracted once with benzene. The benzene solution was dried and the benzene distilled. The residue was then distilled under reduced pressure, taking the temperature up to 100° at 13 mm. pressure. Distillate 61g. Residue, 41.5g. and this higher boiling residue probably consists of self-condensation products of the *cyclo*hexanone.

The distillate was then fractionated under reduced pressure using a Vigreux type column with an outer vacuum jacket. Two fractions were obtained:-

Fraction 1 33g. (26%) b.p. 68° / 16mm.
Fraction 2 17g. (13%) b.p. 84-90° / 13mm.

The values given in the literature for the boiling points are as follows:-

*cyclo*hexanone b.p. 47°/ 15 mm.
2-ethyl*cyclo*hexanone b.p. 67° / 13 mm.

There thus appears to be no unchanged *cyclo*hexanome. The first fraction is predominantly the required 2-ethyl*cyclo*hexanone and the second fraction is probably a diethyl*cyclo*hexanone.

Semicarbazone of fraction b.p. 68° / 16 mm.

Fraction 1 (31.5g., 1 mol.) was added to a solution of sodium acetate (hydrated salt, 102 g., 3 mol.) and semicarbazide hydrochloride (33.5g., 1.2 mol.) dissolved in the minimum quantity of water. Acetic acid was then added until the mixture was homogeneous. The semicarbazone separated as a white solid and was filtered, washed and dried. m.p. 142-146°

More semicarbazone was precipitated by adding water to the filtrate. One crystallisation raised the melting point to 159-160°. Three more crystallisations from ethanol gave 2-ethylcyclohexanone semicarbazone(25g.) m.p. 163°. Yield based on cyclohexanone 14%. Literature value for m.p. of 2-ethylcyclohexanone semicarbazone is 161-162°.

Semicarbazone of fraction b.p.84-90° / 13 mm.

The semicarbazone was prepared as above. After four crystallisations from ethanol a steady melting point of 202-203° was obtained.

(Found: N, 19.6, calculated for monoethylcyclohexanone, N, 22.8%, calculated for diethylcyclohexanone, N, 19.9%).

Meerwein,(Annalen,1913,396,225) gives 2:2-diethylcyclohexanone b.p. 93.5° / 15 mm. and semicarbazone m.p. 202-203°.

2-Ethylcyclohexanone.

A mixture of 2-ethylcyclohexanone semicarbazone (20g.) and 20% hydrochloric acid (100ml.) was boiled gently under reflux for 20 mins. After cooling the 2-ethylcyclohexanone was extracted with ether and the ethereal solution washed and dried over calcium chloride. The ether was distilled and the residue distilled under reduced pressure. 2-Ethylcyclohexanone (14g.) was obtained as a colourless liquid, b.p. 68° / 16 mm. Yield based on semicarbazone is 61%. Yield based on *cyclo*hexanone is 12%.

Interaction of 2-ethylcyclohexanone and *o*-ethylphenyl magnesium bromide.

Magnesium (3.2g., 1.2 atoms) was covered with dry ether (50 ml.) and the Grignard reagent prepared in the usual way by the addition of *o*-bromoethylbenzene (20.6g., 1 mol.). When all the bromo compound was added the mixture was stirred mechanically and heated gently under reflux for 1 hr. 2-Ethyl*cyclo*hexanone (14 g.,1 mol.) dissolved in ether (50 ml.) was then added slowly. Finally the mixture was then heated under reflux for 28 hrs. The product was decomposed with ice-water, treated with concentrated hydrochloric acid and the ether layer separated. The aqueous layer was extracted with ether and the ether solution washed with dilute hydrochloric acdi, with 10% sodium hydroxide and with brine. It was dried over anhydrous sodium sulphate and the ether distilled.

In this case the residue was dehydrated directly by boilihg gently under reflux with 98-100% formic acid (75 ml.) for 4 hrs. After coolimg, the product was extracted with benzene and the benzene solution washed and dried. The benzene was distilled and the residue distilled in vacuum. 4g. of material b.p. 132-133° / 11 mm. were obtained. Yield 17%.

$n_D^{26^\circ}$ 1.5261.
(Found: C, 89.3; H, 10.6. $C_{16}H_{22}$ requires, C, 89.7; H,10.3%). This compound is either a single hydrocarbon or a mixture of two isomeric hydrocarbons since we cannot say for certain which way the carbinol dehydrates.

2:2'-Diethyldiphenyl.

The above hydrocarbon (3.5 g.) was heated with sulphur (1.05g.) for 4hrs. at $240^\circ \pm 3^\circ$ when the product no longer decolourised bromine in carbon tetrachloride. The product was then distilled. After two redistillations under reduced pressure, (from sodium) 2g. of 2:2'-diethyldiphenyl were obtained. Yield 58%. n_D^{25} 1.5574. The ultraviolet absofption spectrum of this specimen agreed well with that of the purer specimen obtained through the Ullmann reaction.

Attempted preparation of complex of 2:2'-diethyldiphenyl with 2:4:7-Trinitrofluorenone.

Attempted preparation of a complex in the same way as the attempted preparation of a complex of 2-ethyldiphenyl (p.79) again yielded only 2:4:7-trinitrofluorenone.

α:α'-Dibromo-2:2'-diethyldiphenyl

2:2'-Diethyldiphenyl (21g., 1 mol.) and N-bromosuccinimide (35.6g., 2 mol.) with approximately 0.1 g. benzoyl peroxide to act as catalyst, in dry carbon tetrachloride (80ml) were boiled gently under reflux for 3 hrs. Another 80 ml. carbon tetrachloride were added and the boiling solution filtered through a preheated sintered glass funnel. The solid succinimide was washed with hot carbon tetrachloride and the solvent distilled off from the filtrate. The residue was transferred to an evaporating dish and the last traces of solvent evaporated on a boiling water bath. The oily product was cooled and eventually solidified. It was dissolved in the minimim quantity of light petroleum (b.p. 40-60°) and crystallised from this in white needles, on cooling in ice. The substance softened at 71° finally melting at 74-78°. Yield 25.5g., 70%.

It could be crystallised from glacial acetic acid in prisms m.p. 83-87°, and from n-hexane (b.p. 67-70°) m.p. 76-81°. Light petroleum (b.p. 40-60°) was the best solvent but repeated crystallisations did not give a sharp m.p. The substance is probably a mixture of stereo isomers.

After 5 crystallisations it softened at 76° and had m.p. 86-89°. A mixed melting point was determined with a specimen of the dibromocompound prepared from the diol. (Hall et. al., J. Chem. Soc., 1956, 3475). This softened at 83° and m.p. 87-90°. Mixed melting point, softened at 79°, m.p. 85-89°. (Found: C, 52.4; H, 4.6; Br, 44.0. Calculated for $C_{16}H_{16}Br_2$ C, 52.2; H, 4.4; Br, 43.4%).

2:2'-Divinyldiphenyl.

A solution of α:α'-dibromo-2:2'-diethyldiphenyl (8g.) in quinoline (30ml., dried over potassium hydroxide and freshly distilled) was boiled under reflux for 5-10mins. The cooled solution was poured into dilute hydrochloric acid. An oil separated which quickly solidified giving an orange-brown solid which was filtered off, washed with dilute hydrochloric acid and water, and finally crystallised from n-hexane. m.p. 79-80°. Yield (3g.) 67%. Two further crystallisations from methanol raised the melting point to 80-81°. A mixed m.p. with a specimen prepared from the dibromo compound obtained from the corresponding diol (Hall et. al., loc.cit.) gave no depression.

(Found: C,93.2;H,6.6, $C_{16}H_{14}$ requires, C,93.2; H,6.8%).

2:2'-Diethyldiphenyl.

2:2'-Divinyldiphenyl(4.1g.) dissolved in ethanol (200ml.) was shaken in a hydrogenator with platinum oxide (0.1g.) as catalyst. The pressure of hydrogen used was 80 lbs./ sq.". After 5½ hours a test portion of the solution no longer decolourised bromine water and the reduction was complete. The alcohol was distilled off and the residue distilled in a vacuum. Pure 2:2'-Diethyldiphenyl (3.5g.) was obtained, b.p. 139-140° / 13.5 mm. $n_D^{25°}$ 1.5626. Yield, 84%.

3:3'-Diethyldiphenyl.

3:3'-Diethylbenzidine.

The method of Schultz and Flachslander, (J. prakt. chem., 1902, 66, 153) was modified.

o-Nitroethylbenzene (60g., 1 mol.) was dissolved in ethanol (150 ml.) in a 3-necked flask fitted with reflux condenser and mechanical stirrer. Sodium hydroxide (104 g., 1.2 mol.) dissolved in water (300ml.) was then added and the mixture heated on a boiling water bath. A total of 105 g. zinc dust (8 mol.) was added in small portions during three hrs. As the reaction proceeded the mixture became red in colour and the heating was continued until the red colour was discharged. The total length of heating required varied from 5 to 14 hrs. on different occasions and the efficiency of the stirring appeared to be the determining factor.

The mixture was then decanted from the unreacted zinc into 1:1 hydrochloric acid (400ml.) and the reaction flask was rinsed with warm ethanol. Concentrated hydrochloric acid, (200ml., 36%) was then added and the mixture shaken. The hydrochloride of the base separated out. This was filtered, washed with ether and finally purified by crystallisation from dilute hydrochloric acid. 3:3'-Diethylbenzidine hydrochloride was obtained in 42-44% yield.

The combined ether washings from different reactions were washed, dried and the ether distilled. The residue in the flask solidified and was crystallised 3 times from ethanol. 2:2'-Diethylazobenzene was obtained in red rectangular prisms, m.p. 45-46°.

3:3'-Diethylbenzidine hydrochloride was used directly in most reactions. The free base however could be obtained by warming with 10% sodium hydroxide solution. It separated as a thick brown oil which was washed several times with water by decantation. It finally solidified to a hard light brown solid which could not be crystallised. m.p. 70°-71°.

Disalicylidine derivative of 3:3'-Diethylbenzidine.

3:3'-Diethylbenzidine (1g.) and salicylaldehyde (1ml.) in ethanol (75ml.) were warmed on a boiling water bath for a few minutes. An orange-yellow solid separated which was filtered off and crystallised from a) cyclohexane and b) light petroleum (b.p.100-120°), m.p. 157-158°.
(Found: C, 79.6; H, 6.3; N, 6.8, $C_{30}H_{28}O_2N_2$ requires, C,80.4; H, 6.3; N, 6.3%).

Dibenzylidine derivative of 3:3'-diethylbenzidine.

3:3'-Diethylbenzidine (1g.) and benzaldehyde (0.5g.) in ethanol (25 ml.) were warmed on a water bath for 1 hr. On cooling the dibenzylidine derivative crystallised in pale yellow platelets, m.p. 129-130°. Recrystallisation from ethanol did not raise the melting point. Schultz and Flachslander, loc.cit.) give m.p. 124-125°.

3:3'-Diethyldiphenyl.

3:3'-Diethylbenzidine hydrochloride (47g.,1 mol.) was dissolved in water(600 ml.) and concentrated hydrochloric acid (45ml.,36%, 3 mol.). The solution was cooled to -4° and diazotised by the addition of sodium nitrite solution, (22.8g., 2.2 mol., in 75 ml. water). Throughout the addition the temperature was maintained at -4° to -2°. The diazo solution was then stirred at this temperature for 30 mins. to ensure completion of diazotisation. 50% Hypophosphorous acid (300 ml., 15 mol.) precooled to 0° was added and the mixture stirred at 0° for 1 hr. Finally the reaction mixture was left overnight in a refrigerator, (5°).

The top oily layer was separated and the aqueous layer extracted thrice with ether. The combined ether extracts and oily layer were washed with 30% sodium hydroxide solution and with water, and then dried over calcium chloride. The ether was distilled off and the residue vacuum distilled. After two distillations 3:3'-diethyldiphenyl(21g.) was obtained in 63% yield as a pale yellow oil, b.p. 154° / 9 mm., 168-169° / 20 mm. A final distillation from sodium removed last traces of phenolic impurities to give a colourless liquid, b.p.154-155° / 9-10mm. $n_D^{25°}$ 1.5768.

(Found: C, 91.5; H, 8.5. Calculated for $C_{16}H_{18}$ C, 91.4; H, 8.6%)

4:4'-Diethyldiphenyl

p-Nitroethylbenzene.

Eastmann Kodak Co., Practical Gtade p-nitroethylbenzene was used, and purified by steam distillation. b.p. 246° / 760 mm. $n_D^{25^\circ}$ 1.5444.

p-Aminoethylbenzene.

Cline and Reid (J.Amer.Chem.Soc., 1927,49,3150)

Reduction by this method with zinc and hydrochloric acid gave better yields than the West method as used in the case of o-nitroethylbenzene.(p.69).

p-Nitroethylbenzene(151g., 1 mol.) and granulated zinc (240g., 3.7 atoms) were placed in a 2l flask fitted with an air condenser. Concentrated hydrochloric acid (420 ml., 36%. 4.2 mol.) was then added in small pottions. After the addition of the acid,the mixture was heated on a boiling water bath for three hours and then made alkaline with sodium hydroxide dissolved in the minimum quantity of water. The product was steam distilled and the distillate was made strongly acid with concentrated hydrochloric acid, It was concentrated to about 400ml. and on cooling the hydrochloride crystallised in white flakes. Further concentration of the mother liquor gave more hydrochloride. Total yield 70%.

The free base was obtained by warming with 30% sodium hydroxide solution. After cooling it was extracted with ether dried over potassium hydroxide pellets, the ether distilled and the base finally distilled. p-Aminoethylbenzene was obtained as a colourless oil by distillation from zinc dust. b.p. 212-213/ 760 mm. $n_D^{25°}$ 1.5519.

Acet-p-ethylanilide.

The acetyl derivative of p-aminoethylbenzene could not be prepared in the cold by the wet method which was successful in the case of o-aminoethylbenzene.(p.70).

p-Aminoethylbenzene (3g.) was boiled gently under reflux for 30 mins. with acetic anhydride (2.5 ml.) and acetic acid (2.5 ml.). The product was poured into 50 ml. water with stirring when a solid separated which was filtered off, washed and dried. m.p. 89-91°. The acetyl derivative crystallised from dilute ethanol in fine needles. Yield 90%. After 3 crystallisations a constant m.p. 91° was obtained. Literature, m.p. 94°.

p-Iodoethylbenzene.

Willgerodt and Bergdolt, (Annalen,1903, 327,285).

The only difference was that these workers used the amine sulphate and diazotised in hydrochloric acid. The yields were the same.

p-Aminoethylbenzene (60.5g., 1 mol.) was dissolved in concentrated sulphuric acid (35 ml., d. 1.84, 1.3 mol.) and water (850 ml.) by warming and then cooled to 5°. It was diazotised at this temperature by the addition of sodium nitrite solution (41.5g., 1.2 mol., in 175 ml. water). The diazo solution was stirred at 0° for 20 mins. and then potassium iodide (124.5g., 1.5 mol.) dissolved in water (200 ml.) added. A vigorous reaction set in and when this had subsided the mixture was allowed to warm up to room temperature. Finally it was warmed on a water bath until no more nitrogen was evolved. A heavy brown oil separated. The solution was decolourised with sulphur dioxide, made alkaline and then steam distilled. The iodo compound distilled as a pale yellow oil which was separated, dried and distilled. p-Iodoethylbenzene was obtained in 80% yield. b.p. 87-88° / 8-9 mm. $n_D^{25°}$ 1.5888.

4:4'-Diethyldiphenyl.

Schreiner (J.prakt. Chem., 1910,(ii) 81, 422).

p-Iodoethylbenzene (116 g., 1 mol.) was heated with an equal weight of copper powder in a metal bath at 240° ± 2°. The copper powder was added in portions during 45 mins ., the mixture being stirred throughout. After 1 hr. the metal bath temperature was raised to 248-250°, and the heating continued for another 1¼ hrs. The product was extracted with methanol and filtered from the copper. The methanol was distilled and the residue distilled in vacuum. 4:4'-Diethyldiphenyl was obtained in 75% yield as a white waxy solid, m.p. 80-83° . It crystallised from methanol or ethanol in white flakes, m.p. 83° . Schreiner (loc.cit.) m.p.81° .

(Found: C,91.6; H, 8.5, Calculated for $C_{16}H_{18}$ C, 91.4; H, 8.6%)

p-Bromoethylbenzene.

Method 1.

By using the Gattermann method, quantities and conditions as used in the case of o-bromoethylbenzene,(p.73) a 34% yield of p-bromoethylbenzene was obtained.

Method 2.

The Sandmeyer method (loc.cit.) gave better yields and this was the method finally used.

p-Ethylaniline (60.5g., 1 mol.) in a 1 l. flask was dissolved in 48-50% hydrobromic acid (250 ml., 1.5 mol.) by warming and then cooled to 5°. Diazotisation was carried out at this temperature by the addition of sodium nitrite solution, (41 g., 1.2 mol., in 75 ml. water). After each addition the flask was stoppered and shaken until all the brown fumes were absorbed. When the diazotisation was complete the diazo solution was poured into a solution of cuprous bromide (72g.) in 48-50% hydrobromic acid (100 ml.). It was warmed on a water bath until the reaction started and then removed from the heat and shaken well. When the vigorous reaction had subsided the mixture was heated on a water bath until no more nitrogen was evolved. It was made alkaline and then steam distilled. The bromo compound distilled as a practically colourless oil which was separated, washed with concentrated sulphuric acid, with 30% sodium hydroxide solution, with water and then dried. Distillation under reduced pressure gave p-bromoethylbenzene in 42% yield. b.p. 93-94° / 23 mm. $n_{D}^{25^\circ}$1.5449.

4:4'-Diethyldiphenyl. (cf. p.75).

Magnesium (5.8g., 1.2 atoms) was covered with dry ether (150 ml.) and p-bromoethylbenzene (37g., 1 mol.) was added slowly. In the first place about ¼ of the bromo compound was added and a crystal of iodine was added to start the reaction. The mixture was then stirred mechanically and the rest of the bromo compound added. The reaction mixture was boiled gently under reflux for 1 hr. and then decanted from the unreacted magnesium into another flask. Anhydrous cupric chloride (30 g.) was added in small portions when a vigorous reaction started. The reaction was completed by warming on a water bath for 2½ hrs. The product was decomposed with ice-water and ferric chloride (36g.) dissoved in the minimum quantity of water, added. The ether layer was separated and the aqueous layer extracted with ether. The ethereal solution was washed, dried and the ether distilled. The residue was then distilled. An appreciable quantity distilled at 185° and was unchanged bromocompound chiefly. The higher boiling fraction was 4:4'-diethyldiphenyl which was purified by crystallisation from ethanol. m.p.83°. Yield 6.5g., 31%.

α:α'-Dibromo-4:4'-diethyldiphenyl.

The method used was identical to that used in the case of 2:2'-diethyldiphenyl. (p.83). The product crystallised from

light petroleum (b.p. 60-80°) in tiny flakes, m.p. 84-87° after 4 crystallisations. Yield 79%.
(Found: Br, 43.0, $C_{16}H_{16}Br_2$ requires, Br, 43.4%).

Attempted preparation of 4:4'-Divinyldiphenyl.

α:α'-Dibromo-4:4'-diethyldiphenyl (1 g.) in quinoline (10ml.) was boiled for 2 mins. and the cooled solution poured into dilute hydrochloric acid. The solid obtained was filtered washed and dried. Difficulty was encountered in finding a solvent for crystallisation. It was initially very soluble in methanol but could be crystallised from n-hexane to give a yellow substance m.p. 152-162°. Further crystallisations did not sharpen the melting point. m.p. softened at 152°, 160-162°. After leaving overnight the product was no longer soluble completely in methanol and after 1 week it was completely insoluble in methanol. The substance started to soften at 132°, and darkened as the temperature was raised, it did not melt. Presumably polymerisation took place.

Complex of 4:4'-Diethyldiphenyl with 2:4:7-trinitrofluorenone.

4:4'-Diethyldiphenyl(o.2g.) was dissolved in glacial acetic acid (3 ml.) and to this solution was added 2:4:7-trinitrofluorenone (0.3 g.) dissolved in glacial acetic acid (5 ml.). On mixing an immediate colour change of the solution to orange-red was observed. The solution was concentrated to

½ volume and left to cool. Orange red needles crystallised out, 0.45 g,m.p. 108-110°. After recrystallisation from dilute acetic acid, m.p. 110-111°.
(Found: N,7.7%, $C_{29}H_{23}N_3O_7$ requires N,8.0%).

On attempted crystallisation from ethanol some decomposition appeared to take place, white crystals appeared in the filtrate. Attempts were then made to prepare a complex as above but using ethanol as solvent. On cooling the solution crystallisation took place and in this case three distinct types of crystals could be seen. White flakes, orange-red needles, and small yellow needles. These were filtered off and separated by hand picking. They were shown by m.p. and mixed m.p. to be 4:4'-diethyldiphenyl, complex and 2:4:7-trinitrofluorenone, respectively.

Di- and Tetraisopropyldiphenyl series.

o-*Bromoisopropenylbenzene*.

Bergmann and Weizmann, (*Trans*.*Farad*.*Soc*., 1936,*31*,1327)

Magnesium (24.9g., 2.2atoms) was covered with dry ether (300ml.) and the Grignard reagent prepared in the usual way by the addition of methyl iodide (66.5 ml., 2.3 mol.) in ether (200 ml.). When the reaction was complete , *o*-bromomethyl benzoate (100g., 1 mol.) was added slowly and the mixture then boiled under reflux for 2 hours. Dilute acetic acid was added and the mixture then extracted with ether. The ether solution was washed with sodium carbonate solution and water, and finally dried over anhydrous sodium sulphate. The ether was distilled and the residue then treated directly with 100ml. acetic anhydride in the presence of five drops of concentrated sulphuric acid. After boiling under reflux for 12 hrs. the acetic anhydride was distilled and then the residue distilled under reduced pressure. A first fraction of 57.5 g. was collected b.p. 72-142° / 9 mm. The residue consisted of a high boiling fraction,(14g.) which did not decolourise bromine,together with a tarry residue. The first fraction distilled over a wide range and no definite cut could be taken. To make sure that all the acetic anhydride was removed the oil was warmed with sodium carbonate solution, extracted with ether and the ethereal solution washed and dried. The ether was distilled and the residue distilled in vacuum.

Fraction 1 : b.p. 64-120° / 9-10 mm. 6 19 g.
decolourises bromine water

Fraction 2 : b.p. 134-140° / 9-10 mm. This fraction gave only a faint test for unsaturation and the last portion which distilled solidified in the condenser.

Fraction 1 was then redistilled and the fraction, b.p. 54-64°/ 4 mm. collected. Yield 14.5 g.,16%. The residue in the flask was slightly coloured and gave a faint test for unsaturation. The fraction collected was a colourless oil with a pleasant smell. It contained bromine and was unsaturated. $n_D^{25°}$ 1.5530.

Bergmann and Weizmann (loc.cit.) obtained o-bromo-isopropenylbenzene in 17% yield, b.p. 55-65° / 0.9 mm. $n_D^{27°}$ 1.5530.

Attempted preparation of 2:2'-di-isopropenyldiphenyl.

The method proposed was to treat the Grignard reagent of o-bromoisopropenylbenzene with anhydrous cupric chloride. (cf. p.75).

All attempts to prepare a Grignard reagent from o-bromoisopropenylbenzene, in the usual way, failed. Since o-bromoisopropenylbenzene could only be obtained in poor yield this route was abandoned.

p-isoPropylbenzoic acid.

p-isoPropylbenzoic acid (cumic acid) was used as starting material and had m.p. 111-117° . This was used without further purification, however one crystallisation from ethanol raised the m.p. to 116-117° which is the value given in the literature.

3-Nitrocumic acid.

Bryan and Foote, (J.Amer.Pharm.Assoc., 1949,38,572 and 1950, 39,644).

p-isoPropylbenzoic acid (100g.) was dissolved in concentrated sulphuric acid (500ml.,d.1.84) and cooled in ice to about 10°. Fuming nitric acid (75 ml.,d.1.5) was then dropped in during 20 mins. 30 Mins. from the start of the reaction the mixture was poured onto crushed ice. The solid was filtered off, washed and dried. Crude yield (124g.) 97%. m.p. 154-155°. This was not purified further before use. It could be crystallised from ethanol in prisms, m.p.158-159°, which is the value given by Bryan and Foote (loc.cit.)

Methyl ester of 3-Nitrocumic acid.

Bryan and Foote (loc.cit.)

To 3-nitrocumic acid (209g., 1 mol.) in a 1 l. 2-necked flask fitted with a reflux condenser and calcium chloride tube, thionyl chloride, (155g., 93 ml., 1.3 mol.) was added slowly from a dropping funnel. The mixture was heated on a boiling water bath for 2 hrs. The excess thionyl chloride was then removed by distillation under reduced pressure.

The acid chloride was then added slowly from a dropping funnel into a good excess of methanol (750 ml.) in a 2 l. flask fitted with a reflux condenser. The acid chloride was added at such a rate to keep the reaction under control. The methanol boiled. On cooling the methyl ester crystallised in large prisms. The solid (162g,) was filtered off and a second crop (47g.) obtained by concentrating the filtrate. Yield 93-94%, m.p.61-63°. This material was pure enough for use in the next stage. One crystallisation from methanol however raised the m.p. to 63-64° which is the value given in the literature.

<u>Reduction of 3-nitrocumic acid and methyl 3-nitrocumate.</u>

Difficulty was encountered in the reduction and several methods were tried. The most successful was that using tin and hydrogen chloride on the ester. This method initially gave a 63-65% yield which was eventually increased to 88%.

Methyl 3-nitrocumate (146g., 1 mol.) was dissolved in methanol (1,250 ml.) by warming. Granulated tin (148.5g., 2 mol.) was added and then dry hydrogen chloride bubbled through the solution until all the tin had dissolved. To complete the reaction the solution was boiled under reflux for 2 hrs. The alcohol was then distilled and the residue dissolved in water. It was completely soluble. Addition of sodium hydroxide solution precipitated the tin salts and the solution was made strongly alkaline to redissolve these and then extracted with ether. The ether extracts were washed, dried over anhydrous sodium sulphate and the ether distilled. The residue solidified and 110 g. base were obtained, m.p. 47-50°. Yield 88%. It was not purified further before use in the next stage.

The hydrochloride of the base could be precipitated with concentrated hydrochloric acid and crystallised from dilute hydrochloric acid in flakes. On dissolving in alkali the base was precipitated as an oil which was extracted with ether. Evaporation of the ether gave a solid which crystallised from benzene-light petroleum in colourless flakes, m.p. 51-52°. Abenius (J.prakt.Chem.,1889,40,425) gives m.p. 51-52°.

Benzoyl derivative of methyl 3-aminocumate.

Methyl 3-aminocumate (1g.) was treated with benzoyl chloride (1.5 ml.) in sodium hydroxide solution (10 ml., 10%). On shaking for a few seconds a solid separated which was filtered off and washed. On crystallisation from dilute ethanol the benzoyl derivative was obtained in white needles, m.p. 118°. Further crystallisations did not raise the melting point. Yield (0.8g.), 62%.

(Found: C,72.6; H, 6.3; N, 4.9. $C_{18}H_{19}NO_3$ requires, C,72.7; H,6.4; N, 4.7%).

Attempted reduction of 3-nitrocumic acid.

Method 1.

Fileti, Gazzetta, 1880,10,12.

3-Nitrocumic acid (5g.) was dissolved in glacial acetic acid (30 ml.) and the solution heated to boiling in a flask fitted with a reflux condenser. Iron powder (10g.) was added down the condenser in small portions during 10 mins. The mixture was then boiled under reflux for 1¾ hrs. After filtering from the iron the acetic acid was evaporated and the reddish-brown solid obtained, extracted with ether. On evaporation of the ether a solid was obtained which crystallised from ethanol in needles, m.p. 120-122°. Yield, 0.05g. The m.p. recorded in the literature for 3-aminocumic acid is 129°.

It was possible that an iron salt of the acid had been formed, therefore the reddish-brown solid was boiled with dilute hydrochloric acid and filtered. On cooling no solid separated and concentration of the filtrate still gave no substance. The solid was then treated with boiling water and filtered. On cooling this filtrate a substance crystallised out. It could be crystallised from ethanol in white needles, m.p. 248-249°. Yield, 0.5 g. The m.p. recorded in the literature for the N-acetyl derivative of 3-aminocumic acid is 248-250°. Finally extraction of the solid residues with ethanol gave 0.5g. of recovered 3-nitrocumic acid, m.p. 154-160°.

Method 2.

3-Nitrocumic acid (5g.) was dissolved in ammonium hydroxide solution (25ml., 6N) and saturated with hydrogen sulphide. The mixture was then heated on a boiling water bath for 1½ hrs. The solution was filtered from the sulphur which deposited and then made neutral with dilute acetic acid. A small amount of solid was precipitated. This was however unchanged nitro acid. Portions of the filtrate were tested at numerous pH values and concentrated. All that could be isolated was starting material. This was crystallised from ethanol, m.p. 159-160°. Yield 3g.

Method 3.

Water (100ml.) was heated to boiling and then ferrous sulphate (50g.,7 H_2O) added and when the solution was again boiling 3-nitrocumic acid (5g.) dissolved in dilute ammonia added. The solution was stirred mechanically. Concentrated ammonia (0.88) was then added in small portions until the solution was strongly alkaline. It was boiled for another 5 mins. and filtered. Careful addition of dilute acetic acid to a portion of the cooled filtrate did not give any solid. The filtrate was then concentrated by distillation under reduced pressure. Again addition of dilute acetic acid to a portion of the filtrate, testing through all pH values did not give a precipitate. On making strongly acid with concentrated hydrochloric acid still no solid could be isolated. Attempts to isolate a product from the original solid obtained on filtration were also unsuccessful.

Attempted reduction of methyl 3-nitrocumate.

Method 1.

Methyl 3-nitrocumate (8g.) was dissolved in ethanol (200ml.) and palladium black (0.1g.) added as catalyst. The mixture was shaken in an hydrogenator for 2 hrs. with an hydrogen pressure of 100 lbs./ sq.". After 2 hrs. it was filtered from the catalyst. A test portion of the filtrate on evaporation gave a solid m.p. 55-61° and a mixed m.p. with starting material showed no depression. Another 0.05g. catalyst were therefore added and the shaking continued for another 10 hrs. After filtration the alcohol was distilled off and the residue treated with water. The insoluble portion was filtered off and crystallised from methanol. 3g. methyl 3-nitrocumate were recovered unchanged, m.p. 60-62°. The filtrate was made alkaline and the white emulsion obtained extracted with ether. After drying over anhydrous sodium sulpate the ether was distilled. The residue would not solidify but on treatment with hydrochloric acid a solid hydrochloride was obtained. Yield 2g. This was later shown to be the hydrochloride of the required amino acid.

Method 2.

Methyl 3-nitrocumate (10g.) was dissolved in ethylacetate (100ml.) and platinum oxide (0.1g.) added as catalyst. After treatment as above in the hydrogenator for 7 hrs., the residue after evaporation of the solvent was treated with dilute hydrochloric acid. The insoluble nitro compound was filtered off and cfystallised from methanol. Yield of recovered methyl 3-nitrocumate, 6.5 g., m.p.59-61°. From the filtrate 0.5 g. of the hydrochloride of methyl 3-aminocumate were obtained.

Methyl 3-iodo-4-isopropylbenzoate.

Diazotisation in either hydrochloric or sulphuric acid gave the same yield. The solution was kept very dilute to decrease any chance of the ester being hydrolysed.

Methyl 3-amino-4-isopropylbenzoate (77g.) was dissolved in water (700ml.) and concentrated sulphuric acid (28 ml., d 1.84) and cooled to 0° - -2° in an ice-salt bath. It was diazotised at this temperature by the addition of sodium nitrite solution (30g. in 50 ml. water). Potassium iodide (80g.) dissolved in water (500ml.) was added when a vigorous reaction started. Finally the mixture was warmed on a boiling water bath until no more nitrogen was evolved. The solution was decolourised with sodium bisulphite and the heavy oil separated and taken up in ether. The ethereal solution was washed with sodium bisulphite solution followed by alkali. The alkaline washings were acidified and extracted with ether. On evaporation of the ether no residue remained and thus no hydrolysis occured.

The ether solution was dried and the ether distilled. The residue was distilled under reduced pressure. After 2 distillations, methyl 3-iodo-4-isopropylbenzoate was obtained as a colourless oil, b.p. $140-142^{\circ}/7$ mm., $n_D^{25^{\circ}}$ 1.5780. Yield, 66%.

(Found: C,43.7; H, 4.2; I,41.6. $C_{11}H_{13}O_2I$ requires, C,43.4; H,4.3; I,41.8%).

3-Iodo-4-isopropylbenzoic acid.

A few drops of the iodo ester were hydrolysed by boiling with 30% sodium hydroxide solution for 30 mins. The solid which precipitated on acidifying was filtered, washed and crystallised from dilute methanol. It crystallised in needles, m.p. 173-174°.

(Found: I,44.0, $C_{10}H_{11}O_2I$ requires, I,43.8%).

Methyl 6:6'-di-isopropyldiphenyl-3:3'-dicarboxylate.

Methyl 3-iodo-4-*iso*propylbenzoate (76g.) was heated with an equal weight of copper powder for 50 mins. in a metal bath at 270-275°. The copper powder was added in portions during the first 20 mins. The product was extracted with boiling monochlorobenzene, the solvent distilled off and the thick oily residue treated with petroleum ether (b.p. 40-60°). A white solid (37g.) was precipitated and this was filtered off and washed with petroleum ether. Two crystallisations from methanol using charcoal gave pure methyl 6:6'-di-*iso*propyldiphenyl-3:3'-dicarboxylate in 74% yield (33g.) It crystallised in prisms m.p. 143-144°.

Further treatment of the oily residue by dissolving in methanol, boiling with charcoal filtering and reprecipitating with petroleum ether gave more product. It was then crystallised from methanol. In this way the yield was increased to 81%.

(Found: C,74.7; H,7.5. $C_{22}H_{26}O_4$ requires C,74.6; H,7.4%).

6:6'-Di-isopropyldiphenyl-3:3'-dicarboxylic acid.

Sodium (4.6g.) was dissolved in ethanol (200 ml.) and added to a solution of the ester (17.7g.) in ethanol (200 ml.), The solution was boiled under reflux for 2 hrs. and the ethanol distilled. The residue was dissolved in water and made just acid. A white solid precipitated which was filtered off and dried. Yield 91-92%, m.p. 285-290°. After two crystallisations from acetic acid the m.p. was raised to 323-324°. It crystallised in rhombs.
(Found: C,69.0; H,6;7. $C_{20}H_{20}O_4,CH_3.CO_2H$ requires C,68.8; H,6.8%).

The solvent free acid was obtained by crystallisation from ethanol.(m.p. unchanged).
(Found: C, 73.4; H,6.9. $C_{20}H_{20}O_4$ requires C, 73.2; H,6.7%).

2:2'-Di-isopropyldiphenyl.

A solution of 6:6'-di-*iso*propyldiphenyl-3:3'-dicarboxylic acid (10g.) in quinoline (100ml., dried over KOH and freshly distilled) was boiled under reflux in the presence of a trace of copper powder , for 7 hrs. Most of the quinoline was distilled off and the product was poured into dilute hydrochloric acid. A thick brown oil was liberated. The solution was extracted with ether and the ethereal solution washed with dilute hydrochloric acid, 10% sodium hydroxide solution and with water. Acidification of the alkaline washings, extraction with ether and evaporation of the ether gave no residue.

The ether solution was dried over calcium chloride and the ether distilled. The residue was then distilled under reduced pressure. 4.35g. of substance were collected, b.p. 150-160° / 12 mm. It solidified rapidly, m.p. 52-63°. From a higher boiling fraction a further 0.25g. material were collected by dissolving in ethanol, boiling with charcoal, filtering and leaving to crystallise. Yield 65%. Two crystallisations from ethanol gave pure 2:2'-di-isopropyldiphenyl, m.p. 67-68°; Yield 4.2g.

(Found: C,90.6; H,9.1. $C_{18}H_{22}$ requires C,90.8; H,9.2%).

Bromination of 2:2'-di-isopropyldiphenyl.

2:2-Di-isopropyldiphenyl(1.19g., 1 mol.) and N-bromosuccinimide (1.78g.,2 mol.) in carbon tetrachloride (10ml.) with a trace of benzoyl peroxide as catalyst were boiled under reflux for 2 hrs. Another 10 ml. carbon tetrachloride were added and after filtration the carbon tetrachloride was evaporated. The pasty residue obtained could not be solidified however addition of light petroleum(b.p. 40-60°) precipitated a white solid which crystallised from light petroleum (80-100°) in tiny needles. m.p. 114-162°. 0.2g.

Two more crystallisations gave a substance, m.p. 141-142°, clear by 189°. This did not analyse correctly for the expected α:α'-bibromo-2:2'-di-*iso*propyldiphenyl but appeared to be a tribromo compound. Repetition of this reaction using 3 mol. N-bromosuccinimide did not improve the yield. Determination of the ultraviolet absorption spectrum of the product gave no clue to its identity. (p.54).
(Found: C,50.7; H,4.1; Br,45.4. $C_{18}H_{19}Br_3$ requires C,50.5; H,4.0; Br,45.5%).

m-Di-isopropylbenzene.

B.D.H. *m*-di-*iso*propylbenzene was used as starting material. It was distilled from sodium before use, b.p. 200-203°, $n_D^{20°}$ 1.4909. (Literature values, b.p.203°, $n_D^{20°}$ 1.4884).

Nitration of m-di-isopropylbenzene.

Newton, *J.Amer.Chem.Soc.*, 1943,*65*,2434.

m-Di-*iso*propylbenzene (98g., 1 mol.), acetic acid (400 ml.) and acetic anhydride (100 ml.) in a 1.5 *l*. beaker were cooled in running water. The mixture was stirred mechanically and fuming nitric acid (52 ml.,96%, 2 mol.) was added from a dropping funnel at such a rate that the maximum temperature reached was 45°. The addition took 20 mins. and the temperature was between 25-40°. 1 hr. after the nitric acid had been added, the mixture was poured into a large excess of water and petroleum ether added to decrease the density of the nitro compound. The oily layer was separated and washed with 10% sodium hydroxide solution, with water and then dried over calcium chloride. The solvent was distilled off and the residue (120g.,95%) was fractionated in a vacuum using an electrically heated packed column. Using this apparatus a preliminary separation into the following fractions was obtained:

8.5 g.,	$n_D^{20^\circ}$ 1.5214
31 g.,	$n_D^{20^\circ}$ 1.5252
31 g.,	$n_D^{20^\circ}$ 1.5200
15 g.,	$n_D^{20^\circ}$ 1.5200
8g.,	$n_D^{20^\circ}$ 1.5204

Each fraction was refractionated separately in a small apparatus using a Vigreux type column. This was repeated several times until no further separation was obtained. The fractions were recombined on the basis of refractive index.

Low boiling fraction, b.p. 95-96° / 2-3 mm.
$n_D^{20^\circ}$ 1.5300
Yield 7g. 5%

This fraction was later identified as impure 4-nitro-isopropylbenzene arising from isopropylbenzene present as impurity in the starting material. (Newton ,loc.cit., $n_D^{20^\circ}$ 1.5347).

High boiling fraction, b.p. 102-~~104~~ $104\frac{1}{2}^{\circ}$ / 2-3mm.
$n_D^{20^\circ}$ 1.5200
Yield 47.5g. 38%

This fraction was chiefly 4-nitro-1:3-di-<u>iso</u>propylbenzene. (Newton, <u>loc</u>.<u>cit</u>., $n_D^{20^\circ}$ 1.5308).

No 2-nitro-1:3-di-<u>iso</u>propylbenzene was isolated. (Newton obtained this as high boiling fraction, $n_D^{20^\circ}$ 1.5161).

<u>4-Amino-1:3-di-isopropylbenzene</u>.

4-Nitro-1:3-di-<u>iso</u>propylbenzene (26g.) in ethanol (150ml.) with platinum oxide (0.2g.) as catalyst was shaken in a hydrogenator with hydrogen pressure 83 lbs./sq.". The reduction was complete in 15 mins. The solution was filtered from the catalyst and the ethanol distilled. Purification via the hydrochloride was not very satisfactory since the hydrochloride was formed very slowly and was not very soluble in water. The residue was fractionated under reduced pressure. b.p. 88-92°/ 2-3 mm.

First drop $n_D^{20^\circ}$ 1.5295

Main fraction $n_D^{20^\circ}$ 1.5295

Last drop $n_D^{20^\circ}$ 1.5293

4-Amino-1:3-di-<u>iso</u>propylbenzene was thus obtained as a colourless oil (21g.). Yield 94%. (Newton, <u>loc</u>.<u>cit</u>. $n_D^{20^\circ}$ 1.5275).

The acetyl derivative was prepared by stirring a suspension of the amine (1 mol.) in water with acetic anhydride (1 mol.). The solid was filtered off, washed and recrystallised from <u>iso</u>-octane in white needles, m.p. 107-107.5°. (Newton, m.p. 108.3-109°).

The benzoyl derivative was prepared in the usual way and crystallised from ethanol in needles m.p. 162.5-163.5°. (Newton, m.p. 162.8-163.4°).

(Found: N,4.7. Calculated for $C_{19}H_{23}ON$ N,5.0%).

The sulpate is very insoluble and crystallises in long thread-like needles. It can be diazotised to give a very stable diazo solution which does not decompose even at 15°. It couples with alkaline β-naphthol to give a bright red dye.

4-Iodo-1:3-di-isopropylbenzene.

4-Amino-1:3-di-*iso*propylbenzene (20g.,1 mol.) was dissolved in concentrated sulphuric acid (9.5 ml., *d.* 1.84, 1.5 mol.) and water (900 ml.) by boiling and diazotised at 7-10° by the addition of sodium nitrite solution (9.4g., 1.5 mol. in 25 ml. water). It was left in an ice bath for 30 mins. and then poured into a solution of potassium iodide (28g., 1.5 mol. in 200 ml. water). The reaction was completed by warming on a boiling water bath. The solution was decolourised with sodium metabisulphite, made alkaline and steam distilled. The iodo compound distilled as a pale yellow oil which was extracted with ether and the ether solution dried. The ether was distilled and the residue distilled under reduced pressure. Even at low pressures the iodo compound decomposes partially on distillation with loss of iodine. 4-Iodo-1:3-di-*iso*propylbenzene was obtained as a pale yellow oil, b.p. 102-104° / 4-5mm. $n_D^{25°}$ 1.5542. Yield, 18g., 55%.

(Found: C,50.2; H,5.7; I,43.7. $C_{12}H_{17}I$ requires C,50.0; H,5.9; I,44.1%)*.

2:2';4:4'-Tetra-isopropyldiphenyl

4-Iodo-1:3-di-isopropylbenzene (11.5g.) was heated with an equal weight of copper powder in a metal bath at 285-295°. The copper powder was added in portions during the first 20 mins. and the heating continued for an additional 40 min. The product was extracted with chlorobenzene and filtered. The chlorobenzene was distilled and the residue distilled under reduced pressure. The distillate was redistilled from sodium. 2:2':4:4'-Tetra-isopropyldiphenyl was obtained as a thick colourless oil, b.p. 152-154° / 4-5 mm. $n_D^{25°}$ 1.5355. Yield (3.5g.) 55%. Further distillation from sodium and separation into 3 fractions gave no difference in refractive index.

(Found: C,89.5; H,10.4. $C_{24}H_{35}$ requires C,89.4; H,10.6%).

Vapour phase chromatography however showed the product to be only c.a. 80% pure. (p.36)

2:4-Di-isopropyldiphenyl.

4-Iodo-1:3-di-isopropylbenzene (13.5g., 1 mol.) and iodobenzene (24g., 2.5 mol.) were heated with copper powder (40g.) in a metal bath at 220-225°. The copper powder was added during the first 15 min. and the temperature of the bath was gradually increased during the next 20 min. to 245° and maintained at this temperature for 15 min. The product was extracted with chlorobenzene, filtered and most of the solvent distilled. The residue was then poured into water and steam distilled. Chlorobenzene and excess iodobenzene distilled first followed by diphenyl which crystallised in the condenser. After about 1 hr. the rate of distillation had decreased considerably and the distillation was stopped. The residue was extracted with ether and dried. The ether was distilled and the residue fractionated under reduced pressure. A rapid preliminary distillation separated the product from a small amount of tarry material. On redistillation the first fraction , b.p. 96-100°/6mm, and this solidified in the condenser and was diphenyl. A total of 0.7g. diphenyl were obtained.

The temperature was then taken up to 142° when the next fraction started to distill.

2.6g. 23% $n_D^{25°}$ 1.5513

Residue $n_D^{25°}$ 1.5521

Two more distillations from sodium gave a product, b.p. 145-152° / 6-7 mm. $n_D^{25°}$ 1.5510.

(Found: C, 90.5; H,9.5. $C_{18}H_{22}$ requires C,90.8; H, 9.2%).

Again the product was shown by gas phase chromatography to contain appreciable impurities.

4-Amino-isopropylbenzene.

The low boiling fraction of nitro compound (p.109) (7g.) was dissolved in ethanol (100 ml.) and reduced in an hydrogenator with platinum oxide (0.1 g.) as catalyst. The hydrogen pressure was 85 lbs./ sq." and the reduction was complete in 15 mins. The product was filtered from the catalyst and the alcohol distilled. The residue was fractionated. The main fraction (5g.) had b.p. 63-80°/ 4-3 mm.

First few drops	1.5340	
Main fraction	1.5400	$n_D^{20°}$
Residue	1.5340	

This represents a 90% yield of amino compound, chiefly 4-amino-*iso*propylbenzene. (Newton, *loc.cit.*, $n_D^{20°}$ 1.5415).

The acetyl derivative was prepared as above and on crystallisation from dilute ethanol, m.p. 104-105° (Newton, m.p. 103°)

The benzoyl derivative was prepared in the usual way and on crystallisation from ethanol had m.p.161.5-162° (Newton, m.p. 162°).

4-Iodo-isopropylbenzene.

The above amine (5g., 1 mol.) was dissolved in concentrated sulphuric acid (2.4 ml., 1.5 mol.) and water (250ml.) and diazotised at 4-5° by the addition of sodium nitrite solution (2.4g., 1.2 mol. in 25 ml. water). The resulting diazo solution was poured into a solution of potassium iodide (7g., 1.5 mol. in 200ml water) and finally the mixture was warmed on a water bath to complete the reaction. After decolourising [illegible] it was made alkaline and steam distilled. The oil which distilled was dissolved in ether, dried and the ether distilled. The residue was then distilled under reduced pressure. 4-Iodo-isopropylbenzene was thus obtained as a pale yellow oil, b.p. 86-92° / 5-6 mm., $n_{D}^{25^{\circ}}$ 1.5725. Yield,(6 g.) 66%. (Found: C,43.8; H,4.5; I,51.7. Calculated for $C_9H_{11}I$ C,43.9; H,4.5; I,51.6%).

4:4'-Di-isopropyldiphenyl.

4-Iodo-isopropylbenzene (5g.) was heated with copper powder (8g.) in a metal bath at 260-270°. The copper was added in the first 15 mins. and the heating continued for another 30 mins. The product was extracted with chlorobenzene, After distilling the chlorobenzene the residue was distilled under reduced pressure. Yield (2g.) 84%. b.p. 155-160/ 4-5mm. The product solidified. It was redistilled from sodium and finally crystallised twice from ethanol. It crystallised in beautiful white plates, m.p. 65-66°.
(Found: C,90.8; H,9.3. Calculated for $C_{18}H_{22}$ C,90.7; H,9.3%).

Two values are recorded in the literature for the m.p. of 4:4'-di-isopropyldiphenyl. In this case only the high melting form was obtained.

m.p. 45° Schreiner, J.prakt.Chem.,1910(ii) 81,422.
m.p 65-66°, Bert and Dorier, Bull.Soc.Chim.,1925,37,1398

4:4'-Diacetyldiphenyl.

Long and Henze, J.Amer.Chem.Soc., 1941,43,1939.

Aluminium chloride (80g.,3mol.) was covered with dry carbon disulphide (75 ml.) and to the stirred solution was added a solution of diphenyl(30.8g., 1 mol.) and acetyl chloride (42.5ml.,3mol.) in carbon disulphide. A vigorous reaction took place and the addition took 20 mins. The mixture was stirred for another 30 mins. and then boiled under reflux for 4 hrs. After distilling off the carbon disulphide the residue was decomposed by the careful addition of ice-water (c.a.750ml.). The solid obtained was filtered off, dried and crystallised from ethanol using charcoal. The solubility in ethanol was poor and the product crystallised in fine needles. Acetone was a more convenient solvent. 4:4'-Diacetyldiphenyl was obtained in 74% yield (35g.), m.p. 189-191°. (Long and Henze, loc.cit. m.p. 190-191°)

Attempted preparation of 4:4'-di-(hydroxyisopropyl)-diphenyl.

The method of Valyi,Janssen and Hark, J.Phys.Chem.,1945,49, 461 was attempted. The only variation was in the use of 2 mol. excess of methyl iodide instead of 4 mol. as used by these workers.

The Grignard reagent was prepared in the usual way from magnesium (10.2g.,4.2 atoms) and methyl iodide (56.8g., 4 mol.) in dry ether (150ml.). 4:4'-Diacetyldiphenyl(23.8g., 1 mol.) was then added,followed by dry toluene (250 ml.). The ether was then distilled off and the mixture boiled under reflux for 6 hrs. It was then decomposed with ice and ammonium chloride, the toluene layer separated and the aqueous layer extracted with toluene. After distilling off the toluene, 20 g. of a solid product were obtained,m.p.120-174°. Crystallisation was difficult and many different solvents and mixtures of solvents were tried. Valyi (et.al.(loc.cit.) used acetal but this was not satisfactory. Finally attempts were made to obtain a pure product by fractional crystallisations from a)butanol b) acetone. After numerous recrystallisations no pure product of sharp constant m.p. could be obtained. Valyi et al. give m.p. 154° & a second form, m.p. 149-150°.

This route to 4:4'-di-isopropyldiphenyl was then abandoned as it was obtained unexpectedly as described above.

2'-isopropyldiphenyl-2-carboxylic acid and 2-isopropyldiphenyl.

Route 1 (Attempted preparation)

Diphenic anhydride.

Roberts and Johnson,J.Amer.Chem.Soc.,1925,47,1396.

Oyster and Adkins, ibid.,1921,43,208.

Diphenic acid (50g.) was dissolved in acetic anhydride (150 ml.) and the solution boiled under reflux for 2 hrs. The mixture was cooled with stirring and the anhydride which crystallised out filtered off and washed with small portions of ice-cold ethylacetate. After drying in vacuum, 40g. diphenic anhydride were obtained, m.p. 223-224°. Mixed m.p. with diphenic acid, 204°. (Roberts and Johnson, *loc.cit.* give m.p. 217° for the anhydride.) . Concentration of the filtrate by vacuum distillation yielded another 3g. diphenic anhydride, m.p. 222-224°. Yield, 93%.

2'-(α-hydroxy-isopropyl)-diphenyl-2-carboxylic acid.

Corbellini and Angeletti (*Atti R.Accad.Lincei.*, 1932, *15*, 968). Jamison and Turner (*J.Chem.Soc.*, 1942, 432).

This reaction was scaled up from 19g. anhydride to 56g. and in practise the lactone or a mixture of acid and lactone were obtained.

A Grignard reagent was prepared in the usual way from magnesium (15,2g., 2.5 atoms) and methyl iodide. (46.5g., 3 mol.) in dry ether (300ml.). Solid diphenic anhydride (56g., 1 mol.) was then added in portions during 45 mins. and the mixture boiled under reflux on a water bath for a total of 6 hrs. A smooth reaction started on adding the diphenic anhydride but later a paste was formed which made stirring difficult. At the end of the heating the mixture was cooled and decomposed with ice-water. The paste was completely dissolved by the addition of dilute acetic acid and ether. The solution was extracted with ether and the ethereal solution washed once with brine. It was then extracted with concentrated sodium carbonate (4 times) and the combined sodium carbonate washings acidified. A thick oil separated and the solution was decanted from this through a Buchner funnel. The oil was washed with hot water when it solidified immediately. The solid was filtered through the funnel and washed with hot water. After drying in a vacuum dessicator over concentrated sulphuric acid it was crystallised from benzene. First crop, 22g., m.p. 127-128°. Second crop, 13g., m.p.125-126°. Yield 55%. Corbellini and Angeletti (*loc.cit.*) ; 2'(α-hydroxy*iso*propyl)-diphenyl-2-carboxylic acid, m.p. 137-138°, Lactone, m.p.123°.

The lactone was used directly without conversion to the acid.

Dehydration of lactone of 2'-(α-hydroxyisopropyl)-diphenyl-2-carboxylic acid.

Method 1.

The above lactone (1g.) was boiled under reflux with anhydrous formic acid (20ml.) for 4 hrs. On cooling a solid crystallised which was filtered off, dissolved in ether and the ether solution washed with brine. The ether solution was extracted with 30% sodium hydroxide solution and the alkaline extracts acidified. A solid was precipitated which was filtered and dried. Yield 0.6g. It was crystallised fron benzene, yield 0.4g.,40%. m.p. 195-196°. Substance A.

Method 2.

Lactone (25g.) and 50% sulphuric acid (250ml.) were boiled under reflux for 1 hr. On heating an oil was formed which soon solidified. After cooling the mixture was poured into ice-water and extracted with ether. The ethereal solution was treated as above. After crystallisation from benzene, 18g. substance A, m.p. 195-196° were obtained. Concentration of the mother liquor gave another 2g., m.p. 193-196°. Yield, 80%.

Ridgwell (unpublished) heated 2'-(α-hydroxy*iso*propyl)-diphenyl-2-carboxylic acid with 48% hydrobromic acid in a sealed tube for 1 hr. and isolated a compound, m.p. 195-197-5°. This is presumably identical with A. It analysed correctly for 2'-*iso*propenyldiphenyl-2-carboxylic acid.

Further investigation of substance A however shows no evidence of unsaturation. It did not decolorise bromine in carbon tetrachloride and could not be reduced catalytically using either platinum oxide or palladium catalysts. Both ethanol and acetic acid were tried as solvent. In all cases substance A was recovered unchanged after 10 hrs. in the hydrogenator at a hydrogen pressure of 100 lbs./sq.".

Esterification of substance A.

Substance A (12g., 1 mol.) and thionyl chloride (5 ml.) were heated under reflux on a water bath for 2 hrs. After

this time the acid had dissolved. Excess thionyl chloride was removed by vacuum distillation and the acid chloride added to methanol (75 ml.). After concentrating and cooling the methyl ester crystallised in hexagonal prisms, m.p. 82-83°, yield, 9 g. Recrystallisation from methanol did not raise the melting point. Concentration of the mother liquor gave more solid which after crystallisation gave another 2 g. of pure methyl ester (B). Total yield, 82%.
Substance B would not decolourise bromine in carbon tetrachlorid chloride.
(Found: C,80.93; H,6.4. $C_{17}H_{16}O_2$ requires C,80.95; H,6.4%).

Attempted reduction of B.

Substance B (2g.) in ethanol (60 ml.) in the presence of platinum oxide catalyst (0.5 g.) was shaken in a hydrogenator for 20 hrs. with hydrogen pressure of 100 lbs./sq.". After filtering from the catalyst the ethanol was evaporated and a solid residue obtained. M.p. and mixed m.p. with B 82-83°.

Decarboxylation of A.

Substance A (2g.) was boiled under reflux in quinoline (20 ml.) in the presence of copper powder for 3 hrs. The cooled solution was poured into dilute hydrochloric acid and the product extracted with ether. The ethereal solution was washed with dilute hydrochloric acid, brine, sodium hydroxide solution and brine. Acidification of the alkaline washings gave no precipitate. The ethereal solution was dried over calcium chloride and the ether distilled. On cooling the residue solidified and was crystallised from dilute ethanol using charcoal. It crystallised in white needles and after two crystallisations had m.p. ~~96.5-97.5~~ 95-96°. Yield of substance C (1.1g.) 69%.

(Found: C,92.7; H,7.3. $C_{15}H_{14}$ requires C,92.8; H,7.2%).

Substance C gave no tests for unsaturation. This reaction gave the final proof that A is not 2'-*iso*propenyldiphenyl-2-carboxylic acid, since C is not identical with 2-*iso*propyldiphenyl.

2-*iso*Propyldiphenyl is a liquid, b.p. 107/ 2 mm. $n_D^{25°}$ 1.5925 (Mowry,Dazzi,Renoll and Shortridge, *J.Amer.Chem.Soc.*, 1948,*70*,1916).

C was finally identified as 9:9-dimethylfluorene from its ultraviolet absorption spectrum (p.55). Anchel and Blatt, *J.Amer.Chem.Soc.*,1941,*63*,1940 give 9:9-dimethylfluorene, m.p. 95-96°.

A is then 9:9-dimethylfluorene-4-carboxylic acid and B its methyl ester.

Amide of 9:9-dimethylfluorene-4-carboxylic acid.

9:9-Dimethylfluorene-4-carboxylic acid (2g.) and excess thionyl chloride (5 ml.) were boiled under reflux on a water bath for 30 mins. The excess thionyl chloride was then removed by vacuum distillation and 0.88 ammonia (40ml.) added to the cooled acid chloride. A white solid separated and after leaving overnight it was filtered, washed and dried. (1.7g.), m.p. 178-180°, yield 85%. Crystallisation from dilute ethanol raised the m.p. to 180.5-181.5°. (Found: N,5.8. $C_{16}H_{15}NO$ requires N,5.9%).

4-(α-hydroxyisopropyl)-9:9-dimethylfluorene.

A Grignard reagent was prepared in the usual way from magnesium (5 g., 4.5 atoms) and methyl iodide (28g., 4.5 mol.) in dry ether (200 ml.). Methyl 9:9-dimethylfluorene-4-carboxylate (11.5g., 1 mol.) was added in small portions during 15 mins. and the mixture boiled under reflux for 5 hrs. It was decomposed with ice-water and dissolved with dilute hydrochloric acid. The solution was extracted with ether and the ethereal extracts washed and dried over anhydrous sodium sulphate. After distilling the ether, the residue (10 g.) solidified. It was crystallised 3 times from dilute ethanol and pure 4-(α-hydroxyisopropyl)-9:9-dimethylfluorene (6g.) was obtained as white prisms, m.p. 118-119°. Yield 52%. Efficient drying in a vacuum desiccator was necessary since the compound appeared initially to be partly solvated, the solvated form having higher m.p.. Before drying, m.p. 118-126°. (Found: C,85.2; H,8.1. $C_{18}H_{20}O$ requires C,85.7; H,7.9%).

4-*iso*Propenyl-9:9-dimethylfluorene.

4-(α-hydroxy*iso*propyl)-9:9-dimethylfluorene (3g.) was boiled under reflux for 2 hrs. in 50% sulphuric acid (75 ml.). The cooled mixture was poured into ice-water and the solid which separated extracted with ether. The ether solution was washed and dried and the ether evaporated. The residue (2.1g.) solidified and had m.p. 67-68°. It crystallised from light petroleum (b.p. 40-60°) in white prisms, on cooling in ice. m.p. unchanged. Yield (1.7g.) 61%. It decolorised bromine in carbon tetrachloride.

(Found: C,92.4; H,7.7. $C_{18}H_{18}$ requires C,92.3; H,7.7%).

4-*iso*Propyl-9:9-dimethylfluorene.

4-*iso*Propenyl-9;9-dimethylfluorene (1.5g.) in ethanol (50 ml.) was shaken in a hydrogenator in the presence of platinum oxide catalyst (0.5g.) with a hydrogen pressure of 95 lbs./ sq.". After 5 hrs. a test portion no longer decolourised bromine in carbon tetrachloride. The solution was filtered from the catalyst and the alcohol evaporated. The residue solidified and was crystallised from dilute ethanol using charcoal. 4-*iso*Propyl-9:9-dimethylfluorene crystallised in white plates, m.p. 48-49°. Yield (1.2g.) 80%.

(Found: C,91.4; H,8.7. $C_{18}H_{20}$ requires C,91.5; H,8.5%).

Route 2.

9:10-Dimethyl-9:10-dihydroxyphenanthrene.

Zincke and Tropp, Annalen,1908,363,302.
Hall,Ladbury,Lesslie and Turner,J.Chem.Soc.,1956,3475.

Commercial 'pure' phenanthraquinone contained acetic acid and was therefore groun~~g~~d, sieved (60 mesh sieve) and left in a vacuum over KOH before use.

A Grignard reagent was prepared from magnesium (20 g., 4 atoms) and sufficient methyl iodide to dissolve all the magnesium, in dry ether (250 ml.). Phenanthraquinone (42g., 1 mol.) was added in about 2 g. portions and then dry benzene (250 ml.) added. The mixture was stirred mechanically and heated om a water bath for 2 hrs. so that the ether distilled off slowly during this time.

After cooling the mixture was poured carefully into a 3 l. beaker containing ice-water which was stirred mechanically. Dilute sulphuric acid was added until the green colour was discharged and the solution was acidic. The benzene layer was separated and the aqueous layer extracted 4 times with ether. The combined benzene and ether extracts were washed twice with brine and then washed with a saturated solution of sodium bisulphite until the latter no longer gave a precipitate on the addition of alkali. From the sodium bisulphite washings on making alkaline, starting material was recovered, which, after crystallisation from acetic acid gave pure phenanthraquinone (1g.).

The ether solution was washed with brine and finally distilled until the volume was approximately 150 ml. On cooling the diol crystallised and was filtered and washed with a little benzene. Yield 33g., m.p. 159.5-161°. After crystallisation from benzene, pure 9:10-dimethyl-9:10-dihydroxyphenanthrene was obtained (31.5g.), m.p. 164-165°. Allowing for the phenanthraquinone recovered, yield 67%.

9:9-Dimethylphenanthrone.

Zincke and Tropp, loc.cit..

9:10-Dimethyl-9:10-dihydroxyphenanthrene (15g.) was dissolved in glacial acetic acid (50ml.) and concentrated sulphuric acid (3 ml.) added to the boiling solution. On the addition of sulphuric acid the solution became pale yellow and then cloudy. A small amount of solid separated which was insoluble in boiling acetic acid. The hot mixture was left to stand for a few minutes and then decanted through glass wool into ice-water. An oil separated which eventually solidified. It was filtered, washed and dried. Yield 13g. It was crystallised from ethanol (75 ml.). A small unidentified portion would not dissolve, 0.5g., m.p. 171-270° with prevoius softening.

9:9-Dimethylphenanthrone crystallised in white plates, m.p. 74-75°, yield, 6.5g. Concentration of the mother liquor gave more pure 9:9-dimethylphenanthrone, yield, 86%.

2'-isopropyldiphenyl-2-carboxylic acid.

Meerwein, *Annalen*, 1913, *396*, 225.

The reaction was carried out on a larger scale and proportionally less potassium hydroxide was used. The yield was finally increased from 31 to 61 % by carrying out the fusion at a lower temperature than that used by Meerwein, (220-240°)

9:9-Dimethylphenanthrone (15g.) was heated in a nickel crucible in a metal bath at 185-190° with solid potassium hydroxide (40g.). The mixture quickly melted and after about 5 mins. the solid potassium salt of the acid began to separate. In one experiment, for no obvious reason solidification did not start until after 30 mins. heating and in this case heating was continued for a total of 45 mins. in place of the usual 30 mins. The final yield was unchanged.

After cooling the fused mass was dissolved in 1 *l.* water with heating since the potassium salt was sparingly soluble. The solution was cooled and then washed by shaking with ether. The aqueous layer was acidified, extracted with ether and the ether extracts washed with brine. After drying over anhydrous sodium sulphate the ether was distilled. The residue solidified and was crystallised from light petroleum (b.p.60-80°), using charcoal. Pure 2'-*iso*propyldiphenyl-2-carboxylic acid (10g.) was obtained as white flakes, m.p. 110-111°, yield

61%. Meerwein (loc.cit.) crystallised the aeid from dilute alcohol, m.p. 104-106°. However it was very soluble in ethanol and tended to come out as an oil from dilute ethanol. (Found: C,80.4; H,6.8. Calculated for $C_{16}H_{16}O_2$ C,80.0; H,6.7%).

2-isoPropyldiphenyl.

2'-*iso*Propyldiphenyl-2-carboxylic acid (2.4g.) was boiled under reflux for 4 hrs. with freshly distilled quinoline (15ml.) in the presence of copper powder. The cooled solution was poured into dilute hydrochloric acid, extracted with ether, washed and the ether solution dried. The ether was distilled and the residue then distilled. Yield 1.6g. It was redistilled from sodium (4 times) until a constant refractive index was obtained. $n_D^{20°}$ 1.5730 and $n_D^{25°}$ 1.5705. Goodmann and Wise, *J.Amer.Chem.Soc.*,1950,*72*,3076, give m.p. 24.46°.

Although the analysis was satisfactory the spectrum showed that impurities were present an inflection being observed in the 2300 Å region instead of the expected maximum and minimum. After 2 crystallisations from ethanol at low temperatures followed by redistillation a specimen m.p. 25-26° was obtained. It crystallised in white needles. Rather surprisingly the refractive index was unchanged although the ultraviolet absorption spectrum now showed the expected characteristics.(p.53).

Found: C,91.9; H,7.9. Calculated for $C_{15}H_{16}$ C,91.8; H,8.2%).

Route 3.

Alternative dehydration of 2'-(α-hydroxy*iso*propyl)-diphenyl-2-carboxylic acid with alumina.

The lactone (3g.) and alumina (1g.) were heated in a metal bath at 150°. The temperature was raised slowly during 20 mins. to 260°. After cooling the product was extracted with ether, the ether solution filtered and washed. It was extracted with alkali and the alkaline extracts acidified. A solid precipitated which was filtered, washed and dried. It was crystallised first from dilute ethanol and then from light petroleum (b.p. 100-120°). It crystallised in prisms, m.p.122°. The acid decolourised bromine in carbon tetrachloride and analysed correctly for 2'-*iso*propenyldiphenyl-2-carboxylic acid. Yield, 2g., 67%.

(Found: C,80.6; H,5.4. $C_{16}H_{14}O_2$ requires C,80.7; H,5.9%).

2-*iso*propyldiphenyl-2-carboxylic acid.

2'-*iso*Propenyldiphenyl-2-carboxylic acid (0.5g.) in ethanol (20 ml.) with platinum oxide catalyst (0.05g.) was shaken in a hydrogenator for 6 hrs. with a hydrogen pressure of 95 lbs./sq.". At the end of this time a test portion no longer decolourised bromine in carbon tetrachloride. The solution was filtered from the catalyst and the solvent evaporated. The residue crystallised from dilute ethanol, m.p. 109-111°. Yield 0.4g. Recrystallisation from petroleum ether (b.p.40-60°) gave an acid and a mixed m.p. with 2'-*iso*propyldiphenyl-2-carboxylic acid gave no depression.

Amide of 2'-isopropyldiphenyl-2-carboxylic acid.

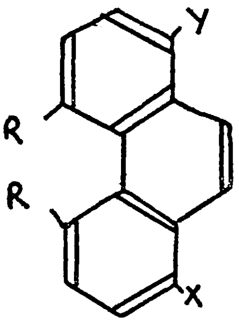
2'-*iso*Propyldiphenyl-2-carboxylic acid (1g.) and excess thionyl chloride (2 ml.) were heated under reflux on a water bath for 30 mins. and the excess thionyl chloride removed by vacuum distillation. To the cooled acid chloride 0.88 ammonia was added and the mixture left overnight. The pale yellow solid was filtered and dried. Yield 1g., m.p. 82-92°. On attempted crystallisation from dilute ethanol the substance came out first as an oil and the crystals were not homogeneous containing some bright yellow impurity, probably fluorenone. The solid was therefore warmed with light petroleum (b.p. 80-60°) and the insoluble portion which was filtered off was white. Yield, 0.2g. m.p.113-115°. Two crystallisations from petroleum ether (b.p. 100-120°) gave pure amide, m.p. 115.5-116.5°.

(Found: N,5.8. $C_{16}H_{17}ON$ requires N,5.9%).

The yellow filtrate on concentration gave more amide the yellow impurity being only a trace.

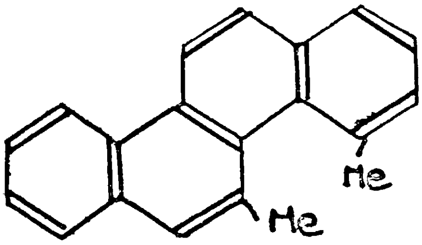
PART 11.

INTRODUCTION.



I

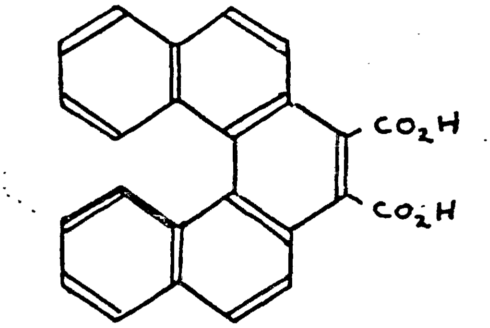
It is well known that compounds of the type 1 are difficult to obtain and for a long time it was thought impossible to prepare such compounds.e.g. Haworth and Sheldrick, J.Chem.Soc.,1934,1950, attempted the synthesis of 1 (R = Me) and concluded 'it is impossible to introduce two methyl groups in the 4:5 positions of phenanthrene without introducing excessive strain in the molecule'. However, Newman,(J.Amer.Chem.Soc.,1940,62,2295) prepared 4:5-dimethylchrysene and also pointed out examples of compounds described in the literature in which the two methyl groups are similarly placed. Although such compounds can be prepared, there is generally great resistance to their formation and they have usually been obtained through ring closures well removed from the interfering groups. This can readily be understood on steric grounds for if the aromatic rings are coplanar the two methyl groups will interfere to a large extent.



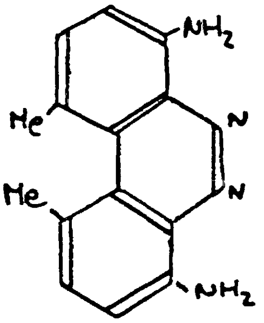
Newman and Hussey (J.Amer.Chem.Soc.,1947,68,978 & 3023) prepared 4:5:8-trimethyl-1-phenanthrylacetic acid (I R = Me, X = Me, Y = CH_2COOH) and obtained it active. In this compound the activity results from the fact that the methyl groups in the

4:5 positions are forced out of the plane of the phenanthrene molecule. This phenomenon of 'molecular overcrowding' has now been observed in a number of compounds, e.g.

Bell and Waring, *J.Chem.Soc.*,1949,2689.

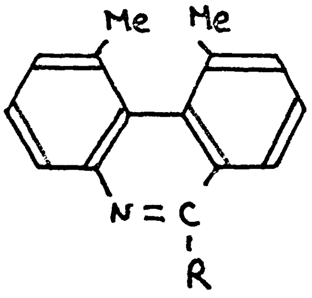


Theilacker and Baxmann, *Annalen*,1953,*581*,117.



These compounds racemise readily, either at room temperature, or in the case of the phenazine in MeOH after lhr. at 60°.

In view of the resistance to the formation of compounds of this type it was surprising to find that Ritchie, (*J. Proc. Roy.Soc.N.S.W.*,1945,*78*,159) described the preparation of 4:5-dimethyl-9(*p*'-nitrophenyl)-phenanthridine, (II, R=*p*-$C_6H_4NO_2$) in 80% yield from 2-(*p*'-nitrobenzamindo)-6:6'-ditolyl by heating with phosphor~~o~~us oxychloride in nitrobenzene at at 180° for 5 hrs. When R = C_6H_5, 4:5-dimethyl-9-phenyl-phenanthridine was obtained.



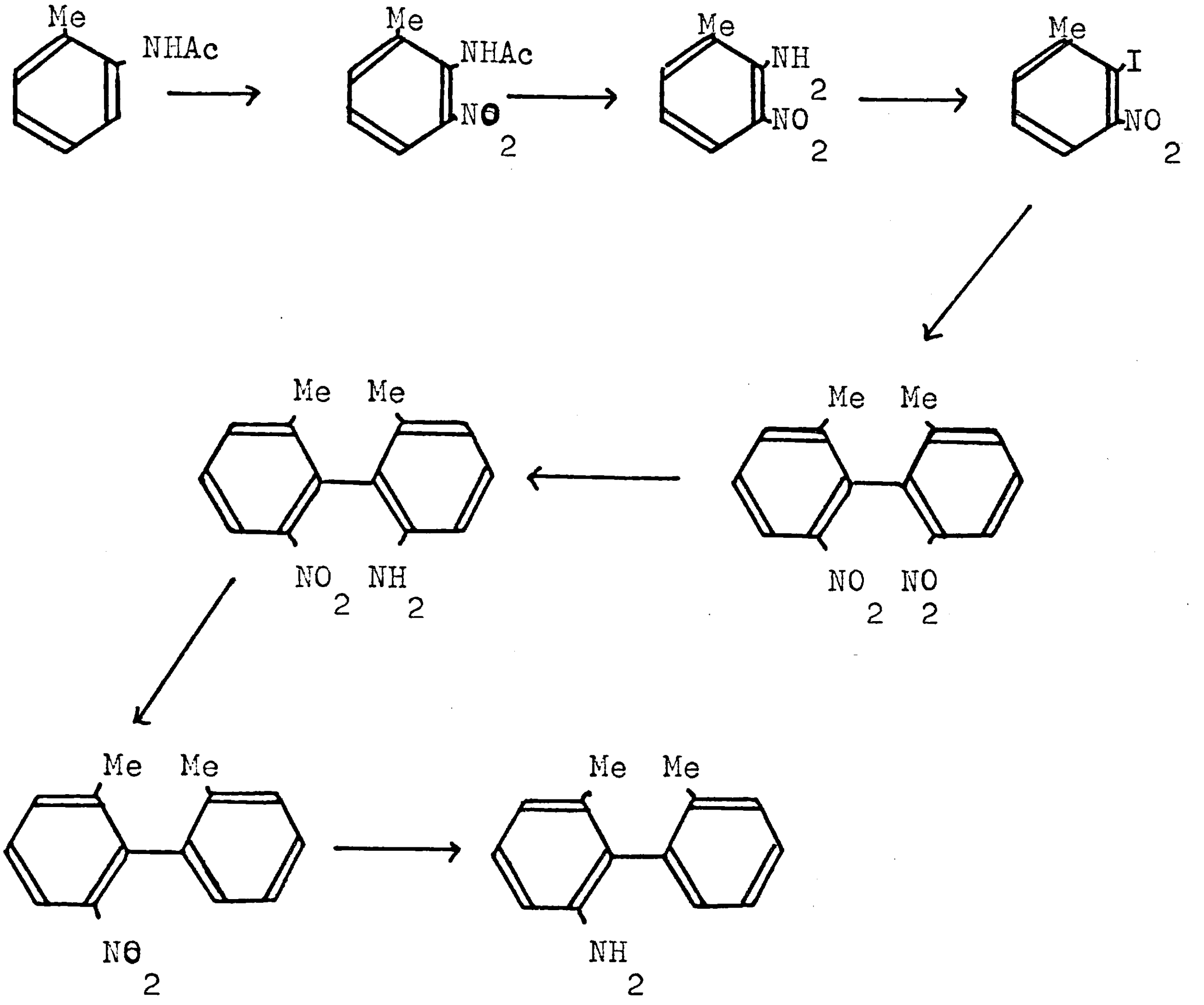
II

It was of interest to reinvestigate the preparation of II, R = p-nitro-C_6H_4. Ritchie (loc.cit.) described the reduction to 4:5-dimethyl-9-(p'-aminophenyl)-phenanthridine.

Phenanthridine itself is planar (Merkel and Wiegand, Z.Naturforsch.,1948,93) and 4:5-dimethyl-9-(p'-aminophenyl)-phenanthridine might provide another example of optical activity arising from 'intramolecular overcrowding'.

DISCUSSION.

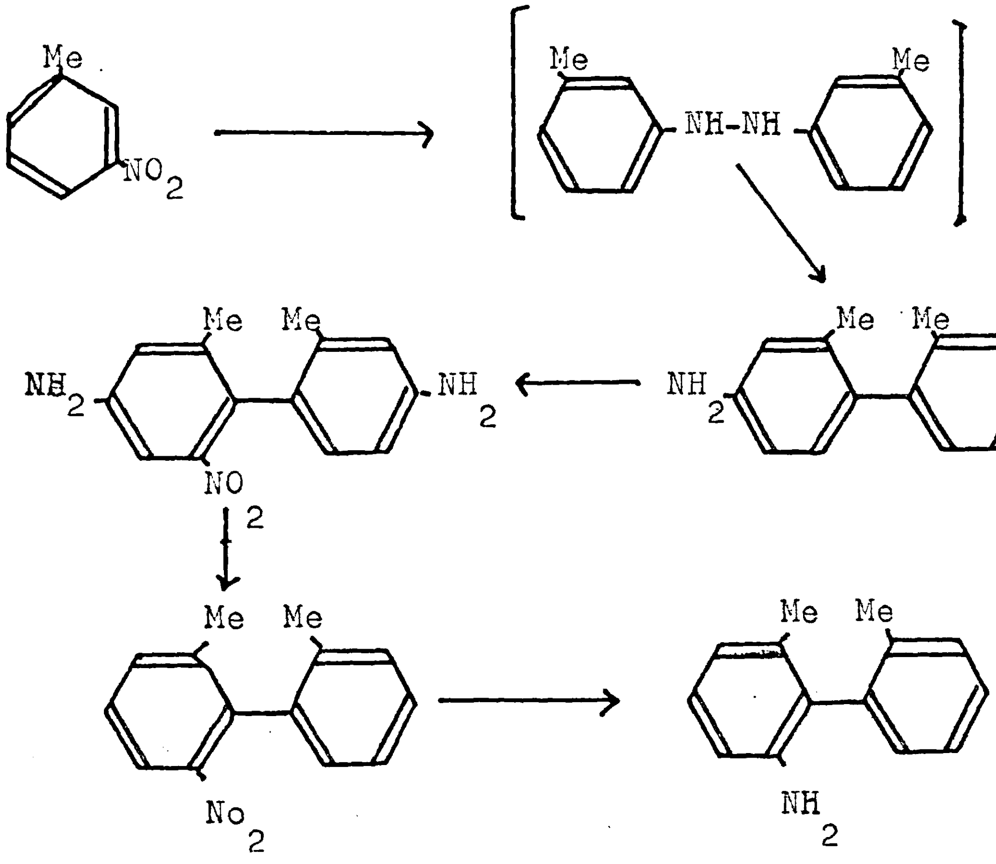
Two routes to 2-amino-6:6'-ditolyl have been described.



Several workers have described the preparation of 2:2'-dinitro-6:6'-ditolyl by the action of copper powder on either 2-iodo-3-nitrotoluene or 2-bromo-3-nitrotoluene. Partial reduction with either sodium sulphide (Sin-ichi Sako, Bull.Chem. Soc. Japan, 1934,9,393) or ammonium sulphide (Angeletti and Guala, Gazzetta,1934,61,651) yields 2-amino-2'-nitro-6:6'-ditolyl.

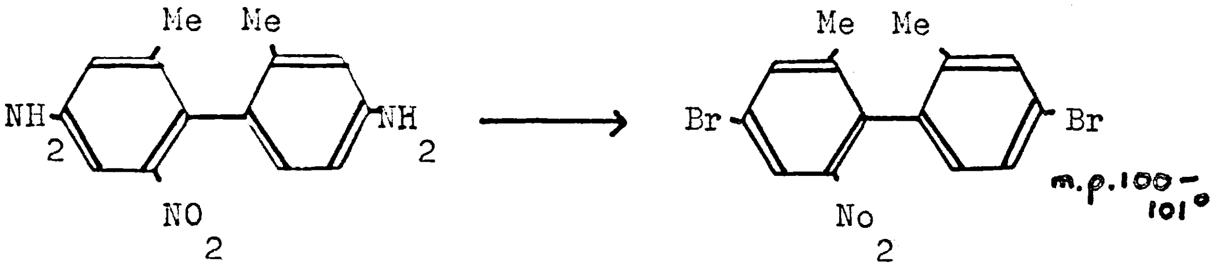
Deamination gives 2-nitro-6:6'-ditolyl, m.p. 45° (Ritchie, <u>ibid</u>. 156) m.p. 42-43° (Mascarelli and Angeletti, <u>Gazzetta</u>, 1938, <u>68</u>, 29) Reduction with stannous chloride and hydrochloric acid in acetic acid solution gave 2-amino-6:6'-ditolyl but there were discrepancies in the properties of this compound. Ritchie described it as a colourless oil, b.p. 169-170°. Mascarelli described it as a light yellow solid, m.p. 105°.

A more convenient shorter route appeared to be that described by Loh (Ph.D. Thesis, 1955).



Loh obtained <u>m</u>-tolidine readily from either <u>m</u>-nitrotoluene or <u>m</u>-azotoluene by reduction with zinc in ethanolic sodium hydroxide followed by rearrangement in acid. (Modified method of Schultz and Rohde, *C.*,1902,*11*,1447). The m-tolidine had m.p. 87°. (Schultz and Rohde,m.p. 87-88°). Later workers have described *m*-tolidine of higher m.p. (see p.148). Loh however confirmed the position of the methyl groups by deamination to 2:2'-ditolyl.

Nitration was carried out in concentrated sulphuric acid with potassium nitrate under conditions which normally favour nitration taking place *meta* to an amino group. The product was thought to be 2-nitro-*m*-tolidine and the following was quoted in favour of this.

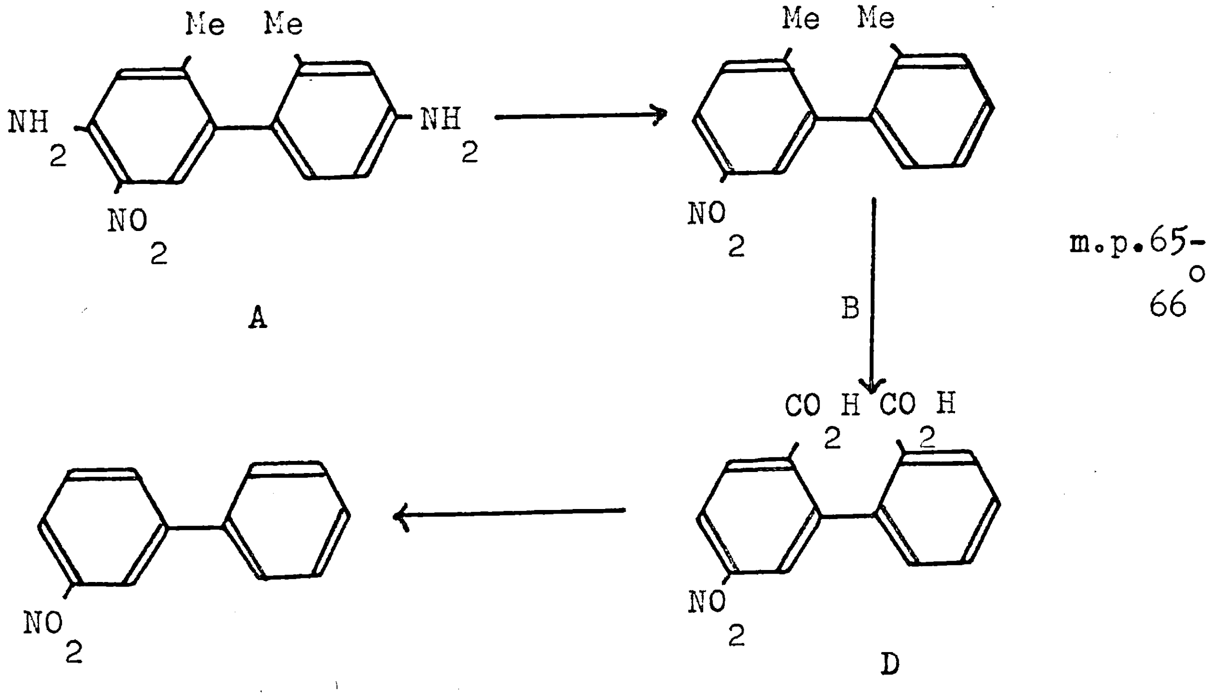


Heating the dibromo compound under reflux with piperidine for 15 mins. gave back the dibromo compound unchanged. (Loh,*loc.cit*.)

Deamination of the nitrotolidine (Loh) gave a product m.p.65° and on reduction the amine had m.p. 54-56°. These values do not agree with the values given by the above workers for 2-nitro-6:6'-ditolyl and 2-amino-6;6'-ditolyl respectively. Previous workers did not describe solid derivatives so checking was difficult. Ritchie however prepared a *p*-nitrobenzoyl derivative, m.p. 122°. Loh, *p*-nitrobenzoyl derivative, m.p. 160-161°.

In the present work the method of Loh for the synthesis of 2-amino-6:6'-ditolyl was first attempted.

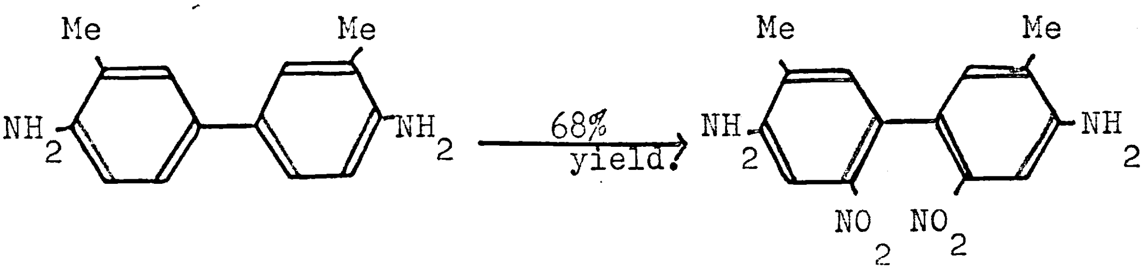
The nitroditolyl,B obtained by deamination of the nitrotolidine, A again had m.p. higher than that recorded by other workers for 2-nitro-6:6'-ditolyl. B was oxidised with alkaline permanganate to give an acid,D, m.p. 266-267°. Oxidation of 2-nitro-6:6'-ditolyl should however give 6-nitrodiphenic acid, m.p. 248-250° (Bell and Robinson,<u>J.Chem.Soc</u>.,1927,1696). A mixed m.p. of D with an authentic specimen of 6-nitrodiphenic acid showed a large depression. D formed an anhydride,m.p.194-195°. 6-Nitrodiphenic acid however does not form an anhydride. Bell and Robinson (<u>ibid</u>.2238) describe 5-nitrodiphenic acid, m.p. 268° and anhydride, m.p.193-195°. Eventually acid D was identified as 5-nitrodiphenic acid by decarboxylation. The product obtained showed no depression of m.p. with 3-nitrodiphenyl. The reactions described are illustrated below.



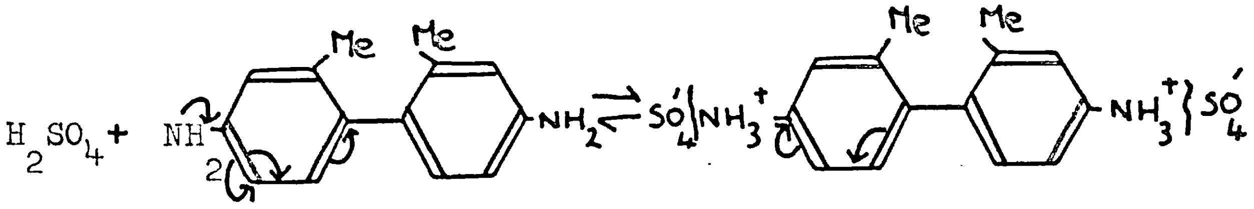
Finally Loh's dibromo compound (p.136) was heated on a water bath for 15 mins. with piperidine. The product had m.p. 105-107° but mixed m.p. with starting material gave a big depression. It analysed for $C_{19}H_{21}N_2O_2Br$ showing that the Br ortho to the nitro group had been replaced by piperidine as would be expected.

Mononitration of m-tolidine thus gave predominantly 3-nitro-m-tolidine and not the expected 2-nitro-m-tolidine.

Case and Koft (J.Amer.Chem.Soc.,1941,63,508) carried out the following nitration with potassium nitrate in 15% oleum and conc. H_2SO_4. The constitution of the product was proved by deamination followed by oxidation to the dinitrodiphenic acid.



m-Tolidine was then nitrated using the exact conditions of Case and Koft but the product was identical with that from previous nitrations. The m.p. of the products is not sharp and although predominantly 3-nitro-m-tolidine is obtained under both conditions, other isomers may be present.



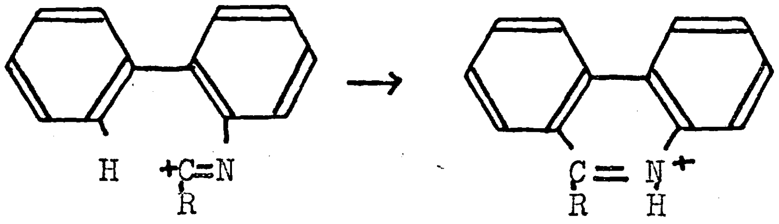
By carrying out the nitration in concentrated sulphuric acid it is hoped to shift the equilibrium well over to the right and the amine is present as the sulphate. The inductive effect of the ammonium group will then direct the electromeric displacements within the ring so that the positions o and p to the ammonium group will be deactivated and nitration will take place in the m-position. Such was the case in o-tolidine, however in this compound the o and p directing influence of the methyl group will enhance the effect of the ammonium group. In the case of m-tolidine however the directing influences of these two groups will oppose one another and the methyl group appears to have the more powerful directing influence. Possibly steric effects will also participate to prevent the nitro group entering the diphenyl in the blocking position.

Having failed to obtain 2-amino-6:6'-ditolyl by this method the alternative route had to be used. 50G. 2-amino-3-nitrotoluene were available and using the methods of Carlin and Foltz (J.Amer.Chem.Soc.,1956,78,1997) this was converted into first 2-iodo-3-nitrotoluene and then 2:2'-dinitro-6:6'-ditolyl in 87 and 81% yields respectively. Partial reduction to 2-amino-2'-nitro-6:6'-ditolyl was effected using sodium sulphide and the nitroamine was diazotised and readily deaminated with hypophosphorous acid to give 2-nitro-6:6'-ditolyl, m.p.42-43°. (cf.Mascarelli and Angeletti, and Ritchie,loc.cit.). Mixed m.p. with 3-nitro-6:6'-ditolyl gave the expected depression, in fact the two compounds melted on mixing. Catalytic reduction gave 2-amino-6:6'-ditolyl, which crystallised from light petroleum in white needles, m.p. 27°. The p-nitrobenzoyl derivative had m.p. 122-123° which is identical with Ritchie (loc.cit.).

No more 2-amino-3-nitrotoluene was available and in order to shorten the synthesis and avoid preparing large quantities of this compound, the commercially available 2-amino-3-nitro-m-xylidine, or the cheaper acetyl derivative, was used as starting material. The final 2:2':4:4'-tetramethyl-6-aminodiphenyl serves the present purpose equally well. A similar series of reactions were carried out and the amine obtained as a white solid, m.p. 50-51°. This compound was difficult to obtain solid and defied all attempts at crystallisation. It was soluble in the cold in all usual organic solvents.

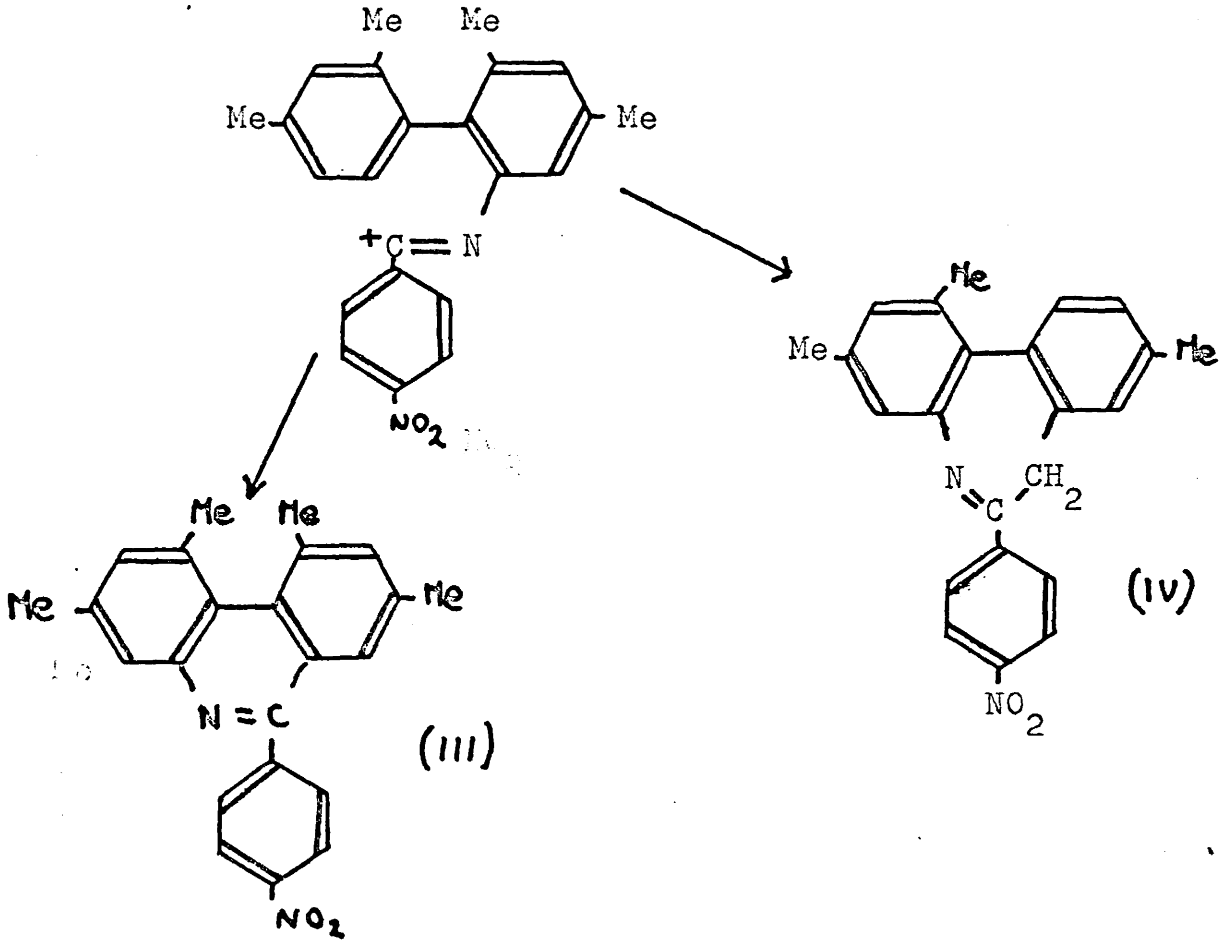
The p-nitrobenzoyl derivative was prepared in the usual way and treated with phosphor~~o~~us oxychloride in nitrobenzene solution at 180°. 2:4:5:7-Tetramethyl-9-(p-nitrophenyl)-phenanthridine was obtained in 78 % yield after heating for 12hrs. It exists in more than one form (p.162). Ritchie (ibid,159) prepared 4:5-dimethyl-9-(p-nitrophenyl)-phenanthridine in the same way and this showed similar behaviour, melting partially at 143° and then at 163°.

Ritchie (ibid.,147) suggests that in the formation of a phenanthridine, the initial step is the formation of a carbonium ion under the influence of the strong acid.



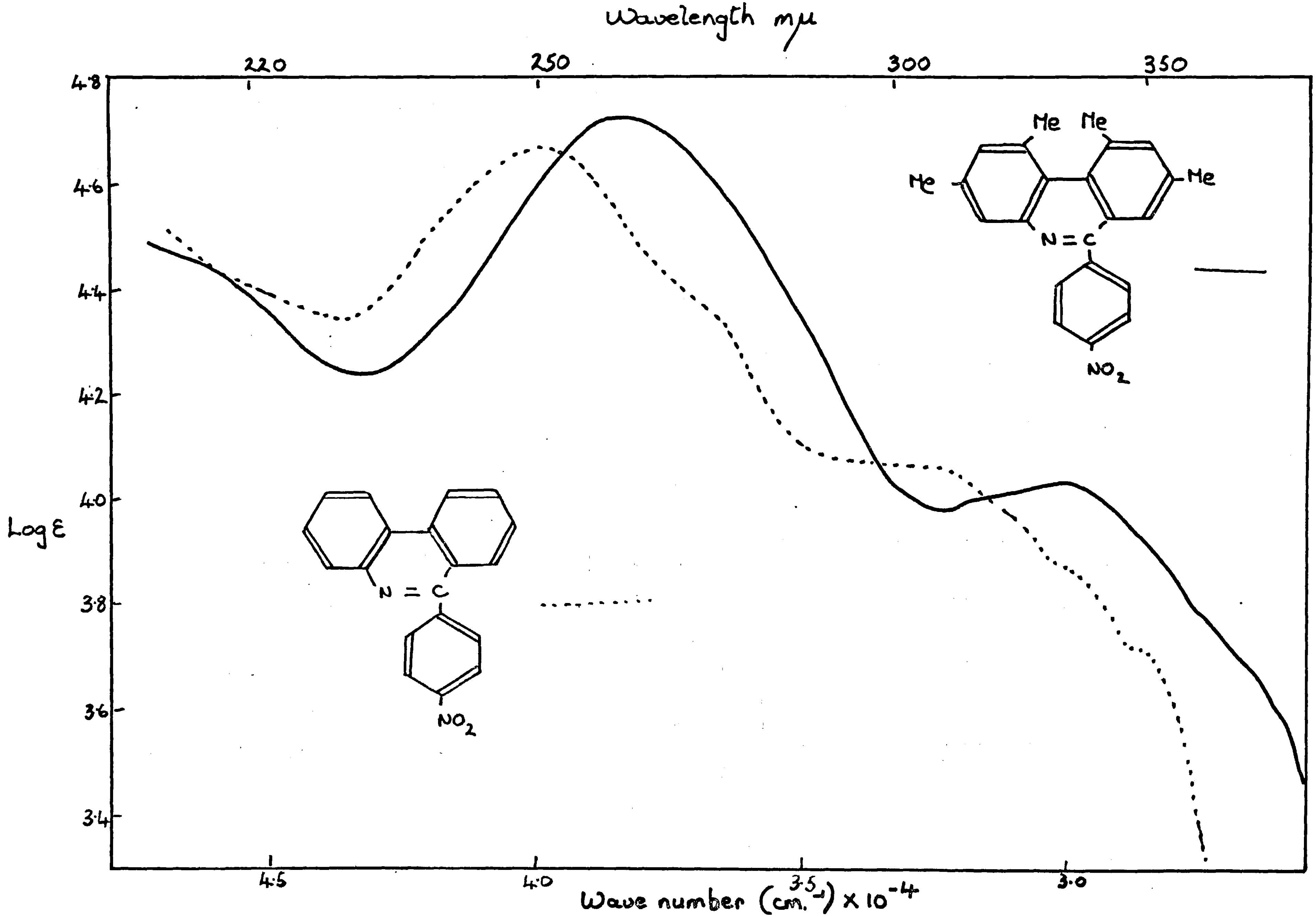
The reaction is completed by loss of a proton.

Considering steric effects one would expect considerable resistance to the formation of a phenanthridine substituted in the 4:5 positions.(111). From the model it seems easier for the attack by the carbonium ion to take place on a methyl group with the formation of a seven-membered ring.(1V). Before studying the tetramethylphenanthridine it was thought necessary to confirm its structure and with this in view 9-(*p*-nitrophenyl)-phenanthridine was prepared. The ultraviolet absorption spectra of these two compounds were then compared.



(111)

(1V)


Wavelength mμ
220
250
300
350
4·8
4·6
4·4
4·2
4·0
3·8
3·6
3·4
Log ε
4·5
4·0
3·5
3·0
Wave number (cm.⁻¹) x 10⁻⁴
Me
Me
Me
Me
N = C
NO₂
N = C
NO₂

Both phenanthridines were sparingly soluble in 95% ethanol and were dissolved by adding chloroform (B.P.Grade). The solutions examined contained 0.1% chloroform.

SUBSTANCE	MAIN ABSORPTION BAND	
	λ max.	ε max.
9-(p-Nitrophenyl)-phenanthridine	250.5	47,000
2:4:5:7-Tetramethyl-9-(p-nitrophenyl)-phenanthridine	260.5	53,000

The spectra of phenanthridine (Friedel and Orchin, U.V. Spectra of Aromatic compounds, No386, and Badger, Pearce and Pettit, J.Chem.Soc., 1951, 3199, Fig.1) and 9-phenylphenanthridine (Govindachari, Nagarajan, Pai and Arumugan, J.Chem.Soc., 1956, 4280 Fig.11) have been determined in ethanol.

FIG 1

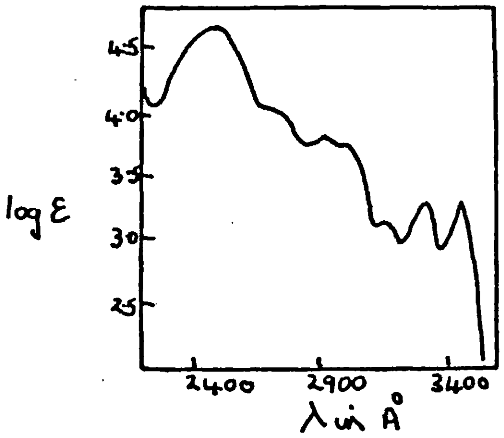
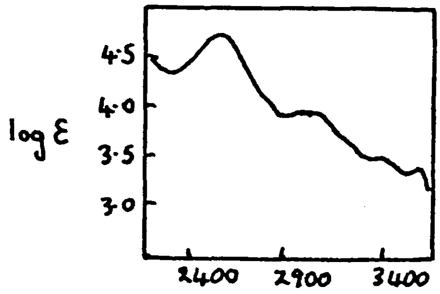


FIG11.



Each shows three main absorption bands. 9-Phenylphenanthridine shows a marked reduction in fine structure as compared with the parent compound. In the ' middle band' and particularly the 'long wave band' of this compound there is an increase in intensity of absorption which may be attributed to the 'conjugation effect' of the phenyl group.

The spectrum of 9-(p-nitrophenyl)-phenanthridine is very similar to that of 9-phenylphenanthridine but there is a further slight reduction in fine structure. The 'middle band' now appears as inflections, ca. λ,2700Å, ϵ 24,500 and λ,3000Å, ϵ,11,600. The two remaining peaks of the long wave band' in 9-phenylphenanthridine are now reduced to inflections, ca. λ,3300Å, ϵ,7,600 and λ,3500Å, ϵ,7,200. The absorption in both the regions is of much greater intensity resulting from the marked 'conjugation effect' of the p-nitro group.

Mills and Schofield (J.Chem.Soc.,1956,4213) studied the spectra of various methyl substituted 5:6-benzophenanthridines and showed that the spectra of 2- and 9-methyl and 2:9-dimethyl-5:6-benzophenanthridines were very similar to that of the parent hydrocarbon. However in 4-methyl and 4:9-dimethyl-5:6-benzophenanthridines, although the curves were still similar there was a decrease in fine structure and a marked bathochromic shift of the whole spectrum. The 'middle' and 'long wave' bands had decreased intensity relative to their isomeric compounds. These changes parallel those in phenanthrene and 1:4:5-trimethylphenanthrene(Newman,J.Amer.Chem.Soc.,1947,69,3023) and benzo-(c)-phenanthrene and 1-methyl-benzo-(c)-phenanthrene(idem,ibid, 1948,70,1913) and indicate considerable molecular overcrowding.

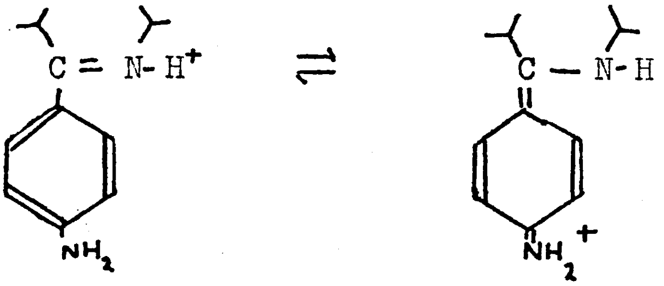
The absorption curves of 9-(*p*-nitrophenyl)-phenanthridine and 2:4:5:7-tetramethyl-9-(*p*-nitrophenyl)-phenanthridine are also very similar but in the methyl substituted compound there is the expected marked bathochromic shift of the whole spectrum accompanied by further loss in fine structure. The increased intensity of the main absorption peak is probably attributable to the normal substituent effect of alkyl groups. The 'middle band' is overlapped by the main peak and as a result the inflection present at *ca*. λ,2700Å, ε,24,500 in 9-(*p*-nitrophenyl)-phenanthridine is now much less distinct and only a trace of this feature remains at *ca*. λ,2800Å, ε,28,000. At longer wavelenghts the overlapping is less and there is a flat peak, λmax. 3310Å, εmax.10,700, λ min.3100Å, εmin. 9,400. The fine structure of the 'long wave band' is now very slight and of lower intensity.

Spectral evidence then definitely shows that (111) is formed rather than (1V). It is difficult to predict the spectrum of a compound of type (1V) but the similarity of the two spectra determined is so striking that the phenanthridine type structure for the methyl substituted compound is unquestionable.

Reduction to 2:4:5:7-tetramethyl-9-(*p*-aminophenyl)-phenanthridine was achieved in acetic acid solution using stannous chloride and hydrochloric acid.

Optical Work.

An unexpected difficulty was encountered at this stage, for in the presence of dilute acid, because of the possibility of resonance within the molecule, the aminophenanthridine has a bright red colour. This is supressed only in the presence of strong acid.



All salts formed between the aminophenanthridine and an optically active acid were orange-red in colour and solutions of these salts were too dark to view in the polarimeter. There was one exception. *l*-Menthoxyacetic acid (0.203g.,1mol.) and the aminophenanthridine (0.309g.,1 mol.) were dissolved in solvent X (20ml.) and had $\alpha_{5791}^{12.2^\circ}$ -1.89° (l = 2dcm.) after 2.5min. No change in rotation was observed at this temperature. The temperature was then increased ($\alpha_{5791}^{41^\circ}$ -1.86°) and again no mutarotation was observed. The solution was orange-yellow and it was difficult to take readings. After leaving at room temperature overnight there was still no change in rotation and the solution was therefore washed rapidly with dilute ice-cold ammonium hydroxide and water to remove the acid. It was then found to be inactive(after 3.5min.).

Attempts to get a second order change were then made. With tartaric, mandelic and menthoxyacetic acids no solvent or combination of solvents could be found to give a suitable crystalline salt. However with d-camphor -10-sulphonic acid (1.16g.,1 mol.) and amine (1.63g.,1 mol.) in benzene (100ml.) after boiling for a few minutes a bright red salt started to crystallise. The mixture was kept warm for about 1 hr. and the salt then filtered and dried. Yield 90%, m.p. 243-245°. (Found: C,71.3, H,7.2, N,5.1,S,5.7. $C_{33}H_{38}O_4N_2S$ Requires, C,70.8, H,6.9, N,5.0,S,5.7%).

The salt was decomposed at low temperatures by grinding with aqueous ammonium hydroxide, filtering the precipitated amine, washing and drying. The amine was then dissolved rapidly in cold chloroform or solvent X and viewed at about 10° in the polarimeter. Alternatively the salt was dissolved in cold chloroform and washed suitably. The chloroform solution was dried by shaking with anhydrous sodium sulphate and filtered into the polarimeter tube. In this way the first reading could be taken after 3-4 min. In all cases the amine obtained was inactive. The amine obtained by decomposition of the salt remaining in the filtrate in the above crystallisation was also inactive. A similar experiment was carried out using only $\frac{1}{3}$ mol. active acid but again the racemate was obtained, as was the case when the solvent used was chloroform/ light petroleum mixture.

Attempts are now being made to effect a resolution.

EXPERIMENTAL.

Attempted preparation of 2-amino-6:6'-ditolyl.

m-Tolidine.

Modified method of Schultz and Rohde (C. 1902,11,1447).

m-Nitrotoluene (411g.,2mol.) was dissolved in ethanol (500ml.) in a 5 l. 3-necked flask fitted with two double surface reflux condensers and an efficient mechanical stirrer. Sodium hydroxide solution (400g.,11mol. in 600ml. water) was then added and the mixture heated to boiling on a water bath. Zinc dust (600g.) was added in small portions as rapidly as possible. Initially on adding zinc a very vigorous reaction started and the rate of addition was slow. Later the zinc could be added more rapidly. At first a red colour developed which gradually faded. Addition of zinc took from 2-3hrs. and the mixture was heated another 30 mins. More alcohol was then added and the solution decanted from the sludge into conc. hydrochloric acid (2 l.). The reaction was very vigorous. The reaction flask was washed repeatedly with boiling alcohol until the washings were no longer coloured. This procedure avoided the necessity of dissolving up large quantities of zinc salts and unreacted zinc. More conc. acid was added to the acid solution until the precipitation of hydrochloride was complete. The cooled mixture was filtered to give the hydrochloride as a blackish solid. Washing with ether to remove traces of azo compound was not necessary. The crude hydrochloride was dissolved in the minimum amount of boiling water and treated with charcoal. It was filtered through kieselguhr on a sintered glass funnel to give a colourless solution. Concentrated hydrochloric acid was then added to the hot filtrate until the hydrochloride started to precipitate. It was then left to crystallise and finally filtered and dried. This reaction was carried out a number of times and the yield of hydrochloride was 230-236g., 54-55%. A total of 845g. hydrochloride were prepared in this way.

The base was obtained in practically theoretical yield by dissolving 285g. hydrochloride in 3 *l*. hot water. The base was then precipitated with 30% sodium hydroxide solution. At first it came down as an oil which eventually solidified. As the solution cooled more base crystallised out. The solid was filtered, ground in a mortar and dried. It was sufficiently pure for use in the next stage. It crystallised from benzene in plates, m.p.87-88°.

(Found: C,79.3; H,7.4; N,13.3. Calc. for $C_{14}H_{16}N_2$ C,79.3; H,7.5; N,13.2%).

Various m.p. have been recorded for *m*-tolidine.

Schultz and Rohde, *loc.cit.*,m.p. 87-88°.

Jacobsen and Fabian,*Ber.*,1895,*28*,2553, m.p. 106-107°.

Buchka and Schachbeck,*Ber.*,1889,*22*,838, m.p.108-109°.

Carlin and Foltz,*J.Amer.Chem.Soc.*,1956,*78*,1992,m.p.105-106°.

Loh, *loc.cit.*, m.p.87°.

60g. Hydrochloride were fractionally crystallised but each crop on conversion to free base had m.p. 87-88°.

The acetyl derivative had m.p. 283-284° on crystallisation from ethanol. Jacobsen and Fabian,<u>loc</u>.<u>cit</u>., m.p. 281°, Carlin and Foltz,<u>loc</u>.<u>cit</u>., m.p. 284-285°. It was hydrolysed by boiling with 70% sulphuric acid for 4 hrs. The base had m.p. 87-88°. Crystallisation from ethanol, light petroleum or water gave a specimen of the same m.p. Previous workers used water as solvent for crystallisation, but the base was found to be sparingly soluble in hot water. On one occassion however on crystallising from water a specimen, m.p.104-105° was obtained. Prolonged drying in a vacuum des~~s~~icator did not alter the m.p. It analysed for anhydrous base.
(Found: C,78.8; H,7.9; N,13.2%).

Mixed m.p. with specimen m.p. 87-88°, was 103-105°. Heating in an oven at 120° for 30 mins. however gave both specimens in low melting form.

<u>Nitration of</u> m<u>-Tolidine.</u>

Loh <u>loc</u>.<u>cit</u>.

<u>m</u>-Tolidine (106g.,1 mol.) was dissolved in conc. sulphuric acid (700 ml.,<u>d</u>.1·84) and cooled to -5° with stirring. Finely ground potassium nitrate (50.5g.,1 mol.) was then added slowly below 0°. Addition took 2 hrs. and stirring was continued for another hr. The solution was poured into 6<u>l</u>. crushed ice and the sulphate which precipitated, filtered and ground in a mortar with 30% sodium hydroxide. The base was filtered and dried. Yield 118g., m.p. 165-170° (92%).

It was crystallised from 2½ l. industrial spirit and filtered from a small amount of brown insoluble material. First crop, 48g., m.p. 170-173°, second crop 35g., m.p. 168-171°. Yield 64%. Repeated crystallisations raised the m.p. to 173-175° but the yield in the next stage was not improved by this further purification of the nitrotolidine. A total of 364g. mononitrated product was obtained from 483g. m-tolidine, representing an overall yield of 62%.

Method 2.

m-Tolidine (1.5g.,1mol.) was dissolved in a mixture of conc. sulphuric acid (15ml.) and 20% oleum (3ml.). It was nitrated as above with potassium nitrate (0.75g.,1mol.) and finally poured into ice-water (400ml.). Yield of base 1.1g. (62%) m.p.159-164°. After crystallisation a mixed m.p. with the product from the above nitration showed no depression.

Deamination of the above nitroamine (A).

Cf. Loh, loc.cit.

This reaction was scaled up with improved yields. On the small scale steam distillation was preferred for isolating the product but this method was too slow for large scale work.

Nitro-m-tolidine(85.7g.,1mol.)was dissolved in hot conc. hydrochloric acid (200ml.,6 mol.) and water (300ml.). It was cooled to 0° - -5° with stirring, and diazotised at this temperature with sodium nitrite solution (48.5g., 2.1mol. in

75ml. water). The solution was then stirred for an additional hour. Hypophosphorous acid (1,100ml.,25mol.) precooled to 0° was added and stood overnight at 5°. (On smaller scale runs this mixture was steam distilled but when 25.7g. nitro-<u>m</u>-tolidine were used, steam distillation of the product took about 7 hrs. The nitroditolyl solidified and was filtered and dried, m.p.63-65°).

The gum which separated was dissolved in ether and the solution extracted with ether. The combined ether solutions were washed well with 10% sodium hydroxide solution, brine, dilute hydrochloric acid,brine and finally dried over calcium chloride. The ether was evaporated and the residue distilled in a vacuum. First fraction,b.p.195-200°/15-16mm, m.p.63-65°, 31g.,41%. A second higher boiling fraction was obtained and both fractions solidified immediately. Fraction 2 crystallised from ethanol in yellow needles, m.p. 63-64°. Yield 5.5g., 7%. This nitro compound was sufficiently pure for use in the next stage, however one further crystallisation of the combined product raised the m.p. to 65-66°. A total of 340g. nitro-<u>m</u>-tolidine A, was converted into 133.5g. nitroditolyl B, Yield 45%.

<u>Reduction of B.</u>

Loh, <u>loc</u>.<u>cit</u>.

B (4g.) was reduced catalytically in ethanol with platinum oxide catalyst and the product worked up in the usual way. The amine was purified by crystallisation of the hydrocloride. Yield 2.4g.,70%, m.p.57-58°. It crystallised from dilute ethanol in white flakes, m.p.59-60°. Loh (<u>loc.cit.</u>) m.p.54-56°.

The benzoyl derivative was prepared in the usual way and crystallised from dilute alcohol in needles,m.p. 129-130°. (Found: N,5.1. $C_{21}H_{19}NO$ requires N 4.7%).

<u>Oxidation of nitroditolyl (B).</u>

B (1g.) was boiled under reflux for 6 hrs. with potassium permanganate (8g.), sodium carbonate (1g.) and water (150ml.). A white solid collected in the condenser. After cooling, the solution was acidified with dilute sulphuric acid and sodium bisulphite added to dissolve the manganese dioxide. The white solid was dissolved in ether and the solution extracted with ether. The ether solution was washed with acid and brine and finally extracted with 30% sodium hydroxide solution. Acidification of the alkaline solution precipitated a white solid, m.p. 262-266°. Yield 0.35g.,29%. Evaporation of the ether gave a yellow solid which was identified as starting material. All attempts to improve the yield by longer heating were unsuccessful, some starting material was always recovered and part of the material was unaccounted for. The acid D crystallised from dilute ethanol in white flakes, m.p.266-267°. (Found: N 4.9. $C_{14}H_{9}NO_{6}$ requires N,4.9%-).

6-Nitrodiphenic acid however has m.p. 248-250° (Bell and Robinson, *J.Chem.Soc.*,1927,1696). A mixed m.p. of D with this acid showed a depression. Mixed m.p. 227-236° .

Anhydride of D.

D,(0.15g.) was boiled with acetic anhydride (2ml.) for 1 hr. On cooling clusters of small white needles crystallised, m.p. 194-195° .

Bell and Robinson,*ibid*.,2238 give m.p. 268° for 5-nitrodiphenic acid and m.p. 193-195° for the anhydride. 6-nitrodiphenic acid does not form an anhydride.

Decarboxylation of D.

D, (0.90g.) was boiled with quinoline (15ml.) in the presence of copper powder. After 1hr. the cooled solution was poured into dilute hydrochloric acid, extracted with ether and the ether extract washed. The ether was evaporated and the residue steam distilled. A light brown oil distilled which solidified on standing. Yield,0.2g.,32%, m.p. 59-62° . It was crystallised from light petroleum (b.p.40-60°), m.p. 63-64° . A mixed m.p. with an authentic specimen of 3-nitrodiphenyl,63-64° .

Hence A is 3-nitro-*m*-tolidine, B, 3-nitro-6:6'-ditolyl, C, 3-amino-6:6'-ditolyl and D, 5-nitrodiphenic acid.

3-Nitro-4-bromo-4'-piperid~~yl~~ino-6:6'-ditolyl.

To 3-nitro-4:4'-dibromo-6:6'-ditolyl(see Loh, *loc.cit.*) (0.4g.) was added piperidine (1 ml.). The solid slowly dissolved to give a dark, red-brown solution.which was warmed on a boiling water bath for 5 mins. On cooling an orange solid was obtained which crystallised from ethanol in clusters of orange needles. It was recrystallised from light petroleum (b.p. 40-60°) and had constant m.p. 105-107°. Starting material, m.p. 100-101°, mixed m.p. 90-92°.

(Found: N,6.9. $C_{19}H_{21}N_{2}O_{2}Br$ requires N,7.2%).

Synthesis of 2-Amino-6:6'-ditolyl.

2-Iodo-3-nitrotoluene.

Starting material was 2-amino-3-nitrotoluene,m.p.95-97°. 2-Amino-3-nitrotoluene (45g.) was converted into 2-iodo-3-nitrotoluene using the exact conditions of Carlin and Foltz (*J.Amer. Chem.Soc.*,1956,*78*,1997). It crystallised from alcohol in pale yellow cubes, m.p. 66-68°. Yield 68.5g., 87%. Carlin and Foltz m.p. 66-68°. (see also p.158)

2:2'-Dinitro-6:6'-ditolyl.

2-Iodo-3-nitrotoluene (25g.) was treated with an equal weight of copper powder at 150°, the addition of copper taking about 1 hr. On each addition,the temperature rose above the bath temperature and in some cases the tube had to be removed from the bath to cool in order to control the reaction. ~~The~~

The mixture was then heated at 150° for another 30 mins. and finally at 190-200° for 15 mins. It was extracted with boiling benzene and filtered from the copper. The benzene was distilled and on cooling the residue solidified. It crystallised from ethanol, first crop 8.5g.,m.p. 110-112°, second crop, 2g., m.p. 109-111°. Yield 81%. Carlin and Foltz, loc. cit.,m.p. 109-110°; They carried out the reaction at 200° but it was found impossible to control the reaction at this high temperature.

2-Amino-2'-nitro-6:6'-ditolyl.

2:2'-Dinitro-6;6'-ditolyl(8g.,1 mol.) was dissolved in boiling industrial spirit (50ml.) in a 250ml. 3-necked flask fitted with mechanical stirrer, dropping funnel and condenser. A solution of sodium sulphide,$9H_2O$, (8.6g.,1.2mol.) and sulpur (2.3g.,2.4mol.) in water (50ml.) was added during 15 mins. and the mixture refluxed for 3 hrs. It was then concentrated to 50ml. and after cooling the solid was filtered and extracted repeatedly with 10% hydrochloric acid. The acid extracts were made alkaline and the precipitated solid again treated with dilute hydrochloric acid. The acid solution was boiled for some time and filtered from an oily substance which was found to be sulphur. The filtrate was made alkaline and the yellow solid filtered and dried. It was crystallised from ethanol(20ml.) 4.7g.,66%,m.p. 123-124°.

Angeletti and Guala,Gazzetta,1931,61,651, m.p.122-123°.

Sin-ichi Sako,*Bull*.*Soc*.*Japan*,1934,*9*,393, carried out this same reduction with sodium sulphide at 50° and obtained a 73% yield of nitroamine, m.p. 121-123°. He stated that in boiling ethanol the product was 4:5-dimethylphenazone oxide, m.p.153°. In our case only nitroamine was isolated.

2-Nitro-6:6'-ditolyl.

The above nitroamine (4.8g.,1 mol.) was dissolved in hot conc. hydrochloric acid (5ml.,2.5mol.) and water (20ml.). It was cooled to 4° and diazotised at this temperature with sodium nitrite solution (1.52g.,1.1 mol. in the minimum quantity of water). After 30 mins., hypophosphorous acid (40ml.,15mol.) precooled to 0° was added with stirring. A vigorous reaction started and an oil began to separate. After standing overnight (10°) the product was extracted with ether and the ether extract washed. After evaporation of the ether the residue was steam distilled from alkaline solution. 2-Nitro-6:6'-ditolyl came over as a pale yellow oil which soon solidified. It was filtered and dried. Yield 3.3g.,73%, m.p. 40-42°. It crystallised from ethanol in flakes,m.p. 42-43°. Yield 2.3g.,51%. It melted on mixing with 3-nitro-6:6'-ditolyl.

Ritchie,*loc*.*cit*.,m.p.45°, Mascarelli and Angeletti,(*Gazzetta*, 1938,*68*,29) m.p.42-43°

2-Amino-6:6'-ditolyl.

2-Nitro-6:6'-ditolyl(1.1g.) in ethanol(50ml.) was shaken in a hydrogenator with platinum oxide catalyst (0.05g.) at a hydrogen pressure of 85lbs./sq.". After 4hrs. the solution was filtered from the catalyst and the alcohol evaporated. The residue was purified by crystallising the hydrochloride and the amine obtained as a white solid, m.p.27°. Yield 0.7g., 73%. It crystallised from light petroleum (b.p. 40-60°) in needles after cooling in ice. M.p. unchanged.

(Found: N,6.9. Calculated for $C_{14}H_{15}N$ N,7.1%).

Mascarelli and Angeletti,loc.cit.,m.p.105°

Ritchie,loc.cit., colourless oil, b.p.169-170°

2-p-Nitrobenzamido-6:6'-ditolyl.

2-Amino-6:6'-ditolyl (0.15g.) and p-nitrobenzoyl chloride (0.15g.) were dissolved in pyridine and warmed slightly. A solid separated which was filtered,washed and dried. It crystallised from ethanol in pale yellow rectangular plates, m.p. 122-123°. Ritchie,loc.cit.,m.p.122°.

(Found: N,8.3. Calculated for $C_{21}H_{18}N_2O_3$ N,8.1%).

Tetramethyl Series.

2:4-Dimethyl-6-nitroaniline.

Willgerodt and Schmierer, Ber.,1905,38,1472.

2:4-Dimethyl-6-nitroacetanilide (200g.) in conc. sulphuric acid (300ml.) and water (50 ml.) was heated at 120-130° for

15 mins. The solution was poured into ice (4*l*.) and the solid filtered and dried. Dilution of the filtrate did not give any more amine. 2:4-Dimethyl-6-nitroaniline crystallised from industrial spirit in orange-red needles, m.p. 70-71°. Yield 143g., 90%. Willgerodt and Schmierer (*loc.cit.*) m.p. 70°. Nolting and Ford, *Ber.*, 1885, *18*, 2688, m.p. 76°. In this way 624g. amine were prepared from 900g. acetyl derivative.

2:4-Dimethyl-6-nitroiodobenzene. (*cf*.p.154).

2:4-Dimethyl-6-nitroaniline (83g.) was dissolved in hot glacial acetic acid (600ml.) and diazotised at 15-20° by the addition of a solution of sodium nitrite (50g.) in conc. sulpuric acid (280 ml.). Addition took 30min. and the solution was stirred for another 30 min. before pouring into ice (2*l*.). Urea (50g.) was added to destroy excess nitrous acid and finally potassium iodide solution (118g. in 600ml. water) was added carefully to the stirred solution when a vigorous reaction started. After about 2 hrs. the solution was decolourised with sodium bisulphite and the iodo compound filtered, washed with alkali and dried. It crystallised in pale yellow rhombs from benzene (200ml.). 72.5g., m.p. 106-107°. Concentration of the mother liqour gave more solid which after recrystallisation gave another 17.5g. pure 2:4-dimethyl-6-nitroiodobenzene. Yield 64%. Further crops were discarded since repeated crystalisations did not raise the m.p. to that of the pure compound. Blanksma, *Rec.trav.chim.*, 1906, *25*, 168, m.p. 105°. From 642g. amine, 690g.

were obtained.

2:2';4:4'-Tetramethyl-6:6'-dinitrodiphenyl.

2:4-Dimethyl-6-nitroiodobenzene (50g.) was treated with an equal weight of copper powder at 130-135°. The reaction was very vigorous and the scale could not be increased. Addition of copper took 1 hr. and after then heating at 155-160° for 30min. the product was extracted with monochlorobenzene. The dinitro compound crystallises from ethanol or benzene in pale yellow prisms, m.p. 136-137°. Yield 23g.,85%. 670g. Iodo compound were converted into 300g. dinitro compound.
(Found: C,63.5, H,4.7, N,9.6. $C_{16}H_{16}N_2O_4$ requires C,64.0, H,5.3, N,9.3%).

2:2':4:4'-Tetramethyl-6-amino-6'-nitrodiphenyl.

The above dinitro compound (60g.,1 mol.) was dissolved in boiling ethanol (600ml.) in a 2l. 3-necked flask fitted with mechanical stirrer. A solution of sodium sulphide,$9H_2O$ (57.6g., 1.2 mol.) and sulphur (15.4g.,2.4 mol.) in water 150 ml. was added during 15 min. and the mixture refluxed 3 hrs. It was then concentrated to about 400ml. and cooled in ice with stirring. The solid was collected by filtration and then extracted several times with boiling dilute hydrochloric acid (1:3, acid:water). The extracts were filtered hot through a sintered glass funnel and a total of 4l. solution was used. On cooling the hydrochloride crystallised and was filtered and dried. Yield 39g. Concentration

of the filtrate to small bulk gave another 6g. hydrochloride. Yield 74%. It was eventually found most convenient to use the hydrochloride directly in the next step without further purification. The hydrochloride is readily hydrolysed by water liberating the amine as a bright yellow solid. 2:2':4:4'-Tetramethyl -6-amino-6'-nitrodiphenyl crystallises from ethanol in needles, m.p. 117-118°.
(Found: C,71.6, H,6.9, N,10.3. $C_{16}H_{18}N_2O_2$ requires C,71.1, H,6.7, N,10.4%).

2:2':4:4'-Tetramethyl-6-nitrodiphenyl.

The above amine was diazotised in the usual way or by the indirect method. The following method gave the best results.

A paste of the above hydrochloride (30.5g.,1mol.) in conc. hydrochloric acid (20ml. 2 mol.) and water (50ml.) was diazotised at 10-12° by the addition of sodium nitrite solution (8.3g.,1.2mol. in 20ml. water). The mixture was left at 10° for 1 hr. and diluted to 300ml. to give a clear solution. A small amount of tar was formed which was removed by decanting through glass wool. The diazo solution was decomposed by the addition of hypophosphorous acid (180ml.). The addition of copper powder speeded up the reaction, which was complete in 1 hour at 15-20°. At lower temperatures the reaction was very slow and the yield was the same. The solid was filtered and then steam distilled from alkaline solution. Steam distillation was very slow, taking 30-40 hrs. but this method gave the purest product. All other methods tried gave the nitro compound contaminated with red impurity. The nitro compound solidified in the distillate and was separated by filtration. It crystallised from ethanol in pale yellow rhombs, m.p. 107-108°, yield, 13.5g., 54%. A total of 74g. 2:2':4:4'-tetramethyl-6-nitrodiphenyl were prepared. (Found: C,75.2, H,6.6, N,5.6. $C_{16}H_{17}NO_2$ requires C,75.3, H,6.7, N,5.5%).

2:2'4:4'-Tetramethyl-6-aminodiphenyl.

The above nitro compound was reduced either catalytically (PtO_2 catalyst, EtOH solvent) or by stannous chloride and hydrochloric acid. Catalytic reduction was preferred since working up was more rapid and the yield nearly quantitative.

In the catalytic reduction of nitro compound (10g.) after evaporation of ethanol the residue was treated with conc. hydrochloric acid and the solid hydrochloride filtered. It crystallised from dilute acid in white needles. The amine was liberated with ammonia as a white oil which was extracted in ether. After evaporation of the ether the residue eventually solidified, 8.5g. 96% m.p. 50-51°. The amine was very soluble in all usual solvents and could not be crystallised. From dilute ethanol it separated as an oil. B.p. 144°/ 5mm.
(Found: C,72.9, H,7.5, N,4.9. $C_{16}H_{20}NCl$ requires C,73.4, H,7.7 N,5.4%).

2:2':4:4'-Tetramethyl-6-p-nitrobenzamidodiphenyl.

This derivative was prepared from the amine in the usual way. Later it was found most convenient to purify the amine directly in this way. In the reduction of nitro compound (10g.) after evaporation of all the solvent the residue was dissolved in dry pyridine and treated with *p*-nitrobenzoyl chloride (8g., 1 mol.) dissolved in pyridine. The solution was warmed on a steam bath for 30 mins. and after standing overnight poured into dilute hydrochloric acid. The oil precipitated soon solidified and was filtered, washed well and dried. It crystallised from ethanol in pale yellow refracting prisms or in needles, m.p. 140-141°. First crop 9.5g., recrystallisation of a second crop gave another 0.5g. Yield, 75%.

(Found: N,7.2. $C_{23}H_{22}N_2O_3$ requires N 7.5%).

2:4:5:7-Tetramethyl-9-(p-nitrophenylphenanthridine).

2:2':4:4'-Tetramethyl-*6*-*p*-nitrobenzamidodiphenyl(8g.) and phosphorus oxychloride (16g.,9.3ml.) in nitrobenzene (25ml.) were heated in an oil bath at 175-180° for 12hrs. The product was poured into alkali and steam distilled to remove nitrobenzene. The residue in the flask eventually solidified, the distillation was stopped and the solid filtered and dried. It crystallised from ethanol (300ml.) in clusters of bright yellow needles. Closer examination revealed also pale yellow rhombs. Yield 5.5g., it melted partially at 160° and then completly at 177-178° (*cf*. Ritchie, *loc*.*cit*.,159). A second crop ,0.5g. of same m.p. was obtained. Yield, 78%.This substance exists in at least two forms, and the exact conditions for producing these forms are uncertain. The rhombs appear to be the stable form for eventually only this form could be obtained, pale yellow, m.p. 177-178°. The brighter yellow needles appeared again in subsequent preparations. A detailed study of the m.p. was carried out on a Kofler block. In different crystallisations flat needles m.p. 159-160° and others m.p. 177-178° were obtained. In all crystallisations varying amounts of rhombs, m.p. 177-178° were obtained. The ultraviolet absorption spectra were identical. (Found: C,77.8,H,5.9,N,8.0. $C_{23}H_{20}N_2O_2$ requires C,77.5, H, 5.7 N,7.9%).

25g. Nitrophenanthridine were prepared from 33g. p-nitrobenzoyl-derivative,(Similar behaviour was shown with benzene as solvent)

6-p-Nitrobenzamidodiphenyl.

This compound was prepared in the usual way and crystallised from large volumes of ethanol in pale yellow needles, m.p. 158°. Morgan and Walls, J.Chem.Soc.,1931,2447, m.p.158.5°.

9-p-Nitrophenylphenanthridine.

6-p-Nitrobenzamidodiphenyl(1.4g.) and phosphorus oxychloride (2ml.) in nitrobenzene (5ml.) were heated at 180° for 8 hrs. On pouring into water a solid was precipitated which was filtered washed and dried. It crystallised from a mixture of ethanol and benzene in long, fine, pale yellow felted needles. Yield, 1.1g., 80%, m.p. 191-192°. Cymerman and Short, J.Chem.Soc., 1949,703, m.p. 190-191°, Morgan and Walls, loc.cit., m.p. 192°.

2:4:5:7-Tetramethyl-9-(p-aminophenyl)-phenanthridine.

2:4:5:7-Tetramethyl-9-(p-nitrophenyl)-phenanthridine (7.3g.,1 mol.) dissolved in hot glacial acetic acid (40ml.) was treated at 70° with a solution of stannous chloride,$2H_2O$ (15g.,3mol.) in conc. hydrochloric acid (18ml.,9 mol.). The solution was boiled under reflux for 15 mins. and the reaction completed by heating on a boiling water bath for 45min. Pouring into excess sodium hydroxide solution (10%) precipitated a pale yellow solid which was filtered and washed with water. It dissolved in dilute hydrochloric acid to give an orange-red solution which was filtered from a trace of impurity. The amine was then reprecipitated with alkali,filtered and dried. It was treated with boiling benzene (100ml.) and after filtering from insoluble tin salts the filtrate was concentrated to about 40 ml. Light petroleum (60-80°) was added until a slight turbidity was produced. The solution was boiled until a clear solution was obtained and then on cooling the amine crystallised in clusters of pale yellow prisms. First crop,4.9g., m.p. 195-196°. Second crop, o.3g., m.p. 193-195°. Yield 77%.

A total of 13g. 2:4:5:7-tetramethyl-9-(p-aminophenyl)-phenanthridine was prepared in this way.

(Found: C,84.3, H,6.5, N,9.2. $C_{23}H_{22}N_2$ requires C,84.6, H,6.8, N,8.6%).

THE RELATION BETWEEN CONFIGURATION AND CONJUGATION IN DIPHENYL DERIVATIVES. PART VI. SOME ALKYLDIPHENYLS

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444. *The Relation between Configuration and Conjugation in Diphenyl Derivatives. Part VI.* Some Alkyldiphenyls.*

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A number of dialkyldiphenyls have been prepared and their ultraviolet absorption spectra studied. In the series of 2 : 2′-dialkyldiphenyls, contributions from a discrete conjugation band are still apparent when the alkyl groups are ethyl or *iso*propyl but are no longer evident when they are *tert.*-butyl.

A re-examination of the ultraviolet absorption spectrum of 2 : 2′-ditolyl (Part III) [1] has shown that slight conjugation between the two benzene rings is still apparent, in spite of the steric effect of the *o*-methyl groups, the inflection at *ca.* 227 mμ being regarded as a vestigial conjugation band displaced to shorter wavelength.

We have now prepared 2 : 2′-diethyl- and 2 : 2′-di*iso*propyl-diphenyl; 2 : 2′-di-*tert.*-butyldiphenyl (Lesslie and Turner, unpublished work) has also been available and we have examined the absorption spectra of these three compounds (Fig. 1, Table 1). The spectra show a progressive decrease in conjugation with increasing size of the alkyl groups until with 2 : 2′-di-*tert.*-butyldiphenyl no trace of a discrete conjugation band remains. In the other three compounds the inflection at *ca.* 227 mμ is apparent, its intensity decreasing slightly from methyl to *iso*propyl. Considering the compounds in the reverse order, it is seen that the absorption at the minimum (between the short-wave band and the long-wave fine structure) at 249·5 mμ ($\varepsilon_{\text{min.}}$ 290) in di-*tert.*-butyldiphenyl moves to progressively longer wavelengths ($\lambda_{\text{min.}}$ 254, 258·5, 260·5 mμ in di*iso*propyl-, diethyl- and dimethyl-diphenyl respectively) and is of correspondingly greater intensity as the contribution from the vestigial conjugation band becomes more important and overlaps the long-wave band. In diethyl- and dimethyl-diphenyl this overlapping has obliterated one of the fine-structure bands of the alkylbenzene partial chromophore which is present as an inflection at 258 mμ in the other two compounds.

Table 1. *Ultraviolet absorption spectra of 2 : 2′-dialkyldiphenyls.*

Diphenyl compound	$\lambda_{\text{infl.}}$	ε	$\lambda_{\text{min.}}$	ε	Long-wave fine structure $\lambda_{\text{max.}}$	ε
2 : 2′-Dimethyl [1]	(*ca.* 227)	6800	260·5	770	263·5	800
					271	600
2 : 2′-Diethyl	(*ca.* 227)	6000	258·5	685	263·5	730
					271	560
2 : 2′-Di*iso*propyl	(*ca.* 227)	5500	254	630	(258)	640
					263·5	720
					271	560
2 : 2′-Di-*tert.*-butyl	—	—	249·5	290	(258)	380
					263·5	430
					270	330

Solvent, 95% ethanol; wavelengths (mμ) in parentheses denote inflections.

All four compounds show at least two bands of the alkylbenzene partial chromophores at 263·5 and 270—271 mμ. The intensities of these bands are slightly reduced for the diethyl and di*iso*propyl compounds in comparison with those for 2 : 2′-dimethyldiphenyl and much reduced for the di-*tert.*-butyl compound (in which they are rather more than twice those of *tert.*-butylbenzene). Thus, except perhaps in di-*tert.*-butyldiphenyl, the long-wave band system is overlapped by the vestigial conjugation band.

The data for the alkylbenzenes are taken from Stair,[2] the Catalogue of the Ultraviolet Spectral Data of the American Petroleum Research Institute Project No. 44, and, in the case of ethylbenzene, from our own work.

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* Part V, *J.*, 1955, 2708.

3 : 3′- and 4 : 4′-Diethyldiphenyl show the expected light-absorbing properties (Fig. 2; Table 2). Both are typical conjugated diphenyls, the second compound showing the long-wave shift and the increased intensity of absorption characteristic of 4 : 4′-disubstituted diphenyls (cf., for example, Williamson and Rodebush[3]); similar behaviour is exhibited by 4 : 4′-di*iso*propyldiphenyl (Table 2). For none of these compounds was long-wave fine structure observed. The 3 : 3′-diethyl compound is thus in marked contrast to 3 : 3′-dimethoxydiphenyl where an intense long-wave band is present.[3] The effect of *mm*′-substituents on the absorption spectrum of diphenyl has been considered by Wenzel[4] (cf. Platt[5]), who suggests that the " hidden " contribution from the phenyl partial chromophores in diphenyl itself becomes evident when the system is strongly perturbed by appropriate substituent groups which interact (by mesomerism) with the phenyl groups. However alkyl groups (unlike alkoxy-groups) exhibit only weak interactions with a benzene ring and in any case the absorption contributions from the alkylphenyl partial chromophores occur at shorter wavelengths than those from the alkoxyphenyl partial chromophores, so that overlapping by the conjugation band will be much greater in 3 : 3′-dialkyl- than in 3 : 3′-dialkoxy-diphenyls.

TABLE 2. *Ultraviolet absorption spectra of* 3 : 3′- *and* 4 : 4′-*dialkyldiphenyls.*

Diphenyl compound	Minimum		Conjugation band	
	$\lambda_{min.}$	ε	$\lambda_{max.}$	ε
Diphenyl	222	4300 *	249	17,300 *
3 : 3′-Diethyl	228·5	6200	251	16,500
4 : 4′-Diethyl	226·5	4500	256·5	22,500
4 : 4′-Di*iso*propyl	226	4600	256·5	23,500

Solvent, 95% ethanol.

* Amended values, means of three determinations each.

FIG. 1.

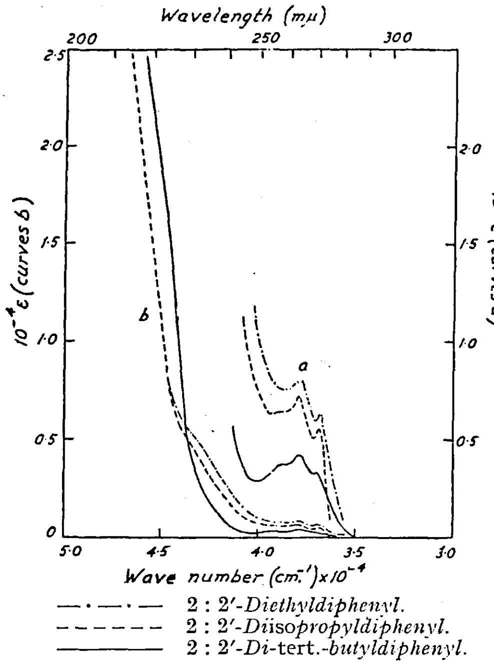
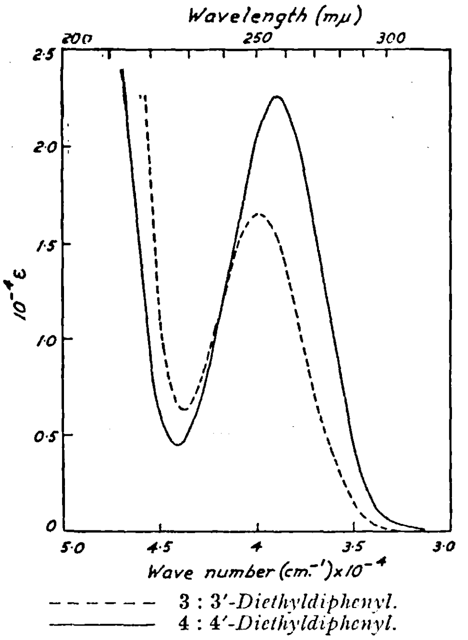


FIG. 2.



2 : 2′-Diethyldiphenyl * was prepared by three methods. It was obtained in 45—50%

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* *Added, May 25th,* 1955.—The 2 : 2′-diethyldiphenyl has now been examined by gas chromatography and found to contain appreciable quantities of impurities. A sample was purified by three crystallisations from ethanol at *ca.* −35° and redistilled; the spectral data now given in Table 1 were determined on this specimen. We are indebted to Dr. E. A. Johnson, who carried out this work, and to Dr. A. T. James for use of the gas chromatography apparatus.

overall yield from *o*-ethylaniline *via* *o*-ethyliodobenzene and an Ullmann reaction (cf. Mascarelli and Longo [6]). Reduction with iron and water and the use of sulphuric acid instead of hydrochloric acid for diazotisation avoided the formation of the 4-chloro-2-ethyl-1-iodobenzene obtained by these authors as a by-product. Treatment of *o*-ethylphenylmagnesium bromide with anhydrous cupric chloride gave 2 : 2′-diethyldiphenyl in 13—14% overall yield from *o*-ethylaniline (method of Krizewsky and Turner [7]). *cyclo*Hexanone was ethylated with ethyl iodide and sodamide. Some 2-ethyl*cyclo*hexanone was obtained, together with 2 : 2-diethyl*cyclo*hexanone, identified as the semicarbazone. 2-Ethyl*cyclo*hexanone was treated with *o*-ethylphenylmagnesium bromide, and the alcohol obtained was dehydrated with formic acid. Dehydrogenation of the resulting 2 : 2′-diethyl-3 : 4 : 5 : 6-tetrahydrodiphenyl gave 2 : 2′-diethyldiphenyl.

For the preparation of 2 : 2′-di*iso*propyldiphenyl an Ullmann reaction was carried out on methyl 3-iodo-4-*iso*propylbenzoate, made from the corresponding 3-amino-compound. The resulting methyl 6 : 6′-di*iso*propyldiphenyl-3 : 3′-dicarboxylate was hydrolysed and the acid decarboxylated.

3 : 3′-Diethyldiphenyl was obtained by the deamination of 3 : 3′-diethylbenzidine with hypophosphorous acid. 4 : 4′-Diethyldiphenyl was prepared by the Krizewsky–Turner method [7] from *p*-bromoethylbenzene or, better, by an Ullmann reaction on *p*-ethyliodobenzene.[8]

4 : 4′-Di*iso*propyldiphenyl was made by an Ullmann reaction on *p*-iodo*iso*propylbenzene; it has been described as existing in two forms [8, 9, 10] with melting points 49° and 65—66°. We obtained only the higher-melting form.

EXPERIMENTAL

o-*Ethylaniline*.—*o*-Ethylnitrobenzene and *o*-ethylaniline were available commercially but initially were obtained from 1-ethyl-2 : 4-dinitrobenzene.[11] This was reduced either with disodium disulphide or with ammonium hydrogen sulphide [12, 13] to 4-amino-1-ethyl-2-nitrobenzene. Deamination by the action of hypophosphorous acid on the diazo-compound gave *o*-ethylnitrobenzene. Cline and Reid [13] record that reduction of this nitro-compound by iron and hydrochloric acid gave a poor yield of *o*-ethylaniline. By carrying out a similar reduction in presence of alcohol [14] a 68—70% yield of pure base was obtained. The crude base was steam-distilled and the total steam-distillate treated with acetic anhydride (102 g.). The acetyl derivative was filtered off and crystallised from aqueous ethanol: it had m. p. 112—113° (126 g. from 151 g. of nitro-compound). By hydrolysis with 20% hydrochloric acid *o*-ethylaniline (85 g., 70%) was obtained, having b. p. 210—211°, $n_D^{22\cdot5}$ 1·5598.

2 : 2′-*Diethyldiphenyl*.—(*a*) *o*-Ethylaniline was diazotised in sulphuric acid, and aqueous potassium iodide added. *o*-Ethyliodobenzene, b. p. 90°/12 mm., was obtained in 80% yield. The iodo-compound (150 g.) was heated with an equal weight of copper bronze in a bath kept at *ca*. 240° for 3 hr. The organic product was extracted with boiling chlorobenzene and, after removal of solvent, the residue was fractionated under reduced pressure. 2 : 2′-Diethyldiphenyl was finally distilled from sodium (yield 42·5 g., 60%) and had b. p. 142—143°/14—15 mm., n_D^{25} 1·5624 (Found: C, 91·4, H, 8·5. Calc. for $C_{16}H_{18}$: C, 91·4; H, 8·6%).

(*b*) *o*-Bromoethylbenzene (b. p. 63—64°/8—9 mm., n_D^{25} 1·5476) was best prepared by a Sandmeyer reaction, the base being diazotised in hydrobromic acid. A Grignard reagent was made from it and anhydrous cupric chloride gradually added, giving 2 : 2′-diethyldiphenyl in 28% yield.

2-*Ethyl*cyclo*hexanone*. *cyclo*Hexanone (98 g., 1 mole) was added gradually during 1 hr. to sodamide (43 g., 1·1 mole) in boiling benzene (800 c.c.). The mixture was heated for 1½ hr. and ethyl iodide (156 g., 1 mole) then added during 1 hr. After further heating (2½ hr.) of the mixture, water was added and the benzene layer separated. Solvent was removed and the residue was twice distilled under reduced pressure. The first fraction (33 g.), b. p. 68°/16 mm., was predominantly 2-ethyl*cyclo*hexanone, the second (17 g.), b. p. 84—90°/13 mm., mainly 2 : 2-diethyl*cyclo*hexanone. The high-boiling residue (42 g.) probably consisted of self-condensation products of *cyclo*hexanone. A semicarbazone made from the second fraction had m. p. 202—203° after four crystallisations from ethanol (Meerwein [15] gives m. p. 202—203° for 2 : 2-diethyl*cyclo*hexanone semicarbazone). The first fraction was also converted into the semicarbazone, m. p. 163° (lit., 161—162°) after four crystallisations from ethanol (yield 25 g.). By hydrolysis with dilute hydrochloric acid pure 2-ethyl*cyclo*hexanone (14 g., 12%) was obtained.

(*c*) 2-Ethyl*cyclo*hexanone (14 g.) in ethereal solution was added to a Grignard reagent prepared from magnesium (3·2 g.) and *o*-bromoethylbenzene (20·6 g.), and the mixture heated under reflux for 20 hr. The product was worked up in the usual way, the ethereal solution dried (Na_2SO_4), and the ether distilled off. The residue was dehydrated by formic acid (75 c.c.) under reflux for 4 hr. The product was extracted with benzene, and the benzene solution washed and dried. After removal of the benzene the residue was distilled under reduced pressure, giving 4 g. (17%) of a hydrocarbon (or mixture of isomeric hydrocarbons), b. p. 132—133°/11 mm., n_D^{26} 1·5261 (Found : C, 89·3; H, 10·6. Calc. for $C_{16}H_{22}$: C, 89·7; H, 10·3%). Dehydrogenation by heating with sulphur for 4 hr. at 240° gave 2 : 2′-diethyldiphenyl (2 g.).

Methyl 3-*Amino*-4-iso*propylbenzoate.*—Methyl 3-nitro-4-*iso*propylbenzoate was obtained in almost quantitative yield by nitration of *p*-*iso*propylbenzoic acid, followed by treatment with thionyl chloride and then methanol.[16] Attempted reduction of the acid with iron and acetic acid, ammonium sulphide, or ammoniacal ferrous sulphate was unsuccessful. The ester was largely unchanged after being shaken with hydrogen in the presence of catalysts (platinum or palladium). However, reduction in 88% yield was achieved by using tin and hydrogen chloride in a methanolic solution of the ester (cf. Abenius [17]). The *benzoyl* derivative of the amino-ester had m. p. 118° (Found : C, 72·6; H, 6·3; N, 4·9. $C_{18}H_{19}O_3N$ requires C, 72·7; H, 6·4; N, 4·7%).

Methyl 3-*Iodo*-4-iso*propylbenzoate* was obtained in 66% yield by the diazo-process. It had b. p. 140—142°/7 mm., n_D^{25} 1·5780 (Found : C, 43·7; H, 4·2; I, 41·6. $C_{11}H_{13}O_2I$ requires C, 43·4; H, 4·3; I, 41·8%). A little was hydrolysed to the *acid*, m. p. 173—174° (Found : I, 44·0. $C_{10}H_{11}O_2I$ requires I, 43·8%).

6 : 6′-*Di*iso*propyldiphenyl*-3 : 3′-*dicarboxylic Acid.*—The above iodo-ester (76 g.) was treated with copper bronze in a bath at 270—275° for 50 min. The product was extracted with chlorobenzene, the solvent removed, and the residue treated with light petroleum. The solid so precipitated, after two crystallisations from methanol, gave *methyl* 6 : 6′-*di*iso*propyldiphenyl*-3 : 3′-*dicarboxylate* as prisms, m. p. 143—144° (36 g., 81%) (Found : C, 74·7; H, 7·5. $C_{22}H_{26}O_4$ requires C, 74·6; H, 7·4%). Hydrolysis with ethanolic sodium ethoxide gave 6 : 6′-*di*iso*propyldiphenyl*-3 : 3′-*dicarboxylic acid* with m. p. 285—290°, which was raised to 323—324° by two crystallisations from acetic acid (Found : C, 69·0; H, 6·7. $C_{20}H_{20}O_4,CH_3{\cdot}CO_2H$ requires C, 68·8; H, 6·8%). The solvent-free *acid* was obtained by crystallisation from ethanol (Found : C, 73·4; H, 6·9. $C_{20}H_{20}O_4$ requires C, 73·2; H, 6·7%) (m. p. unchanged).

2 : 2′-*Di*iso*propyldiphenyl.*—A solution of the above acid (10 g.) in quinoline containing copper bronze was heated for 10 hr. Most of the quinoline was distilled off and the residue poured into water and acidified with hydrochloric acid. The oil which separated was extracted with ether; the extract was washed, dried, and distilled. The fraction, b. p. 150—160°/12 mm., solidified and two crystallisations from ethanol gave pure 2 : 2′-*di*iso*propyldiphenyl*, m. p. 67—68° (4·2 g.) (Found : C, 90·6; H, 9·1. $C_{18}H_{22}$ requires C, 90·8; H, 9·2%).

3 : 3′-Diethylbenzidine was prepared from *o*-ethylnitrobenzene.[18] The dibenzylidene derivative had m. p. 129—130° (Schultz and Flachsländer [18] give 124—125°). The *disalicylidene* derivative crystallised from *cyclo*hexane or from light petroleum (b. p. 100—120°) and had m. p. 157—158° (Found : C, 79·6; H, 6·3; N, 6·8. $C_{30}H_{28}O_2N_2$ requires C, 80·4; H, 6·3; N, 6·3%).

3 : 3′-*Diethyldiphenyl.*—A solution made from 3 : 3′-diethylbenzidine dihydrochloride (47 g., 1 mol.), concentrated hydrochloric acid (45 c.c., 3 mol.), and water (600 c.c.) was diazotised at −4° to −2° with sodium nitrite (22·8 g., 2·2 mol.) in water (75 c.c.). Hypophosphorous acid (50%; 300 c.c., 15 mol.), pre-cooled to 0°, was added and the solution stirred at 0° for 1 hr., then kept overnight at 5°. The oily layer was separated and the aqueous layer thrice extracted with ether. The combined extracts were washed several times with 30% sodium hydroxide solution, then with water, and dried ($CaCl_2$). Removal of the ether, followed by distillation and redistillation, gave 21 g. (63%) of crude material. Small amounts of phenolic impurities were eliminated by distillation over sodium, whence pure 3 : 3′-*diethyldiphenyl*, b. p. 154—155°/9—10 mm., n_D^{25} 1·5768, was obtained (Found : C, 91·5; H, 8·5. $C_{16}H_{18}$ requires C, 91·4; H, 8·6%).

p-*Ethyliodobenzene.*—*p*-Ethylnitrobenzene was reduced with zinc and hydrochloric acid.[13] *p*-Ethylacetanilide had m. p. 91° (lit., 94°). *p*-Ethyliodobenzene, b. p. 87—88°/8—9 mm., n_D^{25} 1·5888, was prepared by a modification of Willgerodt and Bergdolt's method,[19] the *p*-ethylaniline being diazotised in sulphuric acid solution.

4 : 4′-*Diethyldiphenyl.*—(*a*) *p*-Ethyliodobenzene was heated with copper bronze,[8] and the resulting 4 : 4′-diethyldiphenyl distilled under reduced pressure; it crystallised from methanol or ethanol in flakes, m. p. 83° (Schreiner [8] gives m. p. 81°) (Found : C, 91·6; H, 8·5%).

(*b*) *p*-Bromoethylbenzene, b. p. 93—94°/23 mm., n_{D}^{25} 1·5449, was obtained in 42% yield by a Sandmeyer reaction, the base being diazotised in hydrobromic acid. A Grignard reagent was prepared from it and treated with anhydrous cupric chloride, giving 4 : 4′-diethyldiphenyl, m. p. 83°, after crystallisation as above.

p-*Iodo*iso*propylbenzene.*—*p*-Nitro*iso*propylbenzene was reduced in ethanolic solution by hydrogen and Adams platinum oxide. The acetyl and the benzoyl derivative had m. p.s 104—105° (Newton [20] gives 105·8—106·6°) and 162·5—163° (lit., 161·4—162°) [20] respectively. *p*-Iodo*iso*propylbenzene, b. p. 86—92°/5—6 mm., n_{D}^{25} 1·5725, was obtained by diazotising the amine in sulphuric acid and adding the diazo-solution to aqueous potassium iodide.

4 : 4′-*Di*iso*propyldiphenyl.*—*p*-Iodo*iso*propylbenzene (5 g.) was heated with copper bronze (8 g.) at 260—270° for 45 min. The mixture was extracted with hot chlorobenzene; the solvent was removed and the residue distilled, giving 2 g. of 4 : 4′-di*iso*propyldiphenyl, b. p. 155—160°/4·5 mm. It was redistilled from sodium and crystallised twice from ethanol, forming plates, m. p. 65—66° (Found : C, 90·8; H, 9·3%).

Absorption Spectra.—Spectra were measured on a Unicam S.P. 500 spectophotometer.

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