POLYCYCLIC AROMATIC HYDROCARBONS

with an additional paper on

MOLECULAR REARRANGEMENTS.

T H E S I S

for the Degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF GLASGOW

Submitted by

JOHN W. WRIGHT, B.Sc.

March, 1949.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

PREFACE.

The author desires to thank Dr. E. Clar, under whose supervision the work on Polycyclic Aromatic Hydrocarbons was carried out, and Dr. T.S. Stevens, who supervised the work on Molecular Rearrangements.

Thanks are also due to Professor J.W. Cook for his help and suggestions during the course of research, to Mr. J.M.L. Cameron and Miss R.H. Kennaway who carried out the micro analysis, and to the Department of Scientific and Industrial Research for a maintenance allowance.

C O N T E N T S.

Part I.

POLYCYCLIC AROMATIC HYDROCARBONS.

FOREWARD TO PART I.

The nomenclature used in this work on Polycyclic Aromatic Hydrocarbons is that of E. Clar[57,57a], where the terms Acene and Phene are used to denote condensed ring aromatic compounds of linear and angular structure respectively.

In the series of peri condensed naphthalene compounds, the term Rylene is used and in the similar anthracene series the members are referred to as Anthenes[12].

A copy of a letter to 'Nature' on the Meso-Methyl-Acene work is given in the Appendix.

POLYCYCLIC AROMATIC HYDROCARBONS.

Synthesis and Absorption Spectra of Methyl-Acenes and some Perylene and Terrylene Derivatives.

The anellation principle of E. Clar shows a gradual change in the properties of individual members in ascending any aromatic series. In the original paper[1] the absorption curves of anthracene, tetracene and pentacene are examined and the bands of longest wave length, which can be correlated with the meso carbom atoms, are compared. The differences of the square roots of the wave lengths are found to be constant, i.e., $\sqrt{\lambda}$ (pentacene) - $\sqrt{\lambda}$ (tetracene) = $\sqrt{\lambda}$ (tetracene) - $\sqrt{\lambda}$ (anthracene). In naphthalene and benzene also, are found bands of the same form and intensity, which are explained by the contribution of the Dewar structure of the resonance hybrid.

In the complete series, then, benzene - pentacene, we find para bands at the following wave lengths: benzene 2083; naphthalene 2878; anthracene 3776; tetracene 4735; and pentacene 5810Å. An order no. K can be calculated for each member ~~of~~ from the equation, $K = \sqrt{Rp\lambda}$ where Rp is obtained from the constant value of the difference of $\sqrt{\lambda}$. K is found to be represented by the whole numbers 6,7,8,9,10 in the above-mentioned series.

From other bands, known as ortho bands, arising from the Kekulé structure of benzene, a similar equation, $R = \sqrt{Ro\lambda}$

is obtained and it is found that K = 8 for benzene, $8\frac{1}{2}$ for naphthalene and 9 for anthracene or phenanthrene, etc.

In subsequent papers[2-15][16], the theory is developed and new hydrocarbons fitted into the scheme. A direct relationship between the order nos. of the hydrocarbons and the oxidation reduction potentials of their quinones has also been shown[4].

In a more recent publication[12] a new principle is developed which includes the p-polyphenyls and the peri-condensed naphthalenes, i.e., perylene, terrylene etc. (polyrylenes), and can be extended to include the peri-condensed anthracenes (polyanthenes) and so on. In the polyphenyl series the difference between the frequencies of the absorption maxima of the single broad bands is halved as we ascend the series, i.e., ν (diphenyl) - ν (P-terphenyl) = 2(ν (p-terphenyl) - ν (p-quaterphenyl)). In the polyrylene series the differences of the frequencies of the p-bands are quartered from member to member in the ascending series. It is therefore possible, by multiplying the frequency difference between the first two members in 2 (in the polyphenyl series) or by 4 (in the rylenes) and adding the figure obtained to the frequency of the first member, to obtain the frequency of a hypothetical zero member in each case. Extending this scheme, it may be assumed that the difference of the

frequency of the p-bands will be divided by 8 as we pass from anthracene to bisanthene to teranthene, but since only the first two members are known, there was no means of proving this. However, by multiplying the frequency difference

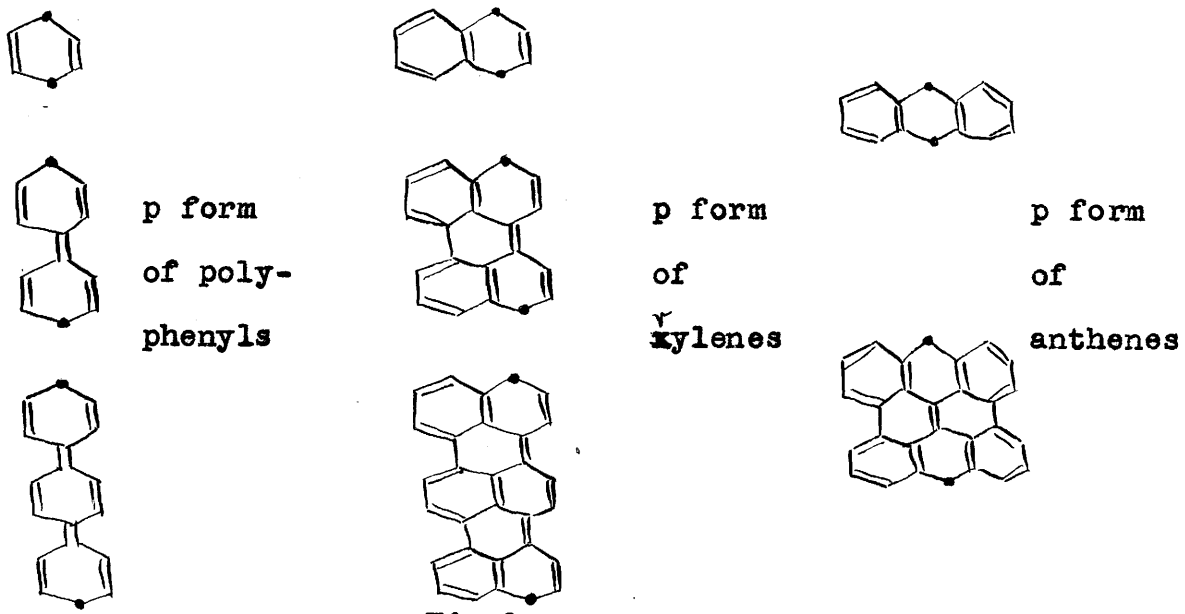


Fig.1

between the p-bands of anthracene and bisanthene by 8, the frequency of the zero member of the series may be found and it is observed that the differences of the square roots of the frequencies of these zero members are constant, and furthermore, the frequencies themselves are directly proportional to the squares of the order nos. 6, 7 and 8. Thus we find that $K = \sqrt{Rp\lambda} = \sqrt{Rp\nu_1} = \sqrt{\nu_0/Rk}$, where ν_1 = the frequency of the first member of the series and ν_0 = the frequency of the zero member. Rp and Rk are constants and are 1,712,800 cm^{-1} and 1,829.9 cm^{-1} respectively. It is

therefore correct to assume that the frequency differences will be divided by 8 on ascending the polyanthene series and by 16, 32 etc. in the series starting from tetracene, pentacene, etc. Thus, it is possible to predict where the p-absorption bands of many peri-condensed hydrocarbons should be.

It is therefore desirable to prepare new hydrocarbons and their homologues and to study their absorption curves, thereby filling up any gaps which may still exist in the various aromatic series.

The present work may be divided into three sections:-

1. Meso methyl acenes.
2. Benzologues of perylene.
3. 7-8 benzterrylene.

---

1. Meso methyl acenes.

It is well known that in ascending the acene series there is a tendency for the meso rings to become less benzenoid and more quinonoid in character. The phenols are a good example of this phenomenon and in the higher members of the series tend to exist entirely as ketones of the anthrone type.

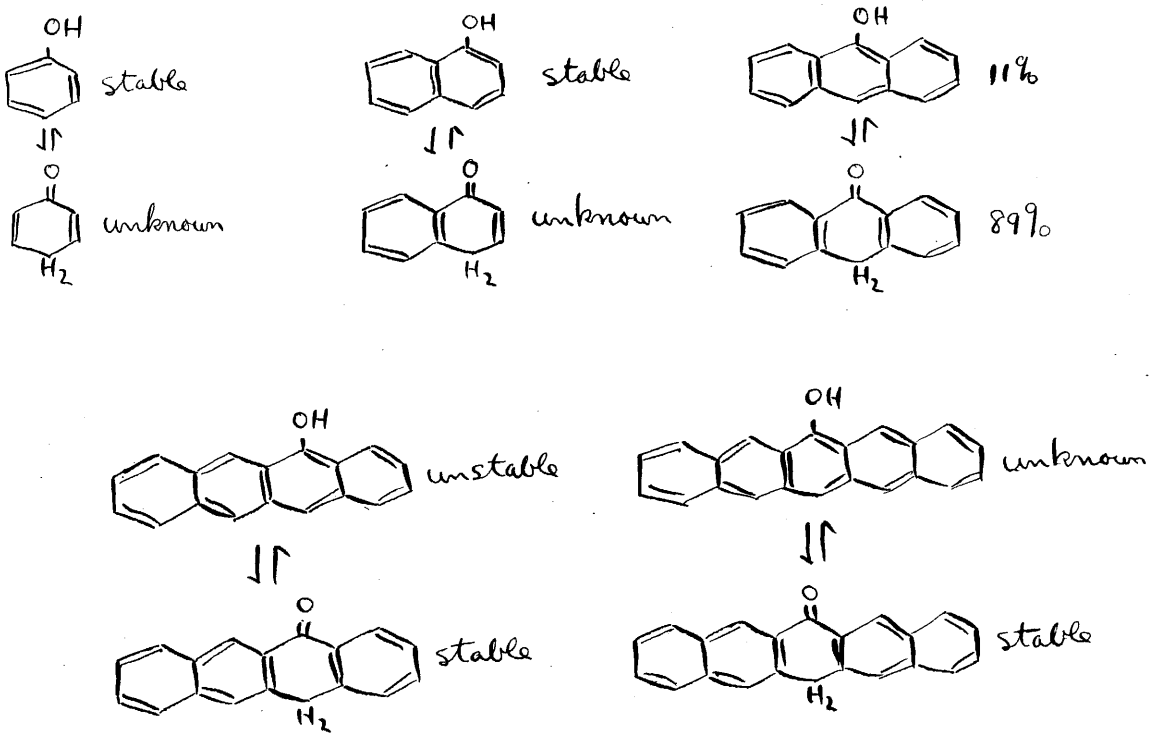


Fig.2[17]

The increasing stability of the quinones and a study of their oxidation reduction potentials leads us to the same conclusions[18].

In meso methyl acene series, tautomerism between the methyl acenes (I, II, III, IV and V) and the methylene dihydro acenes (Ia - Va) has been postulated to explain side chain reactivity, but hitherto no methylene dihydroacene has been isolated. The synthesis of 6-methylene-6-13-dihydro-pentacene (Va) by E. Clar[19] has removed this weakness in the hypothesis. Since the anellation principle requires a

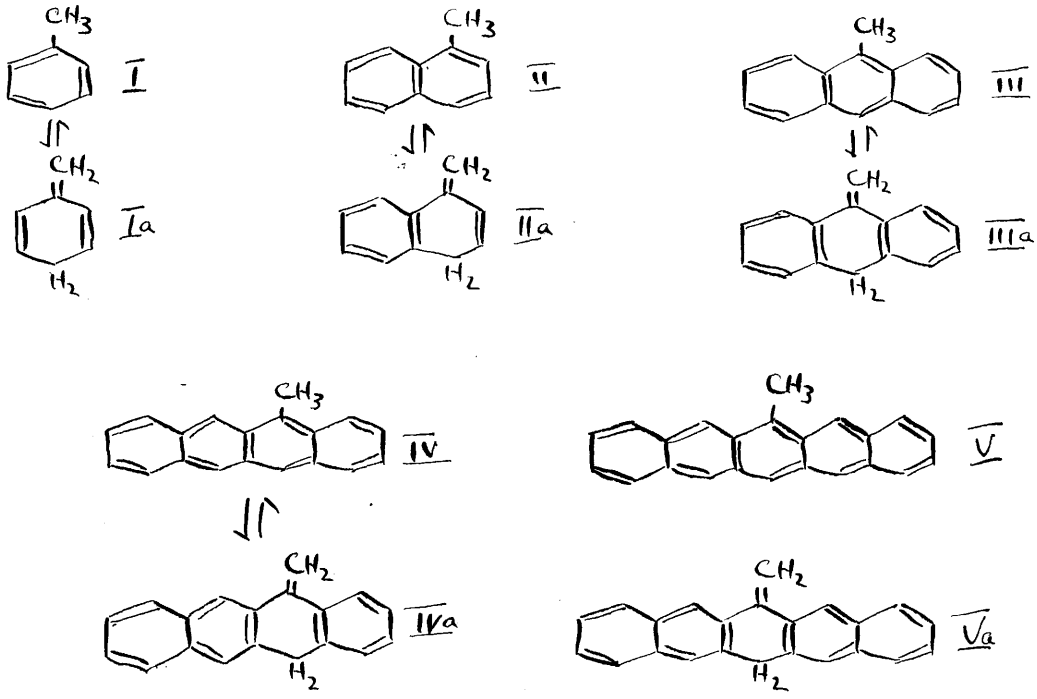


Fig. 2a.

gradual change in properties in the acene series, it is likely that IV, III, II and I will also contain decreasing proportions of the methylene form.

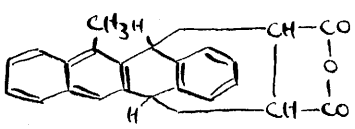
The possibility of isolating methylene dihydrobenzene (Ia) or methylene dihydronaphthalene (IIa) is remote, but it seemed likely that the tautomers 9-methylanthracene and 9-methylene-9-10-dihydroanthracene (III and IIIa) and the corresponding tetracene derivatives (IV and IVa) might exist in equilibrium. 9-Methyl-anthracene and 5-methyl-tetracene were therefore prepared and examined to see if the two methylene compounds were indeed present.

In the case of 9-methyl-anthracene which was prepared by the action of methyl magnesium iodide on anthrone,

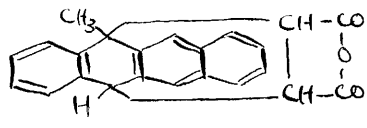
followed by the dehydration of the crude carbinol[20], a small amount of a compound which crystallised in small red needles (m.p. 163-5°) was obtained among the yellow plates of the main product (m.p. 81°) (mixed m.p. 79°). The red compound could not be isolated in sufficient quantity for careful examination, but from its colour alone it is unlikely to be the methylene compound. A pure homogeneous maleic anhydride adduct was obtained.

5-Methyl-tetracene was prepared in a similar manner from tetracenone but no indication of a second compound or crystalline structure was observed, although Fieser and Hershberg[21] claim to have obtained 1-6-dimethyl-tetracene in two readily convertible modifications.

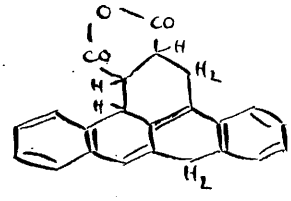
On treatment with maleic anhydride, 5-methyl-tetracene gave two distinct adducts which were readily separated by the different solubility of their sodium salts (see Experimental, p. 38 for comparison). It was at first thought that these might be VI or VIa and VII[cf.22], but since both decomposed at their melting points to regenerate 5-methyl-tetracene it seems more probable that they were VI and VIa. There is also the possibility that the two compounds obtained may be cis-trans isomers.



VI



VIa



VII

Fig.3.

Fig 4.

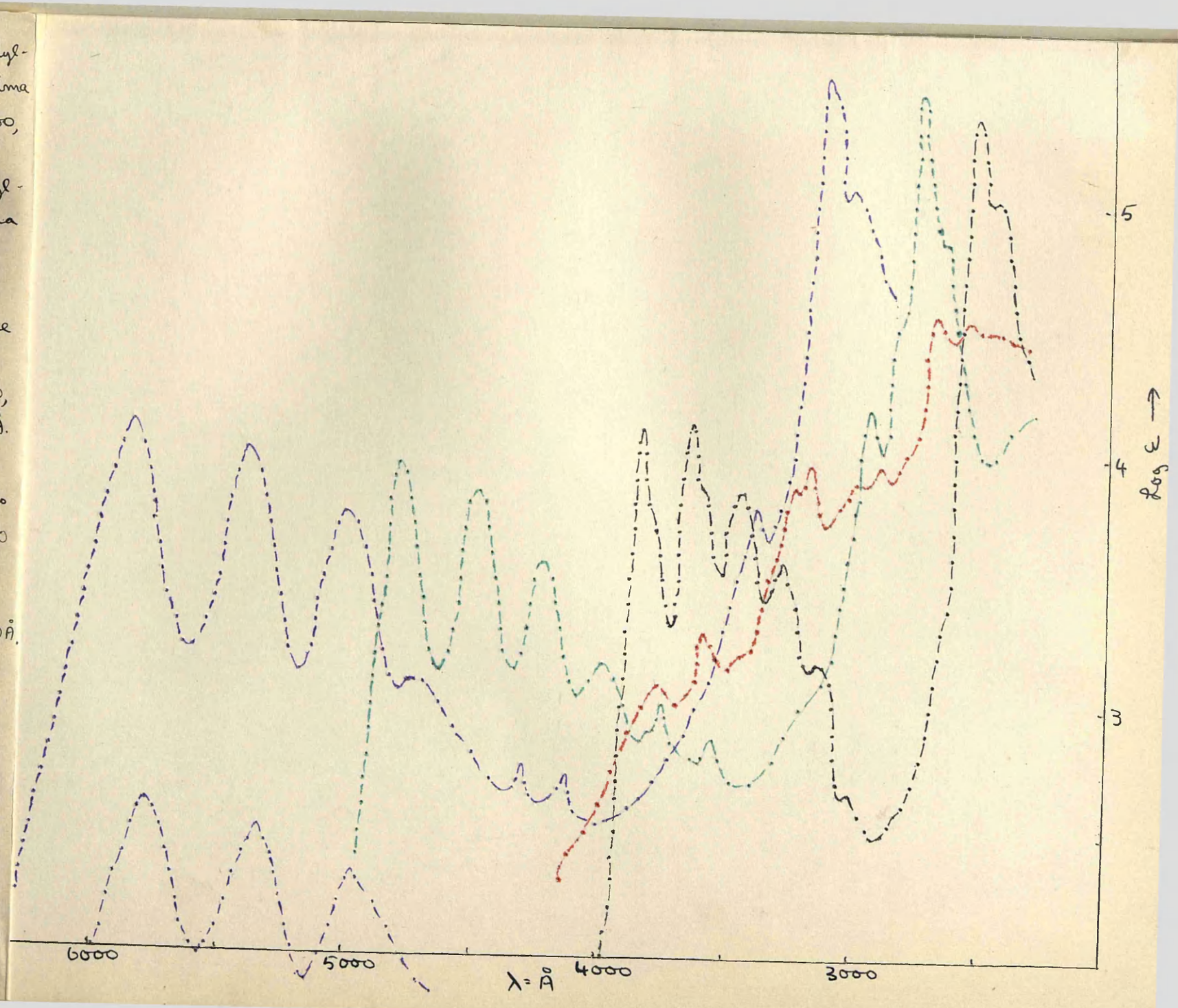
-.-.-.-.- Absorption Curve of 9-methyl-anthracene in alcohol. Band maxima at 3850, 3640, 3460, 3290, 3140, 3000, 2540 and 2460 Å.

-.-.-.- Absorption Curve of 5-methyl-tetracene in alcohol. Band maxima at 4805, 4490, 4220, 3980, 3750, 3560, 2950, 2755 and 2650 Å.

-.-.-.- Calculated Absorption Curve of 6-methyl-pentacene in 1-methyl-naphthalene. Band Maxima at 5850, 5410, 5010, 4300, 4120, 3390 and 3150 Å.

-.-.-.- (Lower Curve) Observed Absorption of 6-methyl-pentacene at 210° in 1-methyl-naphthalene:- 5790, 5360 and 4960 Å. (Intensity Qualitative). On rapid cooling the fading band maxima shift to 5850, 5410 and 5010 Å.

-.-.-.- Absorption Curve of 6--methylene-6·13-dihydropentacene in alcohol. Band maxima at 3770, 3585, 3420, 3175, 3020, 2900, 2690, and 2570 Å.



A comparison of the absorption curves of the two hydrocarbons (Fig.4) gives some indication as to the actual structure of the compounds. Thus the spectrum of 9-methyl-anthracene is very similar to that of anthracene, though the intensity of the bands is somewhat greater (cf. Willemart[23]). The presence of a small proportion of the methylene form which would only have a very feeble absorption is not excluded. In the case of 5-methyl-tetracene, an absorption curve resembling that of tetracene is observed, but here the intensity of the bands is considerably lower than that of tetracene. This seems to suggest that the % of the weakly absorbing methylene compound (IVa) is appreciably greater than in the case of methyl-anthracene. The absorption curve of the meso methyl derivative of pentacene is entirely different and is shown in the figure for comparison along with the curve calculated for 6-methyl-pentacene by means of the anellation principle. A solution of the pentacene derivative in 1-methyl naphthalene at 200°C gave a similar absorption curve to that calculated[19]. It is also shown in Fig.4.

---

2. Benzologues of Perylene.

In the perylene series the anellation effect has so far not been studied in any great detail. Thus Clar[24] compares the colours of perylene (VIII), 1-2-benzperylene (IX),

1-2-11-12-dibenzperylene (X) and 2-3-10-11-dibenzperylene (XI).

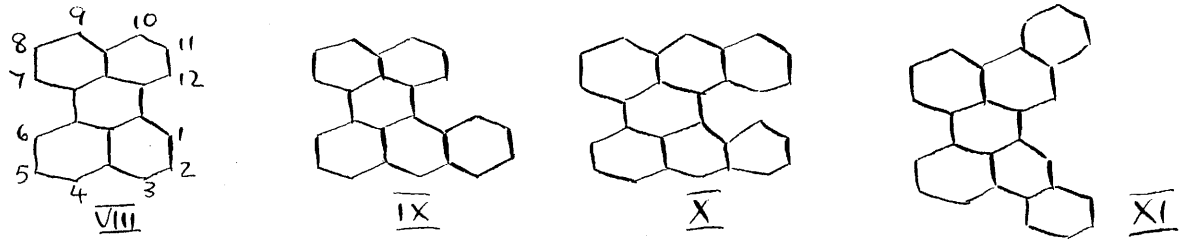


Fig.5

He says, "A calculation shows that the two rings in X increase the order no. for perylene by unity. It is thus shown that the maximum anellation effect comes from a linear parallel anellation." This is similar to the increase found in the series, phenanthrene, chrysene, 3-4-benz-tetraphene, anthraceno-(2'1'-1-2)-anthracene.

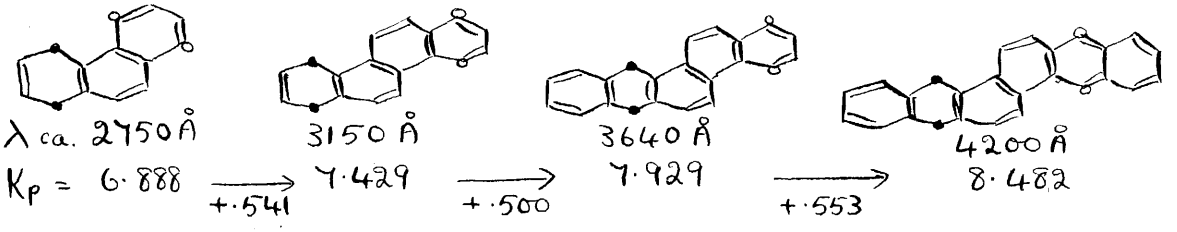


Fig.6 (showing wave lengths and order nos. for p-bands[25]).

In considering the effect of anellation on pyrene, Clar[2] shows there are three series of bands which he refers to as symm.pyr., assym.pyr. and 0-bands as shown by the forms 1, 2, and 3.

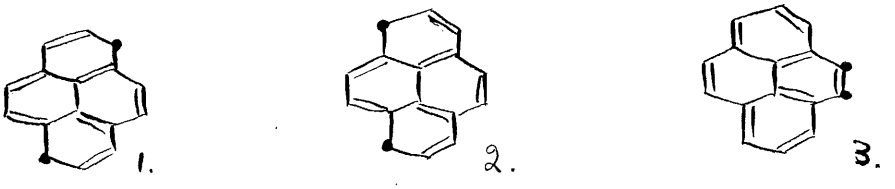


Fig.7.

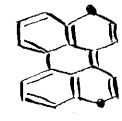
Likewise perylene itself would appear to be a chromophore whose absorption curve is not related to those of phenanthrene or 1-1'-dinaphthyl[26], though Clar has recently shown corresponding relationships between benzene and diphenyl and between naphthalene and perylene[12]. An examination of the double bond distribution in perylene shows a remarkably rigid structure, and the p-form  probably plays a prominent part in determining the absorption curve.

Fig.7a.

A relationship can be developed between the p-forms of diphenyl, perylene and bisanthene, a calculation giving Rp = 1,477,333 cm^{-1}. Using the formula $K = \sqrt{R\lambda}$ we find that K increases by two units from diphenyl to perylene and likewise by two units from perylene to bisanthene. Benzanthrene and the linear benzologues of perylene (IX, X, XII, XIII) can be fitted into this scheme.

1-2-Benzperylene (IX), 1-2-5-6-dibenzperylene (XII), and naphtho-(2'.3':1.2)-perylene (XIII) have been prepared and their properties examined. Their colour range is from orange to violet as shown. An attempt to prepare 1-2-benznaphtho-(2'.3':5.6)-perylene yielded an olive green solution but a rough examination of the spectrum indicated that the molecule had been split.

The method of synthesis of these perylene derivatives which suggested itself was treatment of the corresponding anthrone derivative with 1-naphthyl magnesium bromide followed by dehydration of the crude carbinol and a subsequent Scholl ring closure with aluminium chloride in benzene[27,27a], or with a sodium chloride, aluminium chloride melt[28].

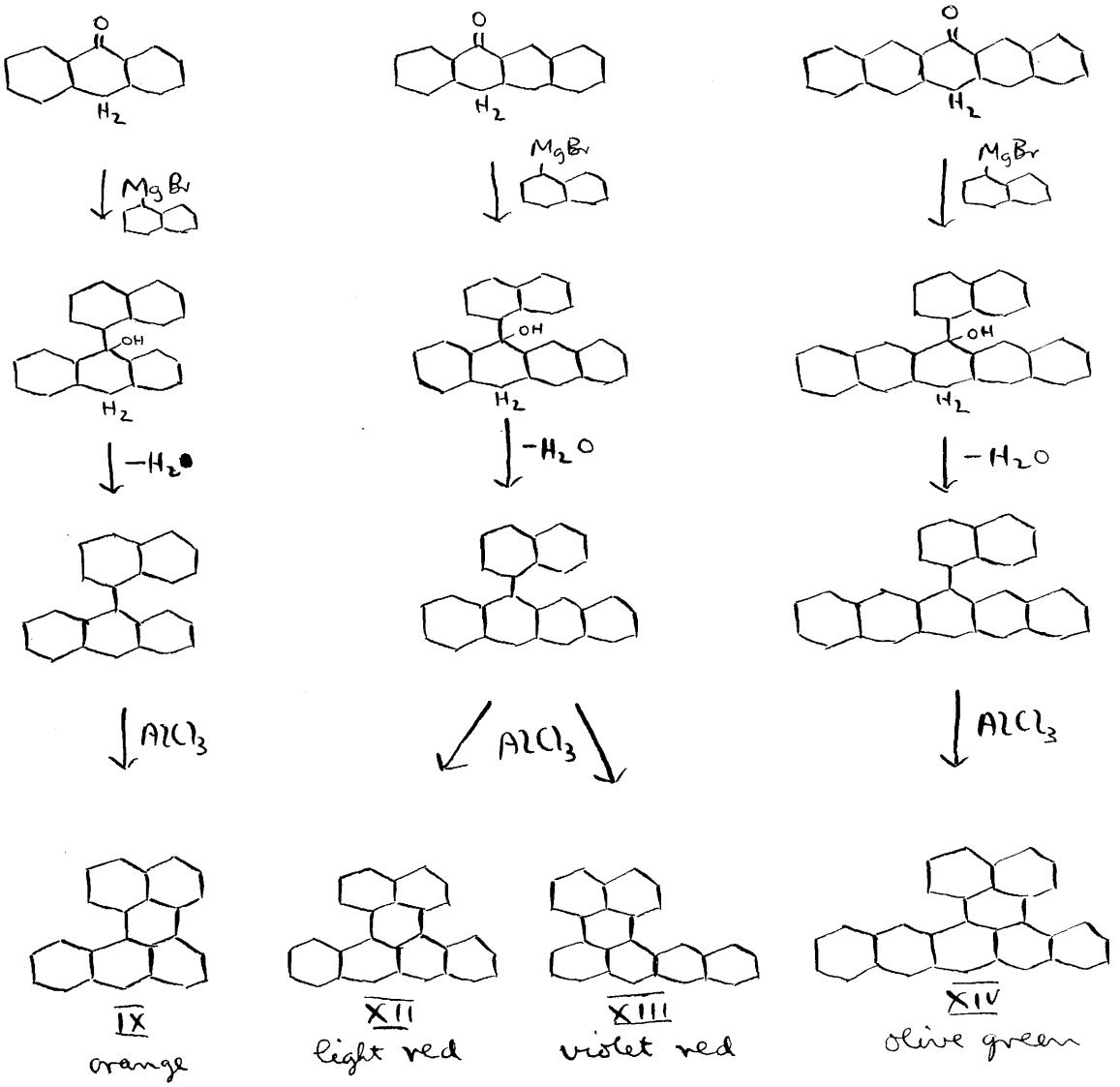


Fig.8.

The attempt to prepare IX by the method outlined was a failure although it is similar to that of Krollpfeiffer[29] for the preparation of meso substituted anthracenes, and to that of Cook[3D] for the preparation of 9-benzyl and 9-phenyl-anthracene. The main products from the Grignard reaction were naphthalene and anthraquinone.

1-2-Benzperylene was obtained, however, as a by-product in the preparation of 7-8-benzterrylene by a process similar to the above, but starting from anthraquinone (see p.54 Clar & Guzzi[31] and Clar[31a]).

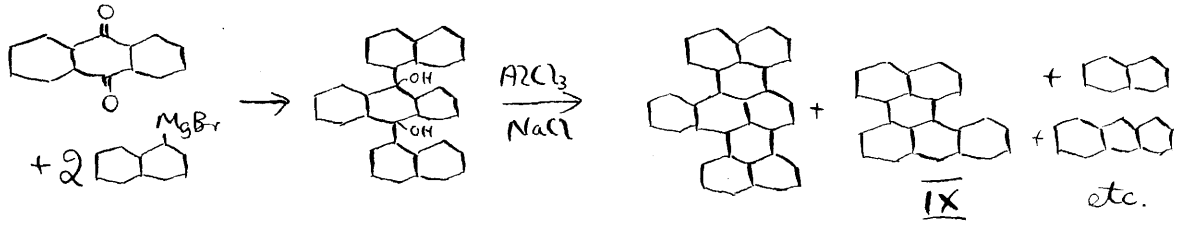


Fig.9

The resulting hydrocarbons from the $AlCl_3$/NaCl fusion were successfully separated on an alumina column which was kept under CO_2 in the dark. Only by taking these precautions was the photo-oxidation of IX prevented.

The reaction between tetracenone and naphthyl magnesium bromide presented no difficulties and the ring closure was readily carried out either with $AlCl_3$ in benzene or in the $AlCl_3$/NaCl melt. On running a petroleum ether solution of the resulting mixture through an alumina column

a large number of bands were observed. The reactions shown in Fig.10 have probably taken place during the $AlCl_3$ treatment.

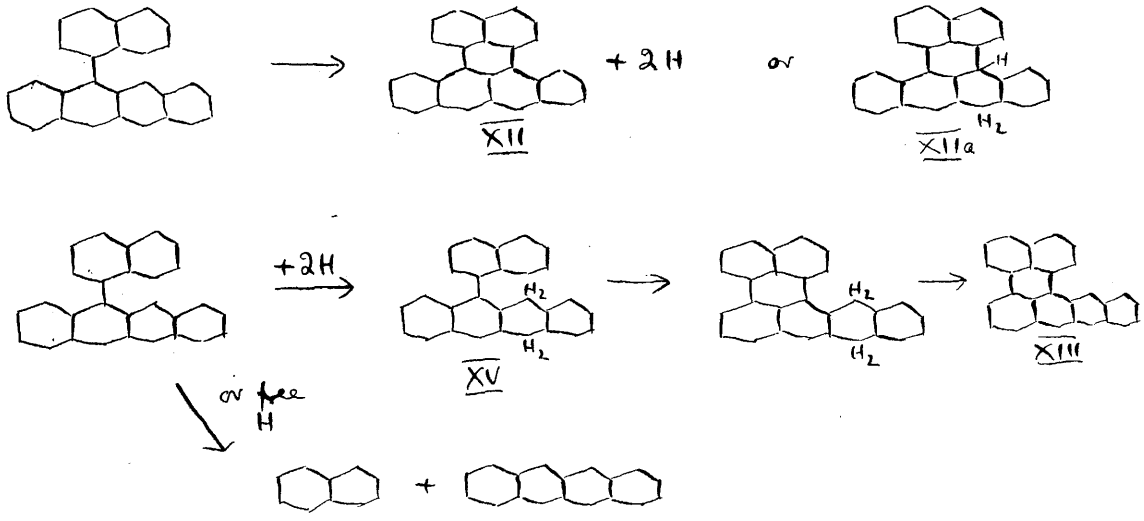


Fig.10

It was expected that this ring closure of 5-(1-naphthyl)-tetracene would take place mainly in the reactive meso or 6-position yielding XII, and the fact that XIII was produced in slightly better yield than XII could be explained by the fact that the free hydrogen produced in the initial ring closure immediately attacked the 6-11 positions in the naphthyl tetracene giving 5-(1-naphthyl)6-11-dihydrotetracene (XV) making further ring closure only possible to the 4 position. The yellow solutions obtained from the chromatogram column probably contained mixtures of the dihydro compounds. Unfortunately the specimens of 1-2-5-6-dibenzperylene and naphtho-(2'.3':1.2)-perylene obtained were found to

be contaminated with tetracene from which they were not separated on the alumina column. The two intense tetracene absorption bands at 4750Å and 4450Å were observed in the extinction curve of the two perylene derivatives. The tetracene is probably produced by a splitting of the molecule across the perylene nucleus into naphthalene and tetracene (cf. Clar and Guzzi[31]).

In the pentacene series the yields were small and only a few milligrams of pure naphthylpentacene were obtained. A rough examination of the spectrum of the olive green solution obtained by the treatment of 6-(1-naphthyl)-pentacene with $AlCl_3$ did not show the expected intense p-band around 6700Å, although bands were observed at 6050Å, 5050Å and 4685Å. The 6050 band may be due to 1.2-benznaphtho-(2'.3':5.6) perylene, though the lower bands at 5050 and 4685 are probably due to a splitting of the molecule.

The compounds IX, XII, XIII and XIV are all extremely sensitive to light, especially the naphtho derivatives. With maleic anhydride in boiling benzene, colourless addition products were formed, naphtho-(2'.3':1.2)-perylene being decolourised particularly rapidly. An examination of the absorption curve (Fig.19) of this addition product showed that it was not the expected endocyclic adduct (XIIIa) which should have given a curve similar to that of perylene. The

actual curve is much more that of an anthracene derivative and would probably correspond closely to that of the pale yellow 1-2-benz-tetraphene, indicating that addition had taken place in the 6-7 position in the perylene nucleus giving XIIIb or XIIIc.

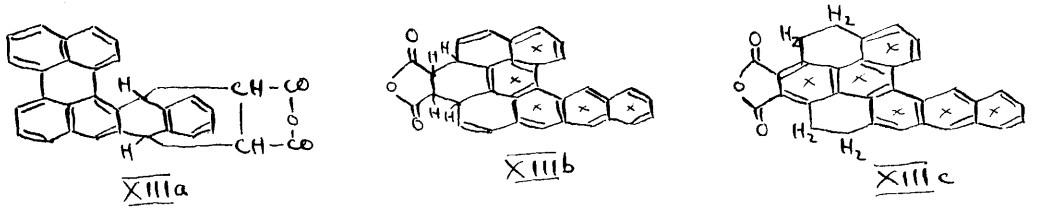


Fig.11.

The absorption curves of 1-2-benzperylene, 1-2-5-6-dibenz-perylene and naphtho-(2'.3':1.2)-perylene are shown in Figs. 16, 17 and 18 and the anellation effect in the P-series, as previously described, is shown in Fig.13, p.17.

Diphenyl (XVI) is the chromophore in this series and we might expect that 1-phenyl-naphthalene (XVII) and 1-1'-dinaphthyl (XVIII) could be included. The absorption curves of these compounds do not, however, have a place in the anellation scheme as the p-bond structure in diphenyl (XVIa) involves a planar molecule which is sterically impossible in 1-phenyl-naphthalene and 1-1'-dinaphthyl, the spectrum of 1-phenyl-naphthalene being similar to that obtained from an equimolecular mixture of benzene and naphthalene[32]. There is, however, a marked similarity in the curves of diphenyl (XVI), 9-10-dihydrophenanthrene (XIX)

and 4-5-dimethylene-fluorene (XX)[33], where the methylene bridges hold the molecule in a planar position. It is therefore clear that a relationship should exist between the curves of diphenyl and benzanthrene (XXII). There is also a marked similarity between the curves of 5-(1-naphthyl)-tetracene (XXII, Fig.14), 9-10-di-(1-naphthyl)-anthracene (XXIII, Fig.24) and their parent hydrocarbons, tetracene and anthracene. This is further evidence of the steric effect preventing the formation of the p-bond forms XXIIa and XXIIIa. The bathochromic shift caused by the 8-naphthyl group in 5-naphthyl-tetracene is almost identical to that caused by the methyl group in 5-methyl-tetracene (Fig.4).

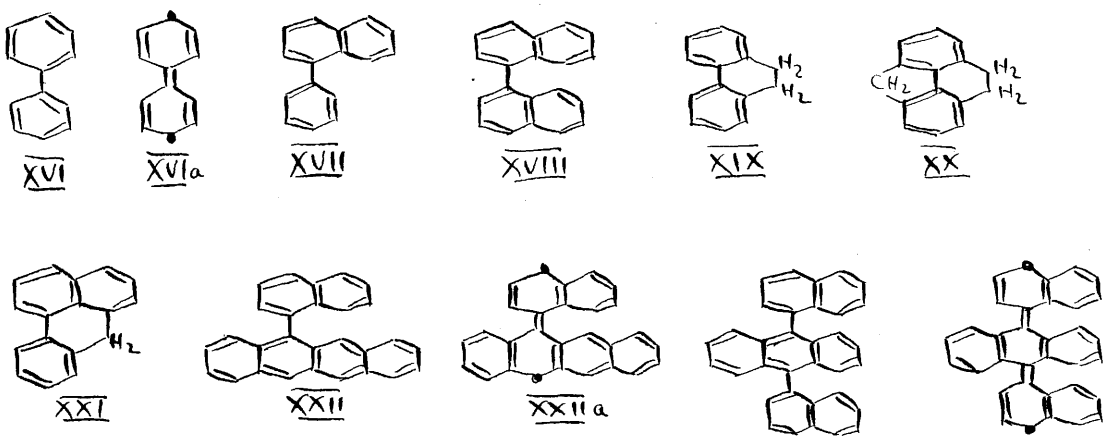


Fig.12

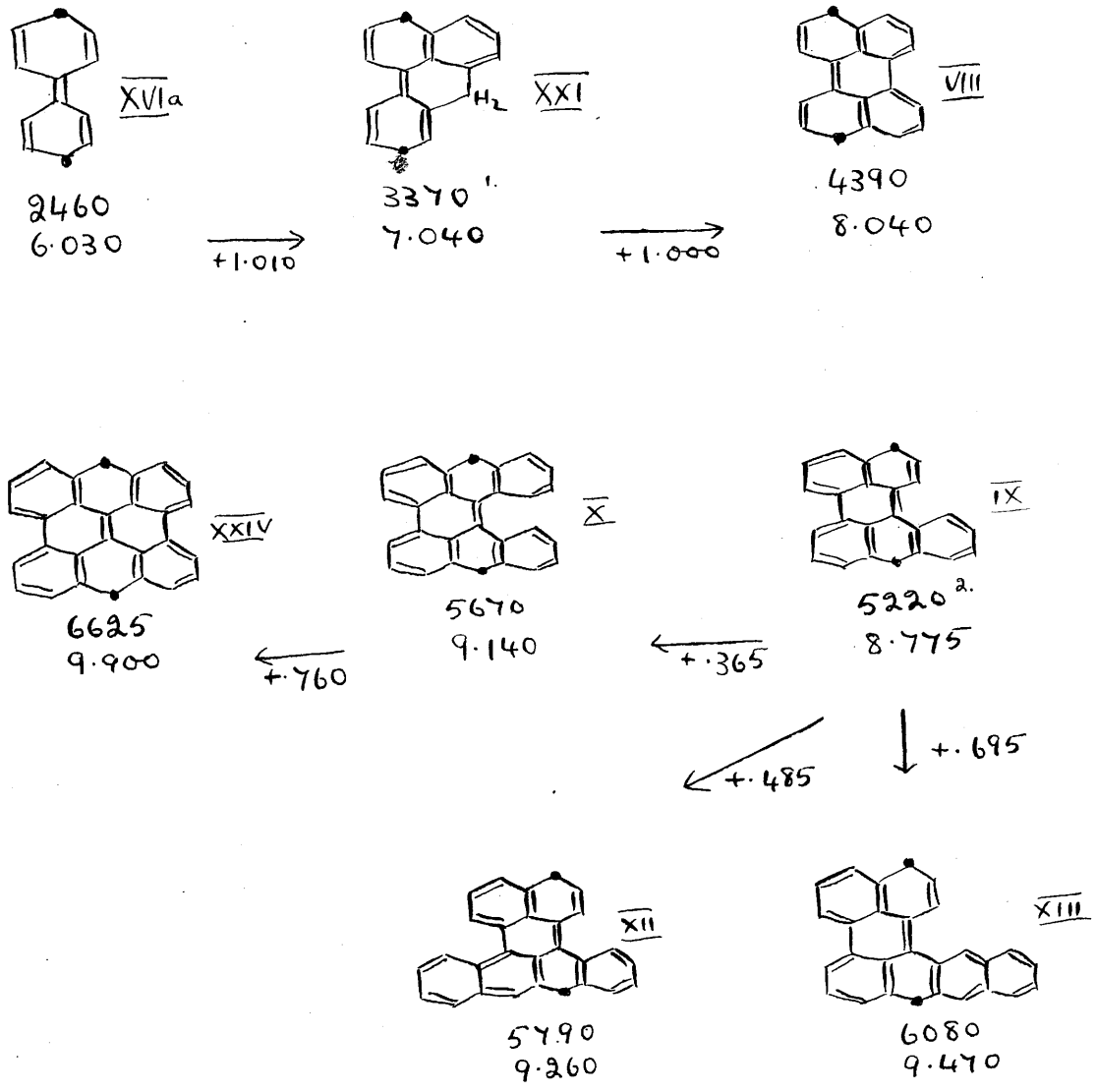


Fig.13

Upper no. = (p-band) in Å
Lower no. = Kp = R_p
R_p = 1,477,333 cm^{-1} for benzene as solvent.

Notes. 1. Correction of 500 cm^{-1} made in frequency for CH_2 group.

2. Correction of 300 cm^{-1} made as spectrum was originally examined in pet. ether

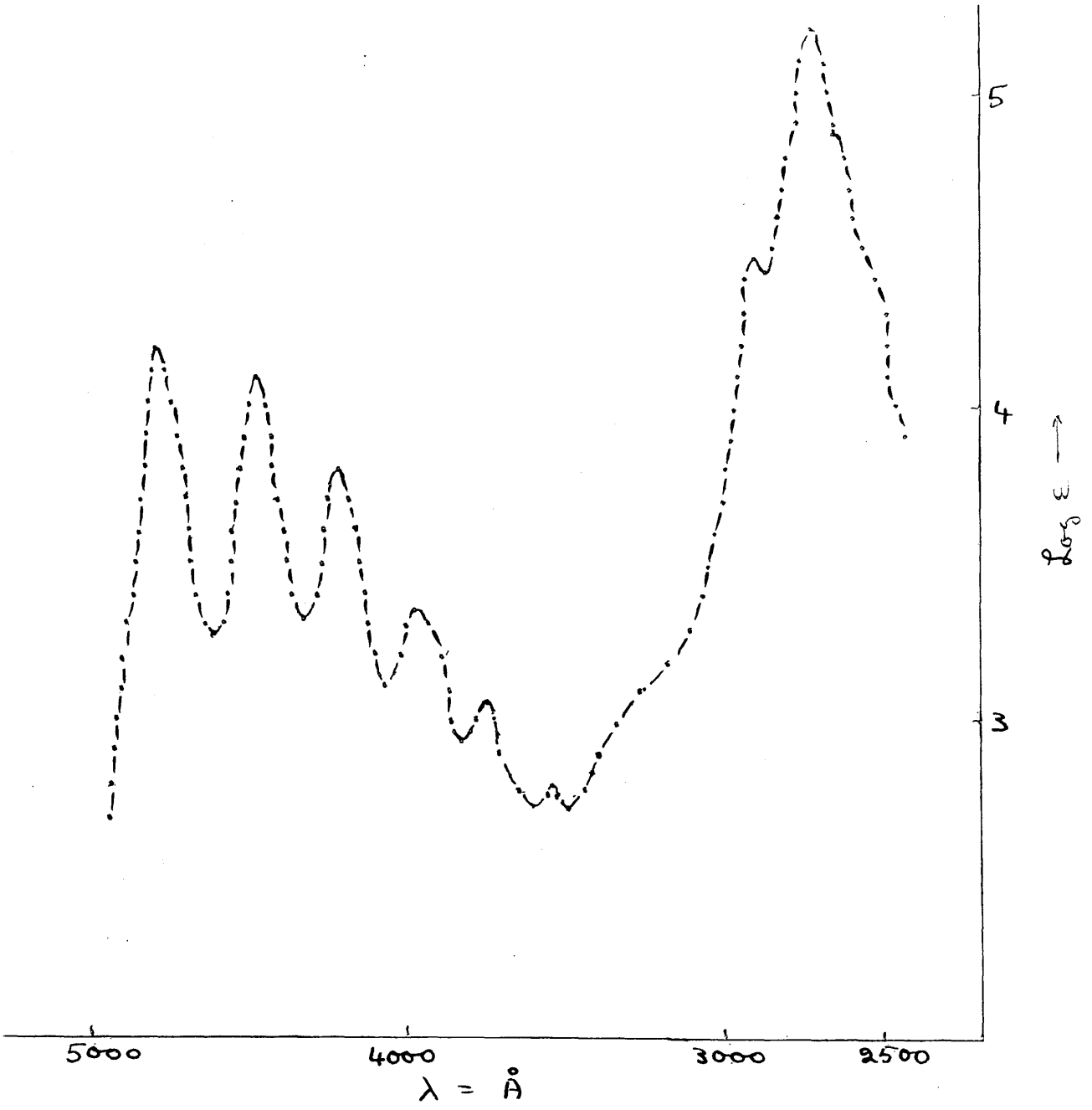


Fig. 14. Absorption Curve of 5-(1-naphthyl)-tetracene in Alcohol. Band maxima in Å at 4810, 4500, 4230, 3980, 3750, 3560, 2940, 2760.

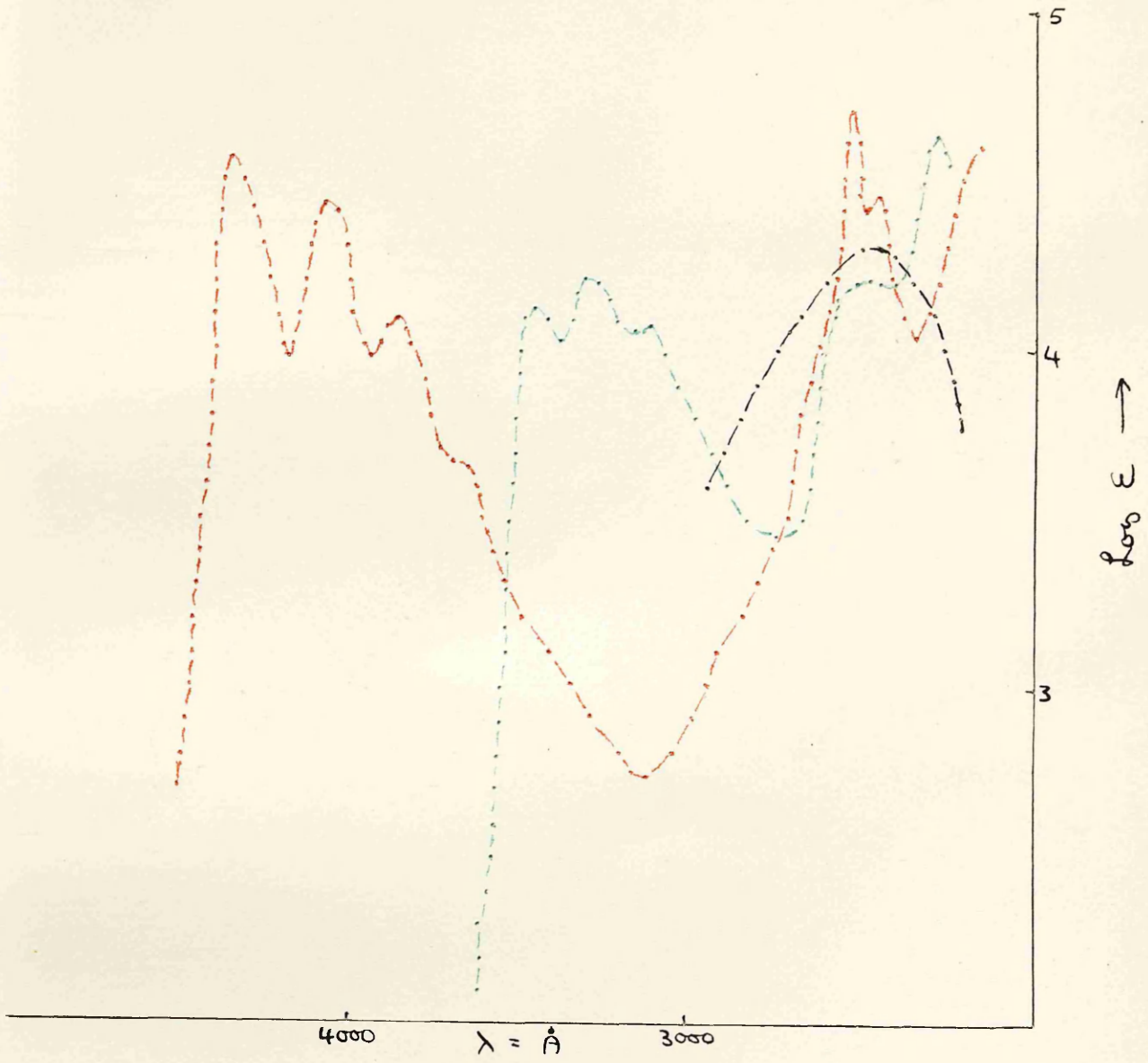


Fig 15

-·-·-·- Absorption Curve of Diphenyl in Alcohol.
Band Maximum at 2460 Å. (58)

-·-·-·- Absorption Curve of Benzanthrene in Alcohol. (59)
Band Maxima at 3440, 3290, 3120, 2500 and 2280 Å

-·-·-·- Absorption Curve of Perylene in Alcohol. Band
Maxima at 4340, 4060, 3870, 3680, 2520 and 2460 Å.
(60)

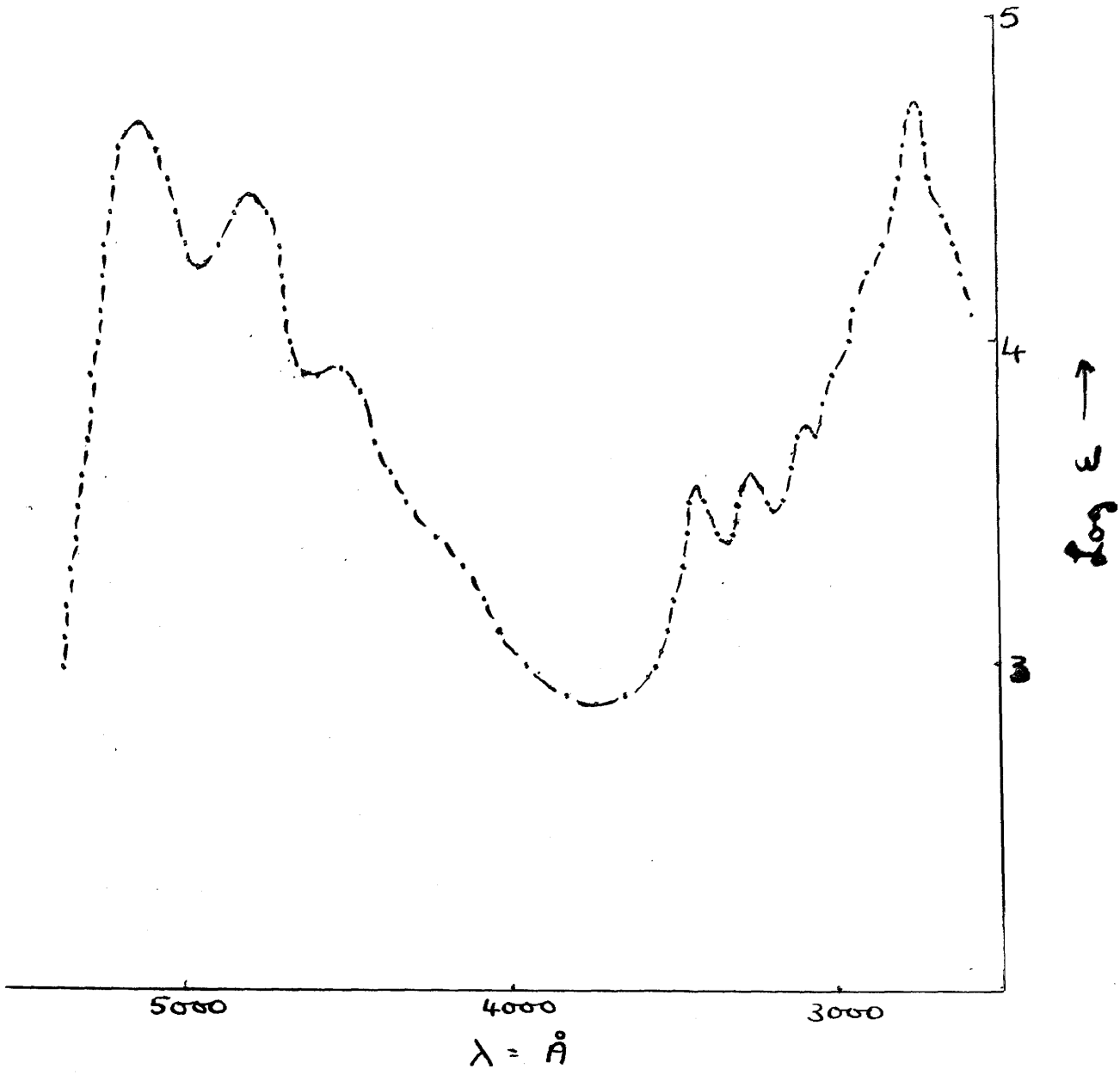


Fig. 16. Absorption Curve of 1·2·Benzperylene in Pet. Ether.

Band Maxima in Å at 5140, 4800, 4540, 3420

3260, 3100, 2760.

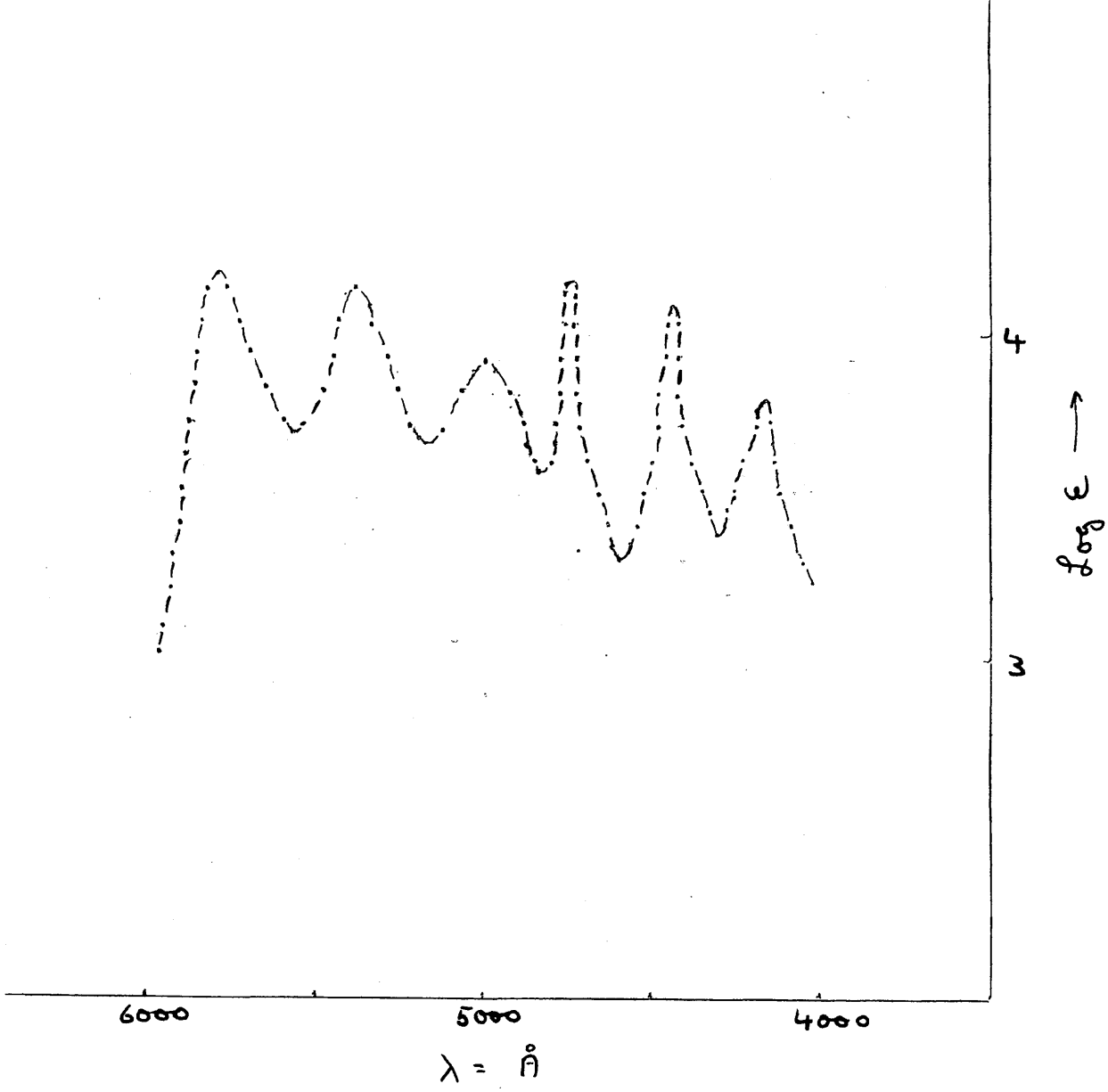


Fig. 17. Absorption Curve of 1-2-5-6-dibenz-perylene in Benzene. Band Maxima at 5490 Å, 5390 Å, and 5000 Å. Those at 4750, 4450 and 4180 Å are due to about 50% of Tetracene.

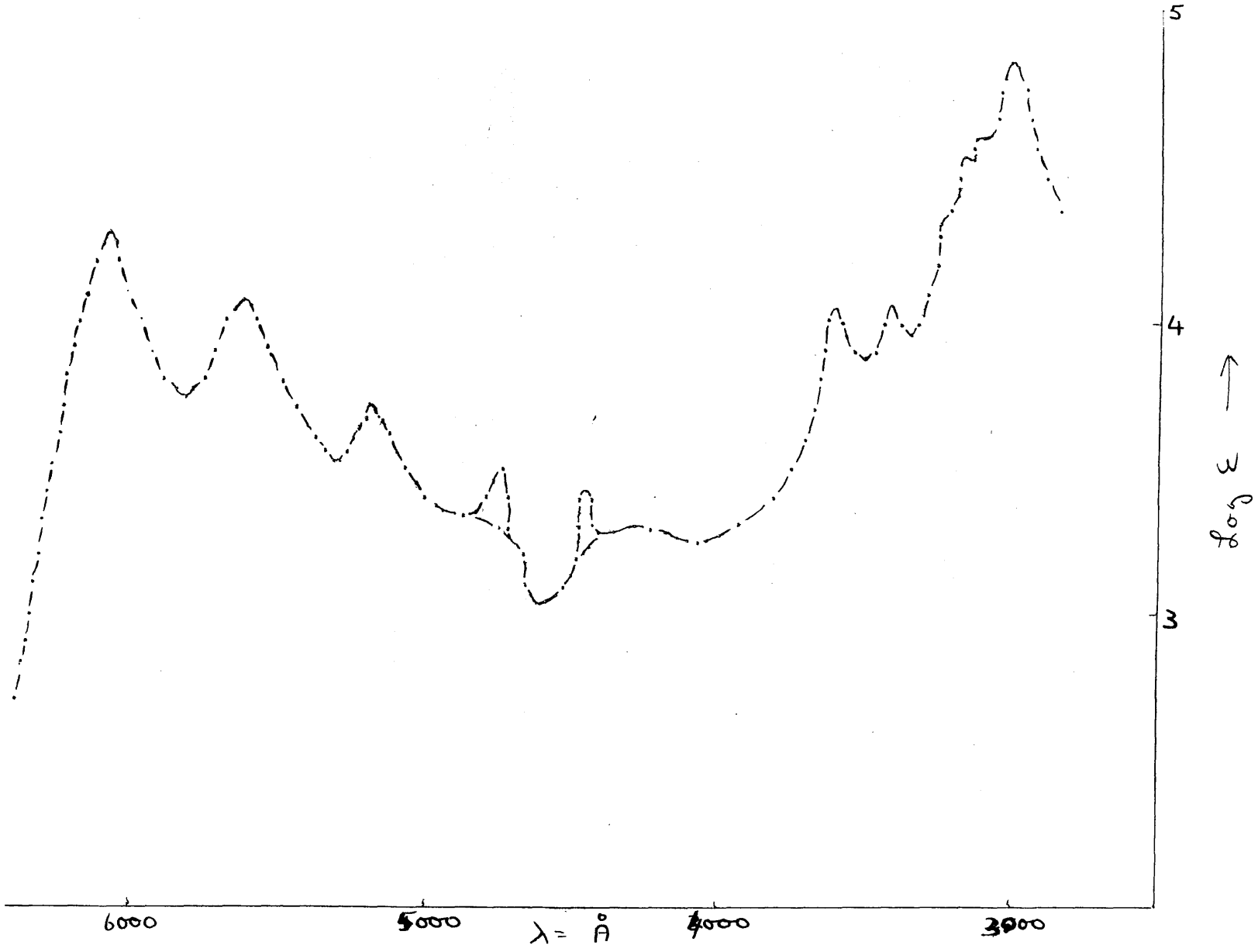


Fig. 18. Absorption Curve of Naphtho [2'-3'- 1-2-]-Perylene in Benzene.
Band Maxima at 6080, 5620, 5190, 4260, 3600, 3420, 3190, 3120 and 3010 Å.
Those at 4740 and 4450 Å due to about 20% Tetracene.

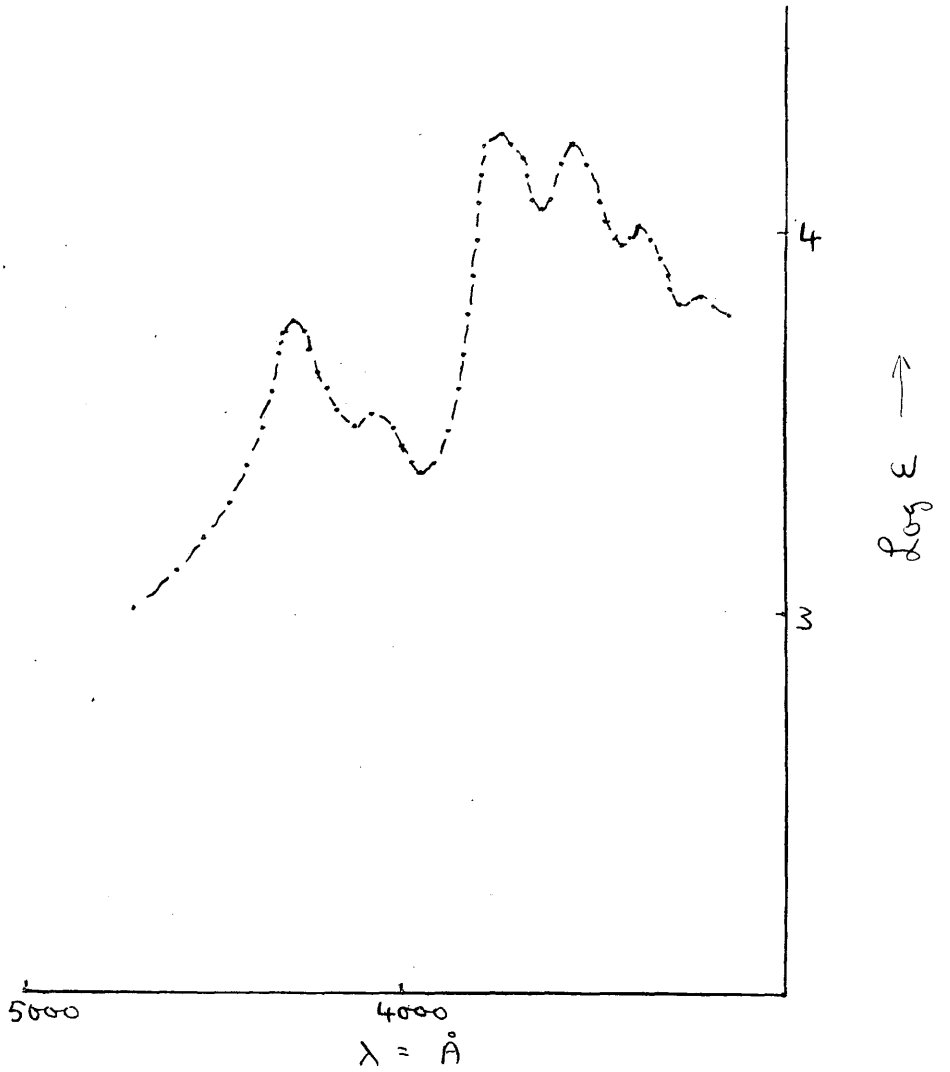
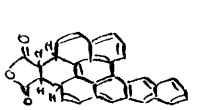
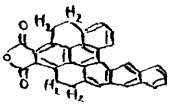


Fig. 19. Absorption Curve of Maleic Anhydride Adduct of Naphtho-[2'-3'-1-2]-Perylene in Benzene. Band Maxima at 4280, 4100, 3750, 3560 and 3400 Å.

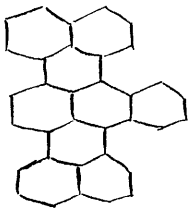
The adduct is probably



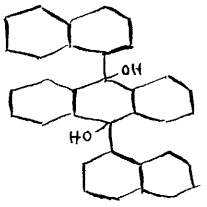
or



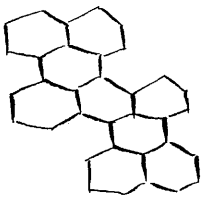
7-8-Benzterrylene.



XXVI



XXV



XXVII

Fig.20

The product obtained by Clar and Guzzi[31], by a ring closure of 9-10-di-1-naphthyl-9-10-dihydroxy-9-10-dihydro-anthracene (XXV) was considered to be either 1-9-5-10-di-peri-naphthalene-anthracene (XXVII) or 7-8-benz-terrylene (1-9-4-10-di-peri-naphthalene-anthracene) (XXVI). (XXVII) was preferred on the rather slender basis that the 1-4-dimethyl derivative of (XXV) gave no similar condensation product on treatment with $AlCl_3$. We have now evidence that their product was 7-8-benzterrylene.

To prepare a specimen of 7-8-benzterrylene whose structure would be without doubt, 1-4-dichloroanthraquinone was treated with an excess of 1-naphthyl magnesium bromide and the resulting diol treated with a melt of $AlCl_3/NaCl$ at 110°C. Reduction of the diol prior to ring closure seemed to make little difference to the final products.

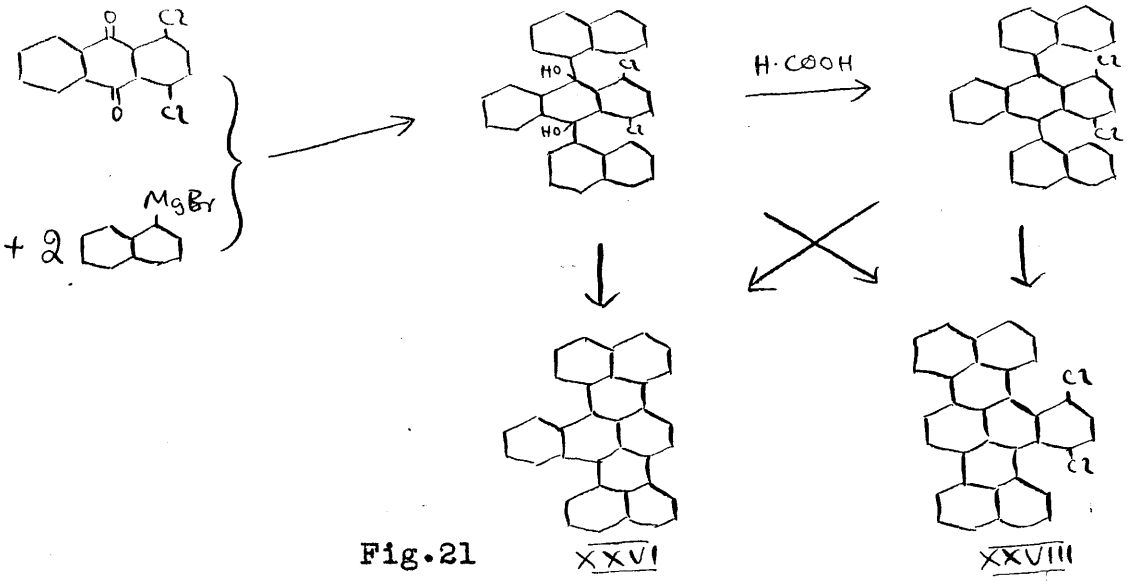


Fig.21

Apart from the fission products, naphthalene, anthracene, benzperylene and their chloro derivatives, 1'4'dichloro-7-8-benzterrylene (XXVIII) and 7-8-benzterrylene (XXVI) were the main substances obtained from the melt. The dichloro compound was green and its absorption spectrum showed an intense band at 6600Å. The hydrocarbon answered the description of Clar and Guzzi's 1-9-5-10-di-peri-naphthalene-anthracene. It was also shown to be identical with a sample prepared from anthraquinone in the way described by them.

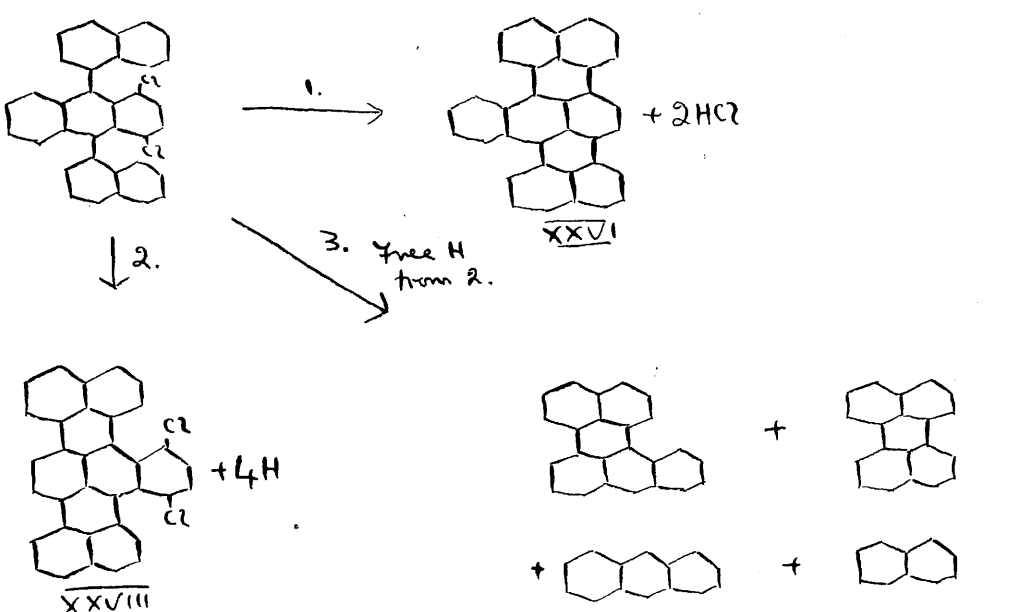
For the ring closures it was found to be much more efficient to use an $AlCl_3$/NaCl melt in place of the fusion with $AlCl_3$ in presence of a small amount of pyridine as described in the original paper. The NaCl seemed to have the same effect as the pyridine and prevented excessive

fission of the dinaphthyl anthracene derivative.

The following scheme (Fig.22) gives an outline of the probable reactions taking place during the fusion. It is purely qualitative as the many variable conditions were not strictly controlled. Generally speaking, the proportions used were - chloranthracene derivative : $AlCl_3$: NaCl : : 1 : 5 : 1. The temperature of the melt was kept about 100-110°C and the time taken was about five minutes. In all cases the chloranthracene derivative was added slowly to the $AlCl_3$/NaCl melt.

Reaction 2 takes place more readily in B than in A as it involves condensation with the elimination of water as well as setting free two atoms of hydrogen. Although in A. reaction 2 releases four atoms of hydrogen, it is likely to be secondary to 1 and probably there will be more nascent

A.



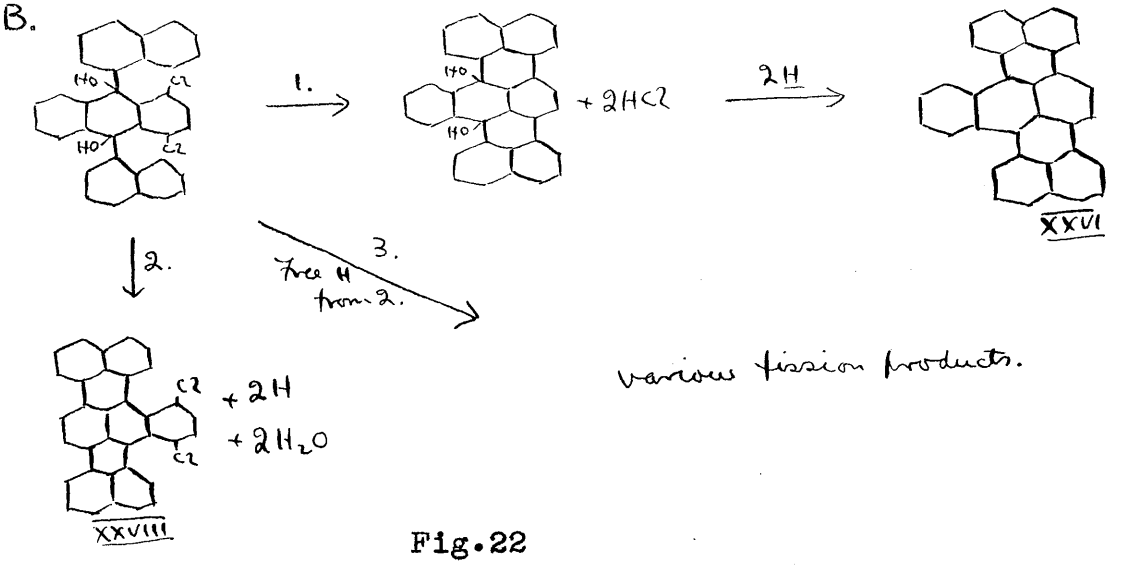


Fig.22

hydrogen available in B than in A. This free hydrogen is probably responsible for the splitting of the dinaphthyl-anthracene molecule into various fission products as shown in reaction 3.

The results bear out this interpretation. Thus, using the reduced (or partially reduced) diol, as in A, a much larger proportion of unsubstituted hydrocarbon (XXVI) was obtained than in B. The proportion of the chlorinated compound (XXVIII) appeared to be much the same in both cases and the proportion of fission products was greater in B than in A. Apart from very small traces of chlorine containing compounds obtained from the first chromatographic elutions, all the fission products were unsubstituted. After the ring closure of the non-chlorinated dinaphthyl-anthranol, some of the higher fractions from the alumina column gave impure, low-melting, blue crystals. On running a solution of these through a second alumina column, no clear separation was

observed but the first runnings were found to contain small quantities of anthracene. The main body of material on the column was pure benzterrylene, while the upper fractions were again impure.

It therefore seems likely that these upper fractions contain a molecular compound of benzterrylene and anthracene.

The absorption curve of 7-8-benzterrylene is the same as that given by Clar and Guzzi[31] for their hydrocarbon (Fig.24).

A pure specimen of the maleic anhydride adduct was prepared by treating the hydrocarbon with excess maleic anhydride at ca. 200°C without any further solvent. An examination of the absorption curve of this 1-9-4-10-di-(peri-naphthalene)-endo-9-10-(1-2-succinic anhydride)-anthracene (XXX) is further proof of the structure of 7-8-benzterrylene.

As with diphenyl, it is possible to build up a linear anellation series from p-terphenyl (XXIX) and we find that the maleic anhydride adduct of 7-8-benzterrylene (XXX) fits in very well. Its basic aromatic structure is that of 2-3-2''3''dibenz-p-terphenyl which is held in a planar state by the rest of the molecule. It is also clear that had the 7-8-benzterrylene (XXVI) been 1-9-5-10-di-peri-naphthalene-anthracene (XXVII), the absorption curve of its 9-10 maleic anhydride adduct (XXXI) should have shown

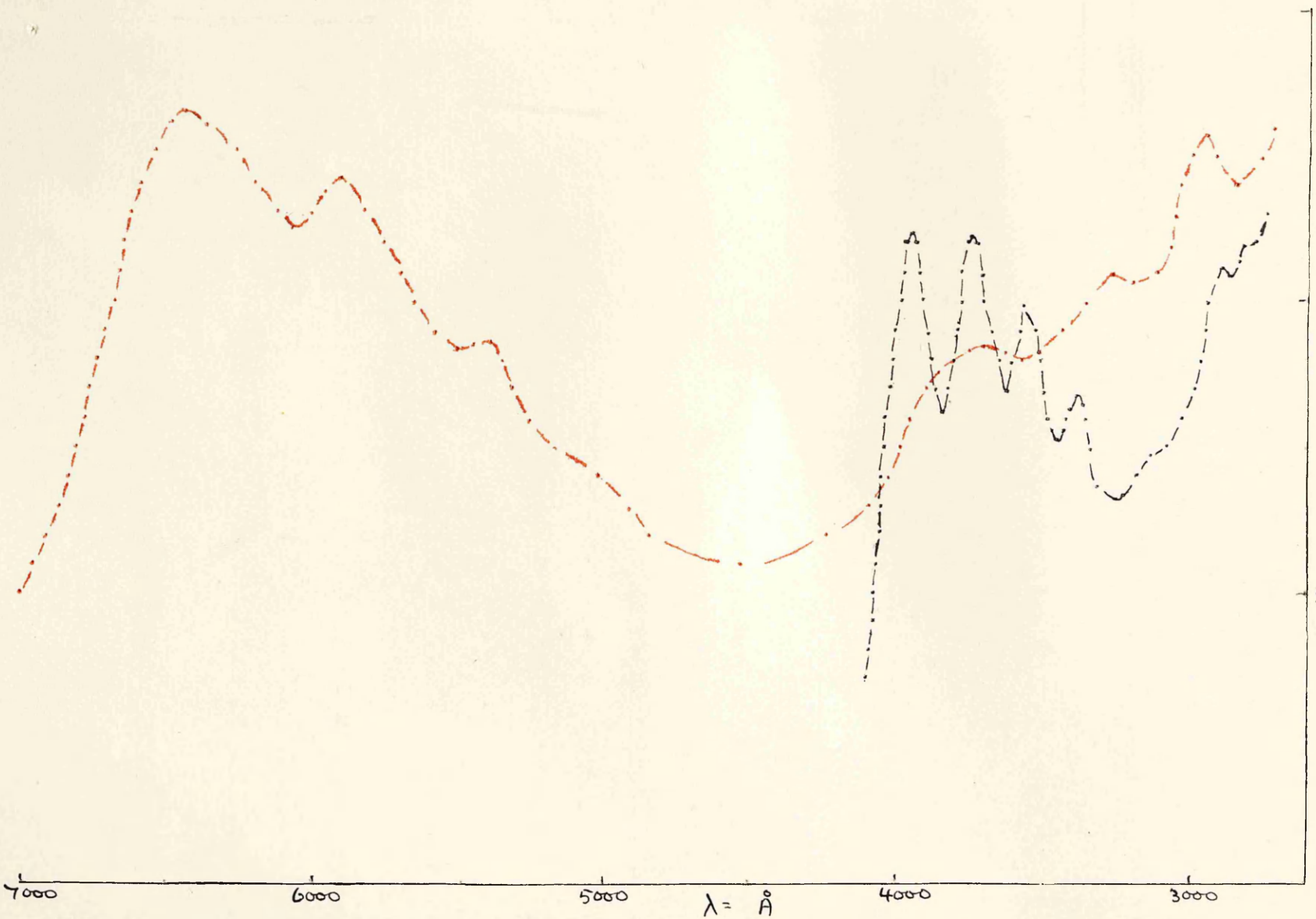


Fig. 24 (cf. Clar e Zanzi (31)) — Absorption Curve of 7-8-Benzterrylene in Benzene. Band Maxima at 6430, 5910, 5440, 3720, 3270 and 2960 Å.

— Absorption Curve of 9-10-Di-(1-naphthyl)-Anthracene in Benzene.

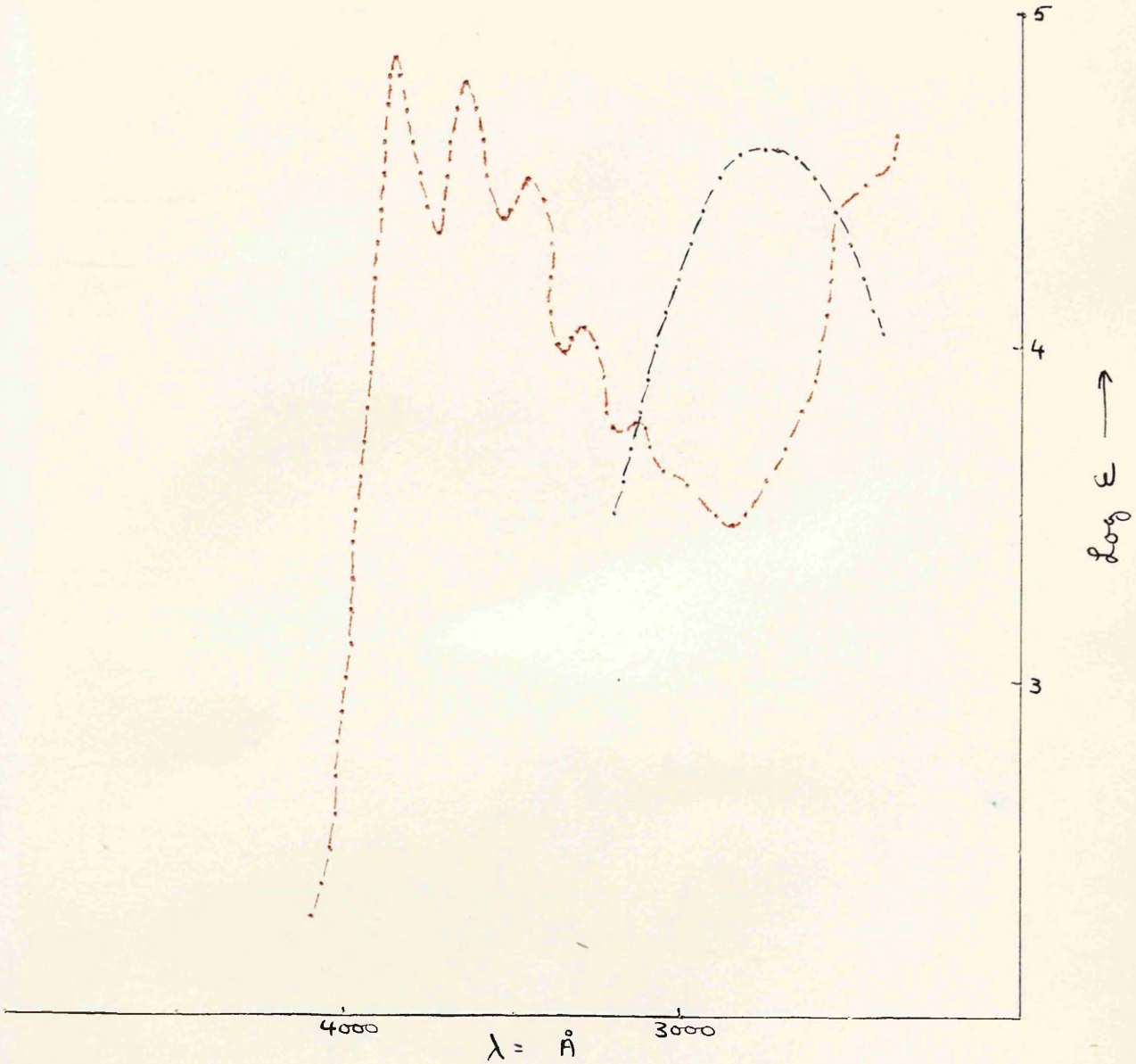
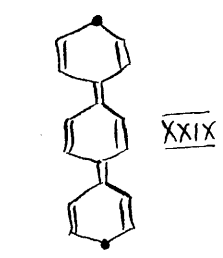


Fig 25.

-.-.-.- Absorption Curve of p-Terphenyl in Alcohol
Band Maximum at 2760 Å. (58)

-.-.-.- Absorption Curve of Maleic Anhydride Adduct
of 4-8-Benzterrylene (Sodium salt) in Alcohol.
Band Maxima at 3870, 3660, 3470, 3300, 3150 and 2500 Å

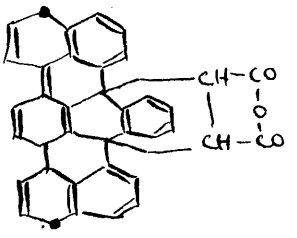
absorption bands at approximately the same wave lengths as benzanthrene with twice the intensity.



XXIX

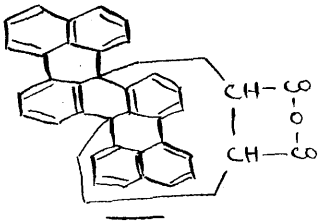
λ 2760
K_p 6·000

$\longrightarrow$ +0·970



XXX

3725 [1].
6·970



XXXI

1. Correction of 300 cm^{-1} made in frequency as spectra was that of disodium salt in alcohol (Fig. 25.)

Fig.23

The syntheses of many of the compounds used in this work involved the use of considerable quantities of tetracenone. This was prepared by the method outlined in Fig.26[34-37]. The yields were good in most stages though the ring closure to dihydrotetracene presented some difficulties, giving a yield of 30-40%. In the final reduction of the quinone to tetracenone considerable modifications were made to Fieser's method. (See p. 32).

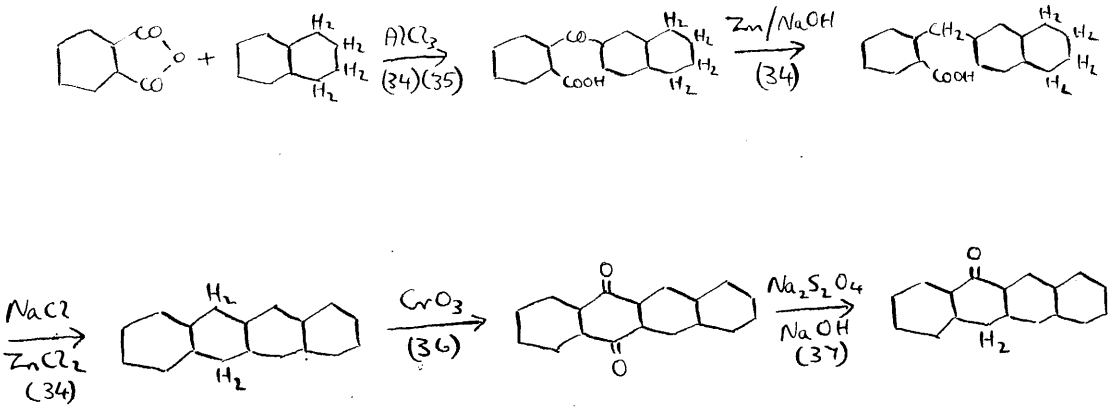


Fig.26

Another method for the preparation of tetracenone is outlined in Fig.27. It was not successful, however, giving either sulphonated material from the boric acid/H_2SO_4 ring closure, or a tarry product from the acetic anhydride/$ZnCl_2$ reaction. Treatment of the keto acid with PCl_5 (42) also gave poor yields.

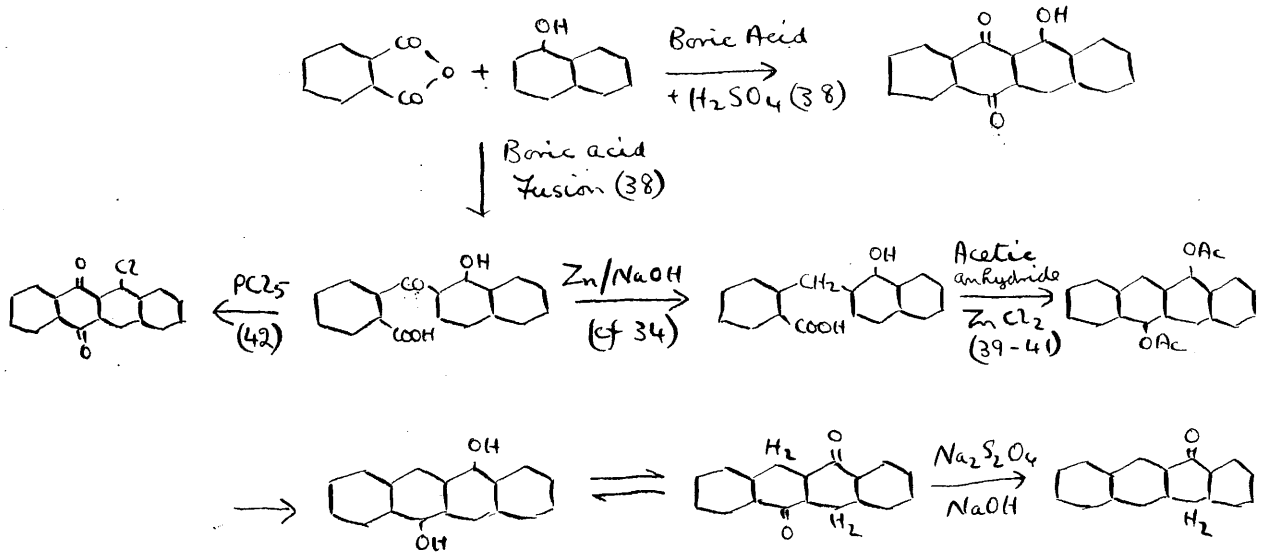


Fig.27

The preparation of pentacenone, required for the 6-naphthyl-pentacene synthesis, is given in Fig.28.

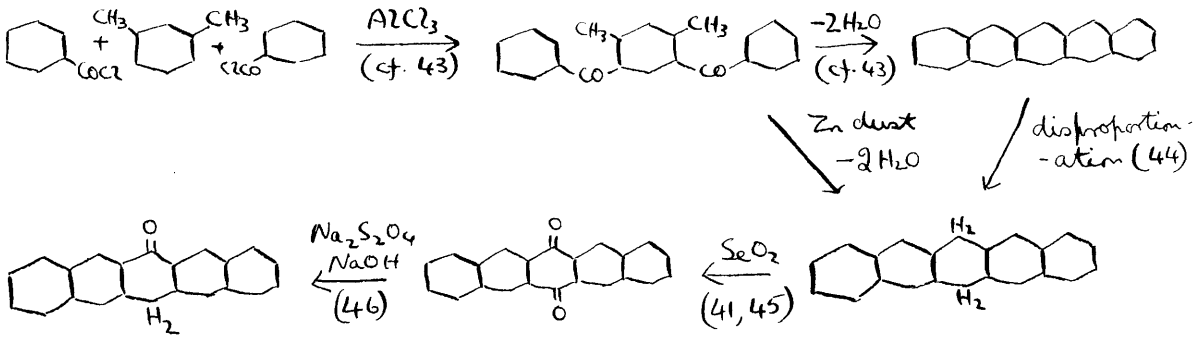


Fig.28

The preparation of the diketone was carried out as described in the experimental part, p.47 (cf.43).

In the Elb's ring closure, the experiment was made, of carrying out the pyrolysis in the presence of zinc dust, with the object of providing a source of hydrogen to form dihydro-pentacene, thereby avoiding excessive disproportionation of the pentacene as described by Clar and John (44).

The oxidation with selenium dioxide was carried out in nitrobenzene (41,45) and presented no difficulty, but the subsequent reduction with alkaline hydrosulphite gave a poor yield (46%, cf. also 37).

The preparation of 7-8-benz terrylene is outlined in Fig. 9. It was also prepared from 1-4-dichloranthraquinone (Fig.21) which was obtained by method (c) Fig.29, methods (a) and (b) both giving poor yields.

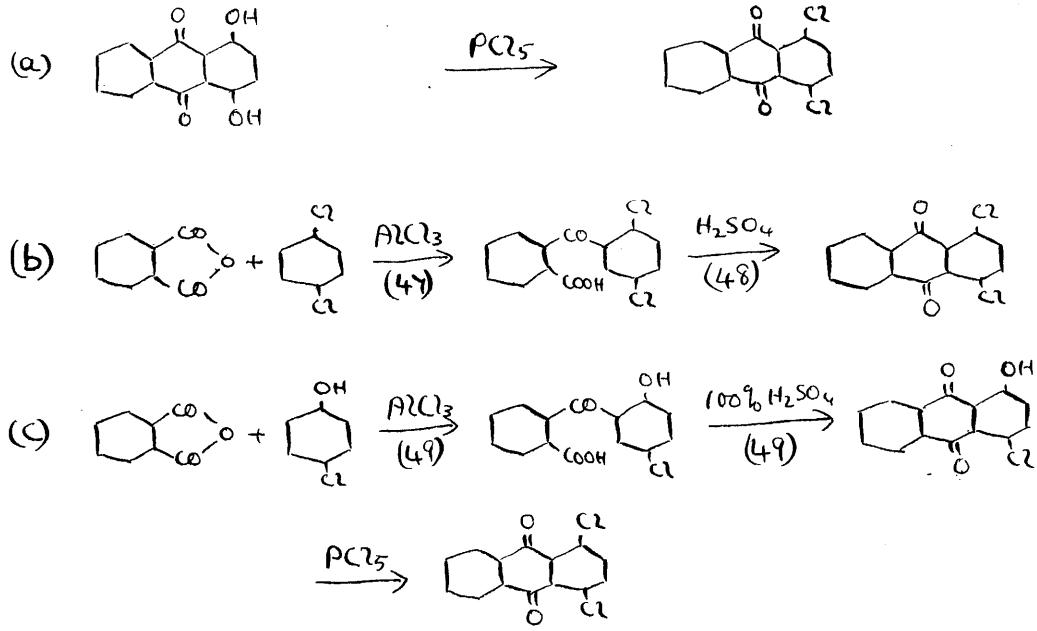


Fig.29

The reduction of the 1-4-dichloro-9-10-di-(1-naphthyl)9-10-dihydroxy-9-10-dihydro-anthracene to 1-4-dichloro-9-10-di-(1-naphthyl) anthracene was attempted with sodium iodide in acetic acid or in a pyridine/acetic acid mixture but was not very successful[50]. Formic acid[51,51a] gave an almost complete reduction, a fine slurry of the diol in acetic acid being used. To ensure the complete exclusion of water, a calculated quantity of acetic anhydride was added to take up the water present in the formic acid (Fig.21).

An attempt to prepare 7-8-benzterrylene from quinizarin (cf. Etienne & Heymes[52]) yielded mainly 1-1'-dinaphthyl in the Grignard stage, large quantities of quinizarin being recovered from the reaction mixture.

A small quantity of material was obtained, however, which on treatment with $AlCl_3$ in benzene gave a deep violet solution showing absorption bands at 6305Å and 5490Å. This is probably 7-8-benzterrylenequinone (XXVIa or XXVIb).

Treatment of the impure dinaphthyl with $AlCl_3$ in benzene gave a blue solution showing absorption bands at 6450Å, 5900Å and 5450Å. It therefore probably contains some 1-4-dihydroxy-9-10-di-(1-naphthyl)-anthracene which should readily ring close to give 7-8-benzterrylene.

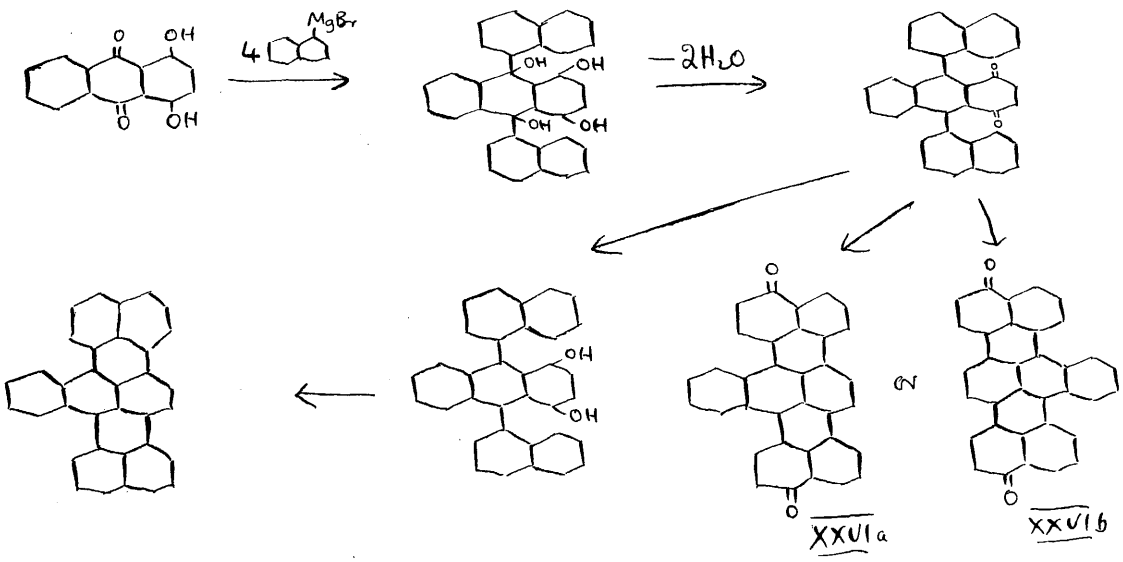


Fig.30

Experimental.

Preparation of 9-methyl anthracene from anthraquinone.

Anthraquinone ⟶ Anthrene

By treatment with tin and HCl in acetic acid solution, Meyer[53].

Anthrene ⟶ 9-methyl anthracene

cf. Sieglitz & Marx[20].

To a cold Grignard solution of methyl magnesium iodide prepared in the usual manner, $^1/_3$ of the molecular proportion of anthrene dissolved in dry benzene was added over a period of about 20 minutes with vigorous shaking. A green colour was observed though the solution gradually became yellow. Decomposition with ice water precipitated a yellow mass which went into solution on the addition of dilute H_2SO_4. The benzene ether layer was separated and shaken several times with a dilute solution of NaOH containing $Na_2S_2O_4$ until no red colouration was observed in the aqueous layer. (This to remove any anthraquinone which may be present.)

After distilling off the benzene, the methyl anthracene was filtered from the aqueous layer, washed and recrystallised from 96% alcohol. Large yellow needles were obtained mixed with smaller red needles. M.P. 81°.

On recrystallisation from benzene, large hexagonal plates were obtained, again along with a considerable quantity of the small reddish needles from which they were readily separated.

The yellow plates melted sharp at 81° and the red needles at 163-165°. (Mixed M.P. 79°).

The maleic anhydride adduct of 9-methyl-anthracene formed very rapidly in xylene solution and melted at 274° decomposing above 305°.

The absorption curve of 9-methyl anthracene is shown in Fig.4.

Preparation of 2-(5-6-7-8-tetrahydro-2-naphthoyl) benzoic acid and its reduction to 2-(5-6-7-8-tetrahydro-2-naphthyl-methyl)-benzoic acid. (Fig.26.)
cf. Clar[34], also Barnett & Lowry[35].

80 gm. phthalic anhydride and 80 gm. tetralin were mixed in ca. 240 cc. tetrachlorethane in a litre flask and 160 gms. of carefully powdered $AlCl_3$ was added fairly rapidly with constant shaking. The HCl gas was liberated in about half an hour. After cooling, the contents of the flask were carefully poured into a 2-litre distilling flask containing a considerable quantity of ice to which about 30 cc. concentrated HCl had been added. When hydrolysis was complete, the solvent was removed by steam distillation,

the acid solidifying when all the solvent had been removed. The liquid was then decanted (filtered if necessary) and the solid mass of acid washed with hot water. It was then dissolved in a solution of 120 gm. NaOH in about 1 litre of water and submitted to further steam distillation to remove any further solvent or tetralin. After filtration the bulk of liquid was made up to 3 litres for the reduction.

This was carried out by adding 160 gm. zinc dust and a trace of copper sulphate to the above alkaline solution which was then refluxed with stirring in a 5 litre flask for 7-8 hours. (A small quantity of a yellowish oil appeared after about 4 hours, but did not appear to affect the reduction). The solution of the sodium salt was then filtered hot from the zinc residue which was washed well with very hot water. The mixed filtrates were then poured while still hot into about 320 cc. concentrated HCl (excess) when the acid separated out and was filtered when cold and washed with a little warm water.

Yield from 80 gm. phthalic anhydride and 80 gm. tetralin was 154 gm. of the reduced acid.

2-(5-6-7-8-tetrahydro-2-naphthyl-methyl)-benzoic acid, ⟶ 5-12-dihydrotetracene. (Fig.26.)

cf. Clar[34].

150 gm. of the crude acid from the reduction experiment was carefully dried and powdered and mixed in a

500 cc. pyrex distilling flask with 100 gm. zinc chloride and 20 gm. sodium chloride. The mixture was fused and heated till all the water was driven off, the temperature of the melt being raised to 300-310°.

When no further steam escaped the dihydrotetracene was distilled from the melt under 10-15 mm. pressure, the temperature being raised to about 280°. Care had to be taken that the side arm of the distilling flask did not choke with solid dihydrotetracene. The distillate was then dissolved in the smallest possible amount of xylene and allowed to recrystallise, being washed on the filter with benzene and alcohol.

The intense yellow colour of the product is due to small quantities of tetracene and may be removed by treatment with maleic anhydride.

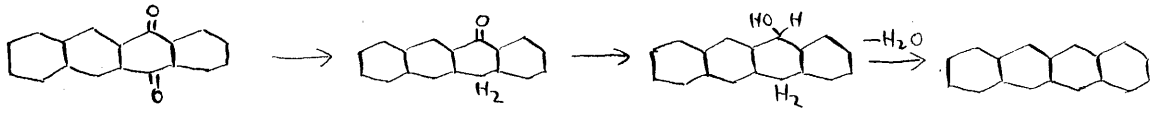
Oxidation of 5-12-dihydrotetracene to tetracenequinone (Fig.26) cf. Gabriel & Leupold[36].

27 gm. of 5-12-dihydrotetracene was carefully ground in a mortar with a little acetic acid to make a fine slurry. This was then washed into a flask with 600 cc. of glacial acetic acid and a solution of 36 gm. CrO_3 in a very little water was slowly run in. After boiling for a short time the quinone was filtered off and washed with acetic acid and water.

Reduction of Tetracenequinone to tetracenone (Fig.26). cf. Fieser[37].

A modification of Fieser's reduction using 30 gm. $Na_2S_2O_4$ with about 9 gm. of the quinone in a solution of 40 gm. NaOH in 250 cc. water and 50 cc. alcohol yielded a precipitate of impure tetracenone which gave only a dirty brown colouration in sulphuric acid instead of the characteristic red of the pure compound.

On examination it was thought that some tetracene was present though Fieser states that reduction further than the tetracenone stage is not possible with hydrosulphite.



tetracene-quinone tetracenone tetracene

Fig.31

The product was therefore dissolved in acetic acid and filtered, tetracene being insoluble in acetic acid. The tetracene thus obtained was recrystallised from nitrobenzene and was about 20% of the total yield from the reduction.

The filtrate was then treated with a small amount of maleic anhydride to remove any remaining tetracene and the tetracenone precipitated by addition of water. It was then recrystallised from alcohol after refluxing with charcoal. M.P. 175° dec. This product gave the characteristic

red colour in H_2SO_4 and the characteristic violet in alcoholic NaOH due to the formation of the sodium salt of the 5-tetracenol.

A further quantity of tetracenone was obtained from the mother liquors of the reduction experiment by acidifying with acetic acid. This gave the characteristic red with sulphuric acid but only a dirty brown colour was obtained with alkali. Attempts to recrystallise after charcoal refluxing in alcohol gave first a few white crystals, M.P. 240° dec. These were also obtained among charcoal with the first crop of crystals and may be the ether, which is formed from two molecules of 12-hydroxy-5-tetracenone which is an intermediate in the reduction of the quinone. Fieser gives the M.P. of the hydroxy compound as 230° (deep red in alkali) and of the ether as 295°.

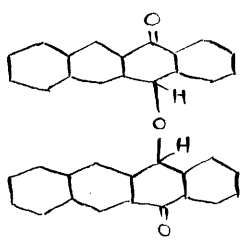


Fig.31a

Another white fluffy compound was obtained from the final wash waters of the reduction experiment. This gave a green colour in concentrated H_2SO_4 and is probably 5-12-dihydrotetracenone-5-ol.

It was then found to be more satisfactory to carry out the reduction in an aqueous medium without the addition of alcohol. Tetracenone, however, is fairly soluble in alkaline solution and fairly large quantities of impure

material were still obtained on acidification of the mother liquors with acetic acid. This material was best utilised by re-oxidising it with CrO_3 back to the quinone.

The following method was then found to give the best yield of tetracenone.

8 gm. of tetracene-quinone was dissolved in concentrated sulphuric acid and re-precipitated in a very finely divided state by pouring the solution into water. After filtering and careful washing with hot water the quinone was placed in a 2 litre flask with a solution of 20 gm. NaOH in 500 cc. water and heated to almost boiling. About 12 gm. $Na_2S_2O_4$ was then added, when the solution went a deep green. After several minutes' refluxing light crystals began to separate and the bulk of the solution became a deep orange brown. Two further 4 gm. portions of $Na_2S_2O_4$ were added at intervals of 15 minutes, and the precipitate tested with H_2SO_4.

A series of such tests showed a gradual change from the deep crimson of the quinone to the orange red of the tetracenone.

After boiling for one hour the tetracenone was filtered off while still hot and washed with a solution of NaOH and $Na_2S_2O_4$ and afterwards with hot water.

(N.B. It is important that the solution should be alkaline and still have reducing properties when the filtration is carried out. A test with litmus paper also showed

a white spot in the centre of the purple area showing that the $Na_2S_2O_4$ had not been completely used.)

The light brown substance thus obtained gave the characteristic red with concentrated H_2SO_4 and the violet colour with NaOH. Its M.P. was 175°d. It recrystallised better from acetic acid than from alcohol and gave a M.P. of 180° dec. (Fieser[37] gives M.P. as 196° dec. but says it varies with the rate of heating.)

Small quantities of tetracene which may be produced become apparent during the acetic acid recrystallisation and can be removed by treatment with a trace of maleic anhydride.

Crystals of tetracenone from the acetic acid solution after treatment with an excess of maleic anhydride gave a melting point of 185-190°. The maleic anhydride even in excess does not appear to react with the tetracenone.

Tetracenone ⟶ (5-methyl-5-hydroxy-5-12-dihydro tetracene) ⟶ 5 methyl-tetracene or 5-methylene-5-12-dihydro-tetracene.

1 gm. tetracenone was dissolved in dry benzene and added to a dry ether solution containing a considerable excess of methyl magnesium iodide prepared in the usual way with activated magnesium and methyl iodide. A precipitate which formed at first went back into solution almost immediately

and further heating was unnecessary. (It may be necessary to reflux for a short time ($\frac{1}{2}$ hour) when larger quantities are being employed.)

The Grignard complex was decomposed by pouring the solution on to ice, when a considerable quantity of methane was given off. A fairly large quantity of concentrated HCl was then added to assist in splitting off the molecule of water and after evaporating the ether and benzene, the aqueous portion was boiled vigorously for some time and finally filtered, giving good red crystals.

An attempt to vac. sublime the product was not very successful, the melting point being too low.

It recrystallised from benzene in beautiful red rosettes and from acetic acid in finer red crystals, M.P. 160°. A solution in conc. H_2SO_4 had a bright green colour.

On treatment of the acetic acid solution with maleic anhydride a white microcrystalline solid slowly separated out on cooling which was not readily resoluble. It was insoluble in NaOH solution and was therefore thought not to be the adduct. It was not readily soluble in xylene and had a very high M.P. about 295° and dissolved slowly in conc. H_2SO_4, giving an olive green colour on heating.

The mother liquors from the acetic acid recrystallisation on standing for several days deposited some light plates which were probably the photo-oxide.

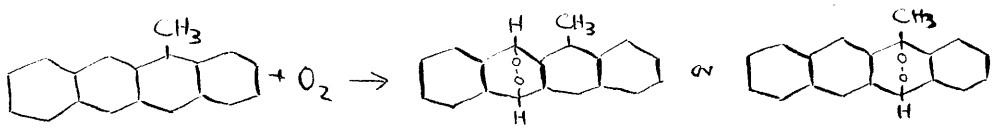


Fig.32

A dilute solution in benzene had a bright green fluorescence which was completely removed after radiation with a 200 watt lamp for 10 minutes.

The absorption curve of 5-methyl tetracene is shown in Fig.4 and discussed on p. 8

Analysis:-

C 94.16%	$C_{19}H_{14}$	C 94.16%
H 5.67%	requires	H 5.82%

Reactions between 5-methyl tetracene and maleic anhydride.

See Fig.3, p.7.

The reaction with maleic anhydride in acetic acid solution seemed to give some indication of polymerisation of the hydrocarbon (viz. the production of a high melting substance which was insoluble in alkali).

In benzene the white compound produced on cooling also formed a rather insoluble sodium salt. Filtration and precipitation of the acid from the filtrate by means of concentrated HCl gave a white compound which appeared to lose water at 100° and finally melted at 285° turning dark brown.

The residue which mostly dissolved in a larger quantity of warm water was likewise reprecipitated with HCl.

It lost water at 100° and melted at 135°.

Preparation of adduct in xylene.

For times, quantities, solvents, etc., cf. Bachmann & Kloetzel[54].

About .5 gm. methyl tetracene was refluxed in xylene for half an hour with 1.2 gm. (large excess) of maleic anhydride. The intense red colour disappeared almost at once. After refluxing a quantity of NaOH solution was added and the xylene distilled off in steam.

As in the benzene experiment the resulting compound appeared to be soluble only with difficulty in water, so was filtered off.

The portion soluble in the NaOH solution and the insoluble residue were then treated separately and the results are best shown in the following summary:

Portion soluble in NaOH soln.	Portion insoluble in NaOH soln.
Precipitated with concentrated HCl filtered and dried	Treated with concentrated HCl and taken up in aqueous KOH solution in which it was much more soluble, a slight residue was filtered off and the acid precipitated with concentrated HCl, filtered and dried.

Portion soluble in NaOH (contd.)	Insoluble in NaOH (contd.)
Vac.sublimation gave white crystals with a slight yellowish tinge later, leaving only a little dark residue.	Vac.sublimation gave light yellow crystals and a yellow glassy substance leaving only a slight dark residue.
Sublimate treated with aqueous KOH in which it was readily soluble.	Sublimate treated with aqueous KOH in which it was soluble.
KOH solution precipitated with HCl gave M.P. 280°. Recrystallised from acetic anhydride/xylene M.P. 290-291°.	KOH solution gave a precipitate on standing but redissolved on heating. Reprecipitated with HCl and dried; M.P. 139°. Recryst. acetic anhydride and xylene. M.P. 200°. 2nd recrystallisation gave a product which softened at 205°, melted at 250° and gradually became red, decomposing above 305°.
Dissolved in concentrated H_2SO_4 on heating with practically no coloration.	Dissolved in concentrated H_2SO_4 on heating; olive green colour.

Analysis:	Analysis:
C 80.21	C 80.99
H 5.01	H 4.78
$C_{23}H_{16}O_3$ requires	$C_{23}H_{16}O_3$ requires
C 81.18	C 81.18
H 4.71	H 4.71
	~~C 4.17~~

Both adducts on fusion yielded a yellowish glassy substance, giving a green solution in H_2SO_4 and a yellow solution in benzene with a green fluorescence. A rough examination of the spectra of these solutions showed the absorption bands to be almost identical with those of 5-methyl tetracene.

Tetracene - maleic anhydride adduct.

A small quantity of the tetracene adduct was prepared for the purposes of comparison with the methyl-tetracene adducts. See Clar[55], and Bachmann & Kloetzel[54].

A small quantity of tetracene was refluxed for about half an hour in xylene with a fairly large excess of maleic anhydride, the xylene partially evaporated and the product allowed to crystallise. After filtration, the crystals were washed with benzene and dried. They were homogeneous and melted without further recrystallisation at 270°. (Clar[55] gives 273-282°).

On vac. sublimation using a "Hyvac" pump the adduct sublimed without decomposition, though on heating to higher temperatures it decomposed to tetracene and maleic anhydride.

Attempt to prepare 9-(1-naphthyl)-anthracene from anthrone. Cf. Krollpfeiffer and Branschied[29].

1-Naphthyl-magnesium bromide was prepared from 20 gms. of 1-bromonaphthalene (dried over calcium chloride), and 2.3 grams (roughly equivalent) of magnesium which had been activated with iodine. Only a very small quantity of ether (ca. 50 cc.) was required and the reaction took place spontaneously, being completed by heating.

The Grignard solution was decanted from excess magnesium into an ice-cooled solution of anthrone in benzene. The reaction mixture was decomposed with ice and acetic acid and the ether, benzene and naphthalene removed by steam distillation. After much washing with NaOH and hydrosulphite, in an attempt to remove unchanged anthrone and anthraquinone, the resulting tar was taken up in ether and allowed to stand for several months. A solid was obtained which, after washing with a petroleum ether/ether mixture, had a pale yellow colour, M.P. 262°C, after crystallising from benzene. Recryst. xylene, M.P. 281-282°C.

The pale yellow needles gave a yellow solution in

H_2SO_4 and a deep red vat in alkaline hydrosulphite solution and were found to be identical with a specimen of anthraquinone.

PREPARATION OF NAPHTHYL TETRACENE, DIBENZPERYLENE AND NAPHTHOPERYLENE.

Tetracene ——————→ 5-(1-naphthyl)-tetracene.

1-Naphthyl-magnesium bromide was prepared as for the previous experiment. The Grignard solution was decanted from excess magnesium into a benzene solution of tetracenone (4 gm.). A deep red colour was immediately produced and the solution was refluxed for half an hour before it was decomposed with ice and acetic acid.

The ether and benzene were distilled off and excess bromonaphthalene and naphthalene were removed by distillation in steam. The red product remained oily and the aqueous layer was finally decanted off, when the product solidified on the addition of cold water. After washing with water it was again submitted to steam distillation to remove further traces of naphthalene. A little HCl was added to promote crystallisation.

The product crystallised from xylene in stout orange needles which gave a dirty green solution in H_2SO_4 and had a

M.P. of 186-194°C. A benzene/petroleum ether solution purified on an alumina column gave crystals of M.P. 204°C; recrystallised from the same solvent 207°C. These formed a bright green solution in H_2SO_4 and a benzene solution had a green fluorescence.

The absorption curve of 5-(1-naphthyl)-tetracene is shown in Fig.14.

Analysis:

C	95.06%	$C_{28}H_{18}$	C 94.88%
H	5.13%	requires	H 5.12%.

Scholl ring closure of 5-(1-naphthyl)-tetracene.

Cf. Scholl & Weitzenbock[27]
Zincke & Dengg[27a]
Fieser & Hershberg[28]

Figs. 8 and 10

Trial experiments of treating naphthyl tetraeene with aluminium chloride in benzene and nitrobenzene were made. That in benzene was quite successful giving a red solution with an orange/gold fluorescence. The nitrobenzene however appeared to be reduced and a blue mass from which it was difficult to remove the aluminium salts was obtained.

A straight fusion with aluminium chloride yielded a maroon coloured substance, whose solution in benzene showed several bands when run on to an alumina column.

The most satisfactory method of carrying out the ring closure was in an $AlCl_3/NaCl$ melt, as follows:

1 gram of naphthyl tetracene was heated for one hour at 150°C with 4 gms. $AlCl_3$ and 1 gm. NaCl, the hydrocarbon being added to a melt of the salts. The melt was then decomposed by pouring into dilute HCl, filtered and extracted with benzene. After distilling off the solvent, a solution was made in petroleum ether and run through an alumina column. An increasing percentage of benzene was added to the pet. ether for development and elution.

The whole column was kept in the dark as far as possible to prevent excessive photo-oxidation of the products. It gradually developed as shown in Fig.33.

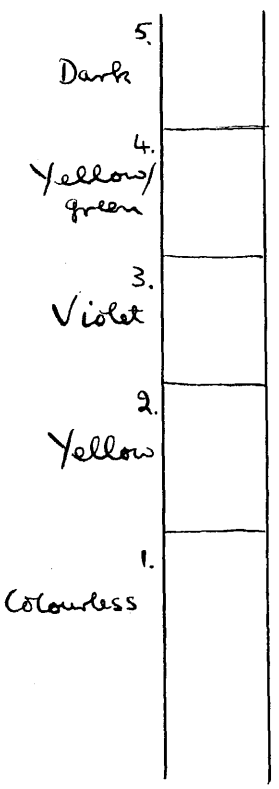


Fig.33

Band 1. Colourless with blue fluorescence; on evaporation yielded light olive green crystals of M.P. 226-230°C which were unidentified.

Band 2 Yellow with a yellow fluorescence: on evaporation yielded a yellowish tar, which in one case after long standing yielded a single red crystal whose solution in benzene gave an absorption curve corresponding to that from band 5.

Band 2 probably contains 5-12-dihydro-5-6-peri-naphthalene-tetracene (XIIa) (Fig.10) which

should be readily oxidised to 1-2-5-6-dibenzperylene.

Band 3. Violet with a red fluorescence; on evaporation yielded dark crystals giving a blue solution in H_2SO_4, M.P. 235-240°C (evac.capill.).

The absorption curve of a benzene solution is shown in Fig.18 and from this it is apparent that the substance is contaminated with about 20% of tetracene, the rest of the curve being characteristic for naphtho-(2'3'1-2)-perylene (XIII).

A benzene solution was decolourised extremely rapidly in light and by boiling with maleic anhydride.

Analysis:

C	94.85%	XIII, $C_{28}H_{16}$	C 95.45%
H	4.90%	requires	H 4.55%

80% XIII + 20% tetracene C 95.35%

$C_{130}H_{76}$ requires H 4.65%

50% XIII + 50% tetracene C 95.17%

$C_{46}H_{28}$ requires H 4.83%.

It is thus clear that in dealing with such polycyclic hydrocarbons, analysis is of little value, while the absorption curves are distinctive. Examination of the latter has therefore been given priority.

Band 4. Yellow/green with green fluorescence. A rough examination of the spectrum of this band showed to be almost identical with that of tetracene.

Band 5. This dark band, when further developed, produced a light red solution which contained a mixture of tetracene and 1-2-5-6-dibenzperylene. The absorption curve is shown in Fig.17 (M.P. 180°C). The tetracene was partially removed by treatment with maleic anhydride, when the red crystals remaining had a melting point of over 360°C (evac. capill.).

Experiments on the absorption spectra of 1-2-benzperylene, 1-2-5-6-dibenzperylene and naphthol-(2'3'1-2)-perylene and their adducts.

Solutions of these substances in benzene or petroleum ether were orange, light red and violet respectively.

The spectrum of benzperylene appeared to be normal but both the dibenz and naphtho derivatives were contaminated with tetracene which had not been completely separated by the chromatogram.

The tetracene bands persisted after photo-oxidation which took about half an hour in the case of the dibenzperylene and about two minutes in the case of the naphthoperylene.

The formation of maleic anhydride adducts in benzene solution was also much slower in the cases of benz and dibenzperylene than in the case of the naphtho compounds.

The absorption curve of the maleic anhydride adduct of naphthoperylene is shown in Fig.19 and is discussed on p.14.

PREPARATION OF PENTACENE DERIVATIVES
(Fig.28)

Preparation of 4-6-dibenzoyl-1-3-xylene.

Cf. Clar & John[43].

106 gm. (1 mole) of pure meta-xylene was mixed with about 350 gm. (2½ moles) of benzoyl chloride and about 300 gm. of powdered aluminium chloride were added fairly rapidly. The mixture was then heated to about 170°C until evolution of HCl had practically ceased. On cooling below 100°C the semi-liquid mass was poured on to ice and hydrochloric acid to hydrolise addition product. About 1 litre of xylene was then added and the mixture boiled to remove any aluminium salts. The xylene solution was separated and washed several times with warm HCl and finally with NaOH to remove excess benzoyl chloride and benzoic acid. It was then carefully washed with hot water and the final wash waters made slightly acid with acetic acid. It was dried over $CaCl_2$ and filtered through a fluted filter to remove all traces of inorganic material.

The xylene was distilled off and the tarry material obtained was used for the next part of the synthesis.

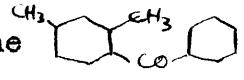
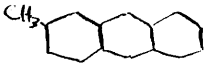
Pentacene and Dihydro-pentacene.

Cf. Clar & John[43,44].

The Elbs ring closure was carried out in the presence of zinc dust which seemed to have the effect of uniting

with water and providing hydrogen to form the dihydro-pentacene without disproportionation of the pentacene.

The tarry product from the preparation diketone, without further purification was heated to 400-420°C in a 500 cc. pyrex distilling flask, the equivalent to two moles of zinc dust being added in three portions during a period of about 90 minutes.

Xylophenone  and 2-methyl-anthracene  were obtained and a small amount of water also passed over. The black residue was sublimed in vacuo and about 80 gm. of dihydropentacene was obtained.

Dihydro-pentacene ⟶ Pentacenequinone

Cf. Badger(41)
Astin, Moulds & Riley(45)

Dihydropentacene was dissolved in nitrobenzene and selenium dioxide in slight excess was added to the boiling solution, which was boiled for about $\frac{3}{4}$ hour. The quinone was filtered from the nitrobenzene solution.

Reduction of Pentacenequinone to pentacenone.

Cf. Marschalk(46).

The reduction of the quinone to pentacenone was carried out by a method similar to that employed for the reduction of tetracenequinone (p. 34). The yield was poor, due apparently to sulphonation which must have taken place

before the reprecipitation of the quinone from its solution in H_2SO_4.

Pentacenone ——→ 6-(1-naphthyl)-pentacene.

This reaction was carried out in the manner described for the preparation of naphthyl-tetracene (p. 42). A deep violet substance was obtained after steam distilling off the excess naphthalene etc.

This substance was purified by running a pet. ether solution through an alumina column and washing through with benzene.

Recrystallised from benzene or xylene, M.P. 245°C.

Naphthyl pentacene is extremely sensitive to light, forming a photo-oxide very rapidly.

Its benzene solution has an orange fluorescence and absorption bands were observed at 5895Å, 5430Å, 5055Å and a low intensity band in the region of 4700Å.

Ring Closure to 1-2-benz-naphtho-(2'3'5-6)-perylene (XIV, Fig.8).

This was attempted with powdered aluminium chloride in a benzene solution, but owing to the small quantity of naphthyl pentacene available and its extreme sensitivity to light, no satisfactory results were obtained.

PREPARATION OF 7-8-BENZ-TERRYLENE AND 1'4'DICHLORO-7-8-BENZTERRYLENE FROM 1-4-DICHLORANTHRAQUINONE. (Figs. 29c and 21).

Phthalic anhydride + p-Chlorophenol

$\xrightarrow{AlCl_3}$ Hydroxy-chloro-benzoyl-benzoic acid

$\xrightarrow[H_2SO_4]{100\%}$ 1-Hydroxy-4-chloro-anthraquinone.

Cf. Ullmann & Conzetti(49).

1-Hydroxy-4-chloro-anthraquinone $\longrightarrow$ 1-4-Dichloranthraquinone. (Cf. 49).

The hydroxy-chlor-anthraquinone was recrystallised from glacial acetic acid and treated with phosphorus pentachloride as described by Ullmann(49). It was found necessary, however, to use a temperature of 180-200°C rather than the 155-160°C, as suggested.

1-4-Dichloranthraquinone $\longrightarrow$ 1-4-Dichloro-9-10-di-(1-naphthyl)-9-10-dihydroxy-9-10-dihydro-anthracene.

Cf. Guyot & Staehling(56)
Etienne & Heymès(52).

A benzene solution of dichloranthraquinone was treated with 1-naphthyl-magnesium bromide (4 moles). A green and then a brown compound were formed in the course of about 15 minutes. After decomposition with ice and acetic acid, excess bromonaphthalene and naphthalene were steam distilled off and the resulting tar treated with ether. The dark

constituents of the tar dissolved leaving a light brown powder. M.P. 283°C dec. Recryst. xylene M.P. 296°C dec. Recryst. nitrobenzene M.P. 313°C.

These crystals dissolved in H_2SO_4 giving a dark green/brown colour.

Analysis:

C	77.38	$C_{34}H_{22}O_2Cl_2$	C 76.56
H	4.39	requires	H 4.13.

Reduction to 1-4-Dichloro-9-10-di-(1-naphthyl)-anthracene.

(a) With Potassium Iodide, Cf. Haller & Guyot[50].

Treatment of the dihydroxy compound with potassium iodide in acetic acid gave a substance which, on recrystallisation from xylene or nitrobenzene, gave the following analysis:

C	77.77	$C_{34}H_{20}Cl_2$	C 81.77
H	4.76	requires	H 5.05

It therefore seems that only a very partial reduction has taken place.

(b) With Formic Acid, Cf. Kovache[51] Schlenk & Bergmann[51a].

5 gm. of 1-4-dichloro-9-10-di-(1-naphthyl)9-10-dihydroxy-9-10-dihydro-anthracene were added to a mixture of 38 gm. of 90% formic acid and 22 gm. of acetic anhydride and refluxed for three to six hours. On filtering a substance of M.P. 332°C was obtained which was more readily

soluble in xylene than the hydroxy compound. Recrystallised from xylene M.P. 335°C (dec.), colourless in H_2SO_4, gradually becoming green. Mixed M.P. with hydroxy compound 300°C.

Analysis:

C	79.38%	$C_{34}H_{20}Cl_2$	C 81.77%
H	3.86%	requires	H 4.01%.

A complete reduction does not yet appear to have taken place.

Further treatment with sodium iodide in a pyridene/acetic acid mixture gave crystals which melted at 342°C on recrystallisation from xylene.

Analysis:

C 80.00%

H 3.25%

Treatment of 1-4-Dichloro-9-10-di(1-naphthyl)-anthracene with an $AlCl_3$/NaCl melt. (Figs. 21 & 22)

1 gm. of the crude product from the formic acid reduction was treated with excess of a 5:1 mixture of $AlCl_3$/NaCl at 110°C and decomposed by pouring into dilute HCl. After careful washing with HCl and water the black product was dried and found to be mainly soluble in benzene or pet. ether.

A dilute solution was therefore made in pet. ether and run on to an alumina column, being developed with a benzene/pet.ether mixture and later with benzene alone. The following bands were obtained:

Band 1. Clear with blue fluorescence; probably naphthalene, anthracene and derivatives.

Band 2. Yellow/red with golden fluorescence; probably benzperylene and chlorinated derivatives.

Band 3. Intermediate green; not further investigated.

Band 4. Blue/green with green fluorescence; on evaporation gave blue/green needles having no M.P. below 360°C. A solution of these crystals showed no fluorescence and had a very intense absorption band at 6600Å. They contained chlorine and were insensitive to light exposure.

Analysis: C 80.31% $C_{34}H_{16}Cl_2$ C 82.43%
H 3.35% requires H 3.23%.

Band 5. Blue with red fluorescence; on evaporation gave copper glistening needles, M.P. 345°C (evac.capill.). These needles contained no chlorine and were identical with those obtained from the non chlorinated dinaphthyl-anthracene experiment. Their absorption curve in benzene is shown in Fig.24.

Band 6. Produced various unidentified compounds.

Treatment of 1-4-dichloro-9-10-di-(1.naphthyl)-9-10-dihydroxy-9-10-dihydro-anthracene with $AlCl_3/NaCl$. (Figs.21 & 22)

This experiment was carried out in a similar manner to that just described, with the reduced compound.

The bands on the chromatogram column were much the same, though the first band contained a higher proportion of unsubstituted anthracene and band 5 was much smaller.

PREPARATION OF 1-2-BENZPERYLENE AND 7-8-BENZTERRYLENE FROM ANTHRAQUINONE. (Fig.9)

Cf. Guyot & Stahling[56]
Clar & Guzzi[31]
Clar[31a]

9-10-Di-(1-naphthyl)-9-10-dihydroxy-9-10-dihydro-anthracene[56].

About 30 gm. of anthraquinone in benzene were treated with naphthyl-magnesium bromide, prepared from 100 gm. of bromonaphthalene and 12 gm. activated magnesium (3 moles). After heating for a short time the yellowish green compound was hydrolysed with ice and acetic acid. Some of the benzene and ether was distilled off but it was unnecessary to steam distil the naphthalene as the desired product appeared to be only very slightly soluble in ether. It was therefore allowed to stand overnight in ether and filtered. (Some unchanged anthraquinone crystallised from the filtrate.) It was then treated several times with $NaOH/Na_2S_2O_4$ solution, to remove further anthraquinone as a vat and when a red colouration was no longer observed, the remaining material was washed and dried. Yield ca. 6 gm.

A large quantity of anthraquinone was recovered from the vat by oxidation and it appears that the low yield is not due to side reactions and could be increased probably by improving the conditions of the Grignard reaction.

Ring closure to Benzperylene, Benzterrylene, etc.(31,31a).

6 gm. of 9-10-di-(1-naphthyl)9-10-dihydroxy-9-10-dihydro-anthracene was finely powdered and added to a melt of 9 gm. NaCl and 45 gm. $AlCl_3$ fused at ca. 100°C. The temperature was kept at 110°C during the addition, which took about five minutes, and the melt was stirred for a further five minutes at this temperature before being poured into dilute HCl. After hydrolysis, the blue black sludge was filtered and carefully washed with HCl and water.

It was then dried and extracted with a small quantity of benzene in a soxlet, in an atmosphere of CO_2. About 1 gm. of residue remained and the benzene solution was added hot to about a litre of warm pet. ether. On cooling, the whole solution was run through an alumina column, from which light and air were carefully excluded.

The first runnings yielded about 1 gm. of anthracene, followed by 1-2-benzperylene which was carefully kept in the dark under CO_2 and evaporated down, giving a small quantity of a red crystalline product from pet. ether, M.P. 172°C.

These crystals gave a green colour in H_2SO_4, turning to a brown/yellow.

With maleic anhydride the red colour gradually faded to a pale brown, though no crystalline material was obtained.

The absorption curve of 1-2-benzperylene is shown in Fig.16.

The next band from the alumina column was thought to be 1-2-benzperylene-3-10-quinone, being a deep brown colour with a green fluorescence. It was very soluble, yielding only a small quantity of crystalline material. This gave no vat in $NaOH/Na_2S_2O_4$ and dissolved in H_2SO_4 to give a bright violet colour. It is probably perylene, formed by the combination of two naphthalene residues.

The next three fractions from the alumina column (about 9 litres of benzene solution), although differing slightly in appearance in solution, all yielded copper glistening needles of 7-8-benzterrylene.

The red fluorescence of the pure benzterrylene gradually became lighter in the higher fractions and finally a substance having a much lower melting point and a white fluorescence in benzene solution was obtained. This was run through another column and a small quantity of anthracene was obtained, followed by pure benzterrylene.

Preparation of Maleic Anhydride Adduct of 7-8-Benzterrylene 1-9-4-10.Di-(peri-naphthalene)-endo-9-10-(1-2-succinic anhydride)-anthracene. (XXX) Cf.(31.)

Small quantities of this adduct were prepared in boiling xylene, but the best method was using excess maleic anhydride as solvent as follows:

A small amount of pure 7-8-benzterrylene was powdered intimately with a large excess of good quality maleic anhydride and the two materials fused together. The blue colour disappeared almost immediately leaving a pale green/brown liquid. After several minutes' heating at 150/200°C, xylene was added and the solid filtered off from the solution. This pale green powder was washed with ether and recrystallised a xylene/acetic anhydride mixture, M.P. 346° (dec.).

The absorption curve of the disodium salt in alcohol is shown in Fig.25.

Analysis:

C	86.10%	$C_{38}H_{20}O_3$	C	87.03%
H	3.37%	requires	H	3.81%
			O	9.16%.

ATTEMPT TO PREPARE 7-8-BENZTERRYLENE FROM QUINIZARIN. (Fig.30)

Quinizarin was obtained by passing air through a solution of 100 gm. of leuco quinizarin in caustic soda. After filtering, the quinizarin was precipitated with

hydrochloric acid, washed with water and dried.

Treatment of Quinizarin with Naphthyl-magnesium bromide.

Cf. Etienne & Heymès[52].

20 gm. of quinizarin in boiling xylene (500 cc.) was treated with a Grignard solution, prepared from 207 gm. 1-bromonaphthalene and 20.5 gm. magnesium (1 mole:12). After distilling off all the ether the xylene solution was refluxed with stirring for about four hours and then hydrolised with ice and acetic acid.

The mixture was filtered and separated, the xylene layer being submitted to steam distillation to remove xylene, naphthalene, etc. The product was then treated with ether, when a number of impurities went into solution. The residue was boiled with acetic acid and filtered. About 20 gm. of 1-1'-dinaphthyl were obtained from the filtrate on cooling, M.P. 154-5°C.

The residue from the acetic acid treatment (ca. 6 gm.) was thought to be 9-10-di-(1-naphthyl)1-4-anthraquinone. This substance, recrystallised from nitrobenzene, melted below 150°C. It was therefore carefully washed with ether and found to be about 80% dinaphthyl. The remainder was recrystallised again from nitrobenzene and gave orange/red crystals, M.P. 364° dec.

Treatment with Aluminium Chloride.

The orange/red crystals from the previous experiment were powdered and partially dissolved in about 25 cc. of benzene and treated in the cold with ca. 1 gm. of powdered $AlCl_3$. The solution went almost immediately a deep reddish violet and then bluish violet. After standing for some time the solution was raised to boiling and finally hydrolysed with dilute HCl.

The benzene layer became green on shaking with caustic soda and the violet colour returned on treatment with hydrosulphite.

Absorption bands were observed in benzene at 6305Å and 5490Å.

It is likely that this solution contains either 7-8-benzterrylene-4-11-quinone or 7-8-benzterrylene-3-12-quinone.

Some of the crude dinaphthyl, which probably contained 1-4-dihydroxy-9-10-di-(1-naphthyl)-anthracene, gave a blue solution on treatment with $AlCl_3$ in benzene, showing absorption bands at 6450Å, 5900Å, and 5450Å. These would appear to be due to 7-8-benzterrylene.

The ether extract from the residue, left after the steam distillation, yielded a considerable quantity of quinizarin.

ATTEMPTED PREPARATION OF TETRACENONE FROM PHTHALIC ANHYDRIDE AND 1-NAPHTHOL BY THE BORIC ACID SYNTHESIS. (Fig.27).

Phthalic Anhydride + 1-Naphthol

$$\xrightarrow[H_2SO_4]{\text{Boric Acid}}$$ 6-Hydroxy-tetracene-quinone.

This reaction, though carried out according to the method of Deichler and Weizmann[38,p.548] yielded almost entirely sulphonated products.

Phthalic Anhydride + 1-Naphthol

$$\xrightarrow[\text{fusion}]{\text{Boric Acid}}$$ 2-(1-Hydroxy-2-naphthoyl)-benzoic Acid.

A good yield of this keto acid was obtained by the method of Deichler and Weizmann[38, p.559].

Reduction to 2-(1.Hydroxy-2-naphthyl)-methyl-benzoic Acid.

Cf. Clar[34].

This reduction was carried out with zinc dust in an aqueous alkaline solution to which a trace of copper sulphate had been added. It was occasionally necessary to add a few drops of sec. butyl alcohol to prevent excessive frothing, but otherwise the method is exactly similar to that described on p.30

Ring Closure with Acetic Anhydride to Tetracenyl-5-11-diacetate.

Cf. Fieser & Hershberg[39]
Blicke & Warzynski[40]
Badger[41].

A mixture of 20 gm. of the reduced acid, 40 cc.

glacial acetic acid, 160 cc. acetic anhydride and 1.6 gm. of anhydrous zinc chloride was refluxed for one hour, during which time the solution became a deep brown colour. It was difficult to get the product out of solution and addition of water only yielded a substance which was sticky even after washing with sodium carbonate solution to remove any unchanged acid.

Recrystallisation yielded small quantities of yellow crystals (M.P. 196°C), but the yield was low and since trial experiments on hydrolysis and reduction were not hopeful, the synthesis was abandoned.

Unsuccessful Attempts to Prepare 1-4-Dichloranthraquinone. Fig.29(a).

Leuco quinizarin was treated with a large excess of phosphorus pentachloride. The resulting tar was vac. distilled but the small quantity of red crystalline material obtained was not the desired compound.

(b) Cf. Egerer & Meyer[47]

The Friedel-Crafts condensation between p-dichloro-benzene and phthalic anhydride gave an almost negligible yield of the dichloro-benzoyl-benzoic acid, so this method of synthesis was abandoned.

PART I.

BIBLIOGRAPHY.

(1)	Clar	Ber.	1936, 69, 607
(2)	"	"	" " 1671
(3)	"	"	1940, 73, 81
(4)	"	"	" " 104
(5)	"	"	" " 596
(6)	"	"	1942, 75, 1330
(7)	"	"	1943, 76, 149
(8)	"	"	" " 257
(9)	"	"	" " 328
(10)	"	"	" " 458
(11)	"	"	" " 609
(12)	"	"	1948, 81, 52
(13)	"	"	" " 63
(14)	Clar & Frommel	"	" " 163
(15)	Clar	"	" " 169
(16)	"	Arom. Kohl.	pp.20-51
(17)	"	" "	p.18
(18)	Fieser	J.A.C.S.	1929, 51, 3102
			1930, 52, 5204
			1931, 53, 793, 1128, etc.
(19)	Clar & Wright	Nature	In Press
(20)	Sieglitz & Marx	Ber.	1923, 56, 1619
(21)	Fieser & Hershberg	J.A.C.S.	1940, 62, 49
(22)	Clar	Ber.	1936, 69, 1686
(23)	Willemart	Compt.rend.	1937, 205, 866
(24)	Clar	Arom. Kohl.	p.42
(25)	"	" "	p.33
(26)	Pestemer & Cecelsky	Monatsh.	1932, 59, 113
(27)	Scholl & Weitzenbock	Ber.	1910, 43, 2202
(27a)	Zincke & Dengg	Monatsh.	1922, 43, 125
(28)	Fieser & Hershberg	J.A.C.S.	1938, 60, 1664
(29)	Krollpfeiffer & Branschied	Ber.	1923, 56, 1617
(30)	Cook	J.C.S.	1926, 2631
(31)	Clar & Guzzi	Ber.	1932, 65, 1521
(31a)	Clar	Arom. Kohl.	pp.230-231
(32)	Jones	Chem.Rev.	1943, 32, 1
(33)	"	J.A.C.S.	1941, 63, 1658
(34)	Clar	Ber.	1942, 75, 1271
(35)	Barnett & Lowry	"	1932, 65, 1650
(36)	Gabriel & Leupold	"	1898, 31, 1277
(37)	Fieser	J.A.C.S.	1931, 53, 2336
(38)	Deichler & Weizmann	Ber.	1903, 36, 547
(39)	Fieser & Hershberg	J.A.C.S.	1937, 59, 1032
(40)	Blicke & Warzynski	"	1940, 62, 3191
(41)	Badger	J.C.S.	1947, 764
(42)	Waldmann & Polak	J.Pr.Ch.	1938, 150, 115

Part I

Bibliography (Contd.)

(43)	Clar & John	Ber.	1929, 62, 3021
(44)	" "	"	1930, 63, 2967
(45)	Astin, Moulds & Riley	J.C.S.	1935, 901
(46)	Marschalk	Bull.Soc.Chim.	1937, 4, 1549
(47)	Egerer & Meyer	Monatsh.	1913, 34, 69
(48)	Ullmann & Billig	Ann.	1911, 381, 11
(49)	Ullmann & Conzetti	Ber.	1920, 53, 831
(50)	Haller & Guyot	Bull.Soc.Chim.	1904, 31, 795
(51)	Kovache	Ann.Chim.	1918, 10, 184
(51a)	Schlenk & Bergmann	Ann.	1928, 463, 152
(52)	Etienne & Heymes	Bull.Soc.Chim.	1947, 1038
(53)	Meyer	Org.Synth.	VIII, 8
(54)	Bachmann & Kloetzel	J.A.C.S.	1938, 60, 481
(55)	Clar	Ber.	1932, 65, 518
(56)	Guyot & Staehling	Bull.Soc.Chim.	1905, 33, 1104
(57)	Clar	Ber.	1939, 72, 2137
(57a)	"	Arom.Kohl.	pp.4-9
(58)	Gillam & Hey	J.C.S.	1939, 1170
(59)	Clar & Furnari	Ber.	1932, 65, 1421
(60)	Clar	"	" " 848.

Arom. Kohl. = Aromatische Kohlenwasserstoffe

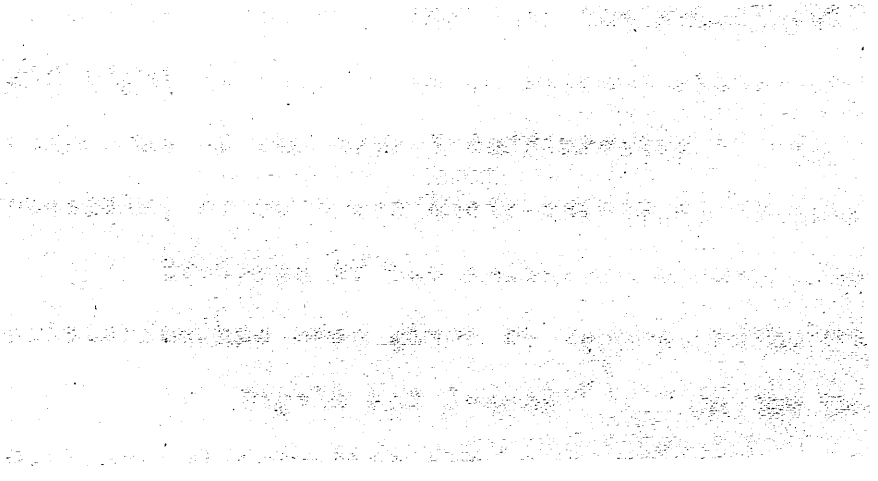
Springer-Verlag 1941.

Part II.

MOLECULAR REARRANGEMENTS

FOREWARD TO PART II.

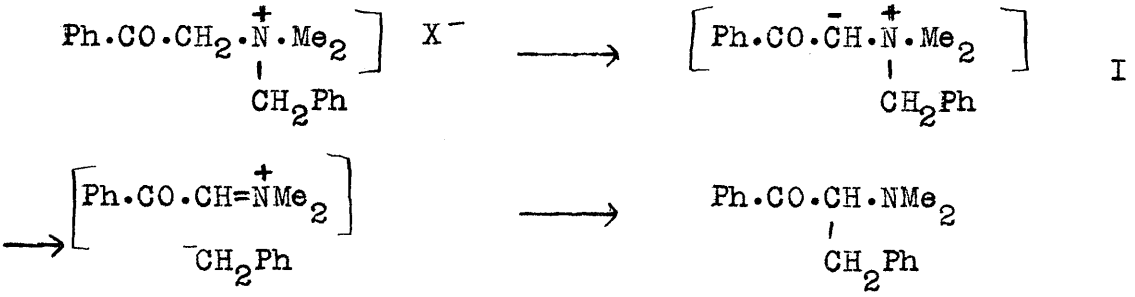
This work on Molecular Rearrangements was carried out before the described work on Polycyclic Aromatic Hydrocarbons. Unfortunately it had to be abandoned in the early part of 1947 when Dr. T.S. Stevens, who was supervising the work, was appointed to the staff of Sheffield University.



MOLECULAR REARRANGEMENTS

Studies in the Mechanism of the Stevens Rearrangement.

The most likely mechanism in the molecular rearrangement of quaternary ammonium salts is suggested by Stevens[1] to be through the zwitterion (I) and the subsequent removal of the migrating group as an anion before its attachment to

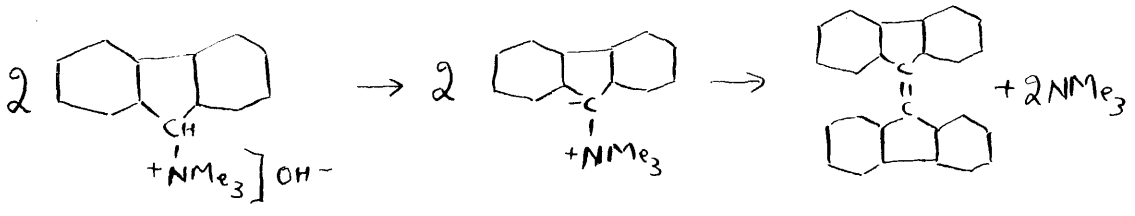


the reactive methylene carbon atom in the receiving group.

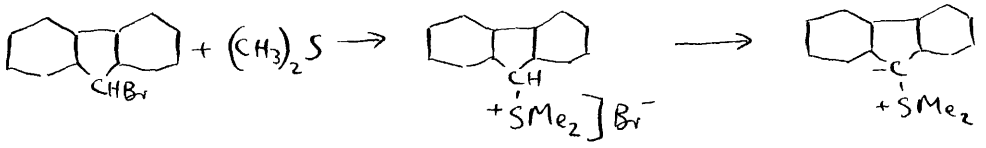
The present research is concerned with the formation of the zwitterion rather than the subsequent rearrangement and might be said to be an attempt either to stabilize compounds of the type I sufficiently to make isolation possible, or to prove their existence by subsequent reactions.

Evidence of the existence of this "Betaine" type of zwitterion has been given by several authors.

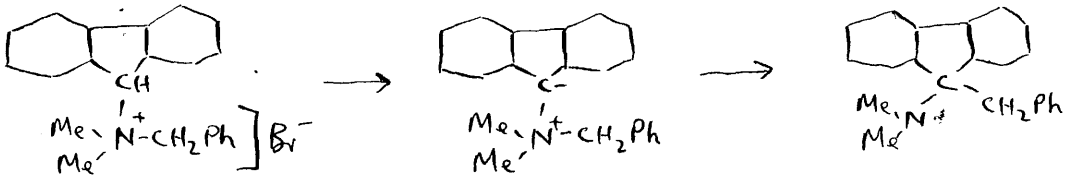
1. Ingold and Jessop[2]. In the decomposition of 9-fluorenyl-trimethyl ammonium hydroxide to the red difluorenylidene by means of silver oxide, a strong purple colour was observed which the authors tentatively suggest was due to the zwitterion.



2. The same authors[3], considering the greater stability of dialphyl sulphoxides over trialphyl amine oxides ($\bar{O}\text{-}\overset{+}{S}R_2$ & $\bar{O}\text{-}\overset{+}{N}R_3$) were led to investigate the fluorenyl sulphonium compounds. They therefore prepared 9-fluorenyl-dimethyl sulphonium bromide by treatment of 9-bromofluorene with dimethyl sulphide in nitromethane. Treatment of this bromide with NaOH or ammonia gave a yellow crystalline precipitate which analysed as the dimethyl-sulphonium-9-fluorenyl-ide.



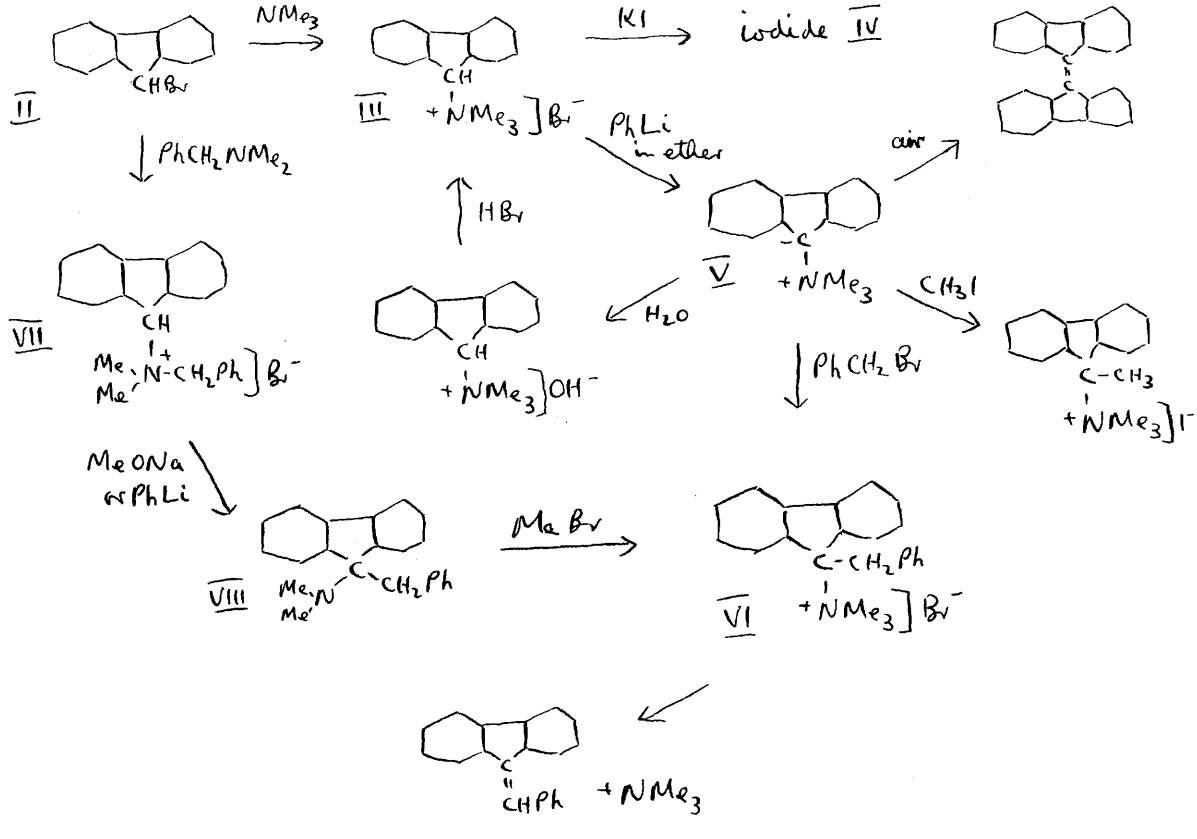
3. Marrian and Stevens[4]. In the rearrangement of 9-fluorenyl-benzyl-dimethyl ammonium bromide to 9-benzyl-9-fluorenyl-dimethylamine a red colouration was observed lasting for about five minutes. This is probably due to the intermediate compound as shown.



4. Wittig and Felletschin[5], having discovered that by treatment of tetramethyl ammonium chloride with phenyl lithium, a metallic product and finally a methylide was obtained, were thus led to use phenyl lithium in an attempt to prepare the trimethyl-ammonium-9-fluorenylide that Ingold and Jessop had observed.

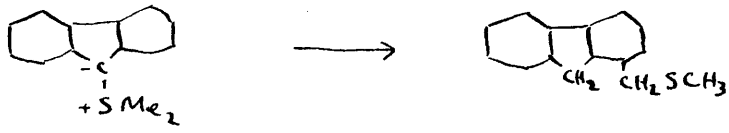
$$(CH_3)_4\overset{+}{N}\Big]\,\bar{C}l + PhLi \longrightarrow Li{\cdot}CH_2{\cdot}N(CH_3)_3\Big]\,\bar{C}l \longrightarrow \bar{C}H_2\text{-}\overset{+}{N}(CH_3)_3$$

They obtained the desired compound by treating the quaternary ammonium bromide with phenyl lithium in an atmosphere of nitrogen and though no analysis results are given, the reactions shown in the following scheme leave little doubt as to its constitution.

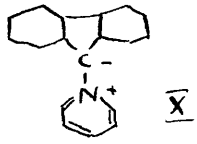


In the rearrangement of VII to VIII, Wittig also reports the formation of the red compound described by Marrian. Even working with phenyl lithium in an atmosphere of nitrogen they failed to isolate the benzyl-dimethyl-ammonium-9-fluorenylide.

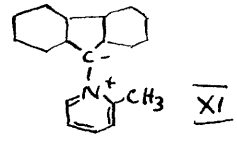
5. Pinck and Hilbert[6,7,8] have recently repeated Ingold's preparation of dimethyl-sulphonium-9-fluorenylide and have shown that it rearranges under the influence of alkali to methyl-1-fluorenyl-methyl sulphide[6].



They also claim to have prepared the compounds X and XI, which they name fluorenylidene pyridinium and fluorenylidene ∝ -picolinium respectively[7]. In keeping with Wittig's nomenclature it seems that pyridinium or ∝-picolinium-9-fluorenylide would be more suitable.

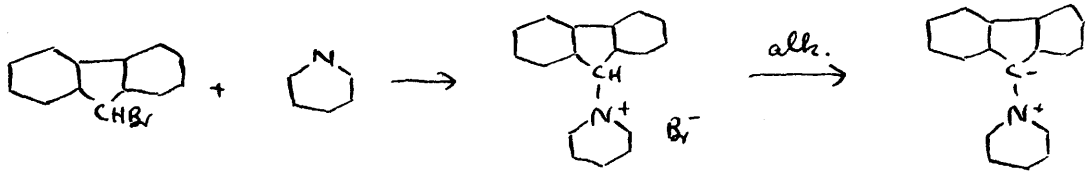


X

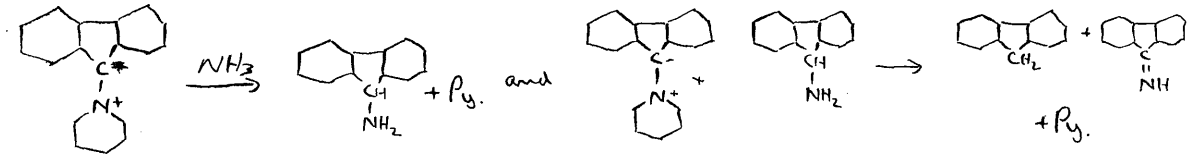


XI

The method of preparation is simple, being the treatment of 9-bromofluorene with excess of either pyridine or ∝-picoline, followed by alkali or liquid ammonia treatment.

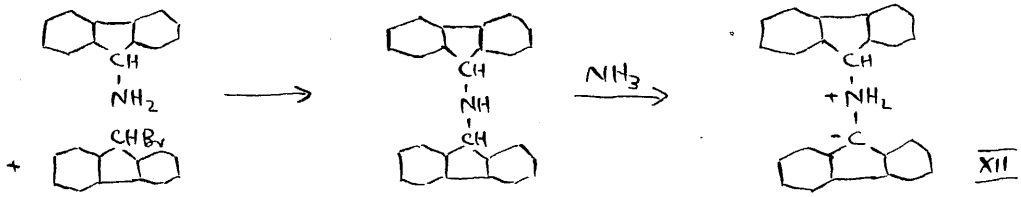


The fluorenylides were deep blue in colour and were not stable enough to be isolated. They gradually decomposed, even in sealed tubes, to fluorene, 9-fluorenylamine and pyridine or ∝-picoline. The authors suggest the following reactions to account for these products.



The unusual action of 9-fluorenylamine as a reducing agent is similar to that described by the same authors in an earlier paper[9].

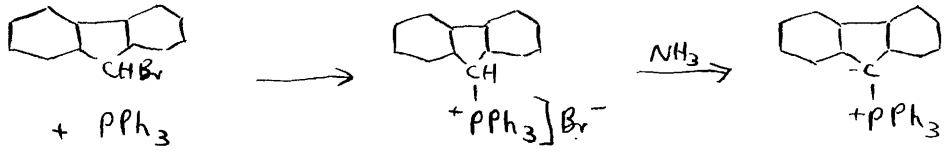
Fluorenylidene-9-ammonium fluorene or 9-fluorenyl-ammonium-9-fluorenylide (XII) is described along with the pyridinium compound[7]. It was prepared by the interaction of 9-fluorenylamine and 9-bromofluorene in acetonitrile, followed by treatment with liquid ammonia.



It is an indigo blue compound, but like the pyridinium and ∝-picolinium compounds, was too unstable to be isolated.

Pinck and Hilbert's latest publication[8] records the preparation of a yellow triphenyl-phosphine-fluorenylidenide (triphenyl-phosphine-9-fluorenylide). It is prepared in a similar manner to the other compounds mentioned,

but is apparently stable, having been refluxed in aniline and other solvents without decomposition.



These papers of Pinck and Hilbert serve to emphasise the instability of the ammonium fluorenylides which Wittig had obtained only under very rigorous conditions.

At the commencement of the present research (January, 1946) neither Wittig's nor Pinck and Hilbert's papers were available. A lithographed copy of Wittig's paper became available in June, 1946, when we had already started on attempts to produce a more stable fluorenylide.

Stevens has shown[1] that quaternary phenacyl ammonium salts will neutralise alcoholic potash (thymolphthalein) immediately and that this reaction is followed by a slow rearrangement which is apparently dependent on the stability of the zwitterion. Since substitution of NO_2 or halogen in the nucleus of the receiving group retards the rearrangement[10], it seemed likely that the introduction of bromine atoms into the fluorenyl nucleus would stabilize the compound sufficiently to allow the isolation of the zwitterion.

Schemes similar to that of Wittig were therefore

drawn up with the 9-fluorenyl radicle replaced by 9-(2-7-dibromo)-fluorenyl or by p-phenyl-phenacyl, and later some work was carried out on fluorenylidene-fluorenyl-alkyl-ammonium salts.

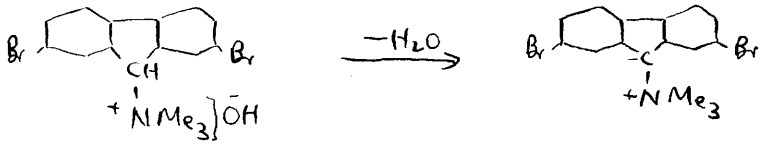
Fluorenylidene-9-fluorenyl-alkyl-ammonium Salts.

The introduction of the bromine atoms into the fluorene nucleus has quite a marked effect. The melting point is raised from 104°C (9-bromofluorene) to 196-7°C (2-7-9-tribromofluorene) and the solubility in organic solvents is considerably reduced. The tendency of two molecules to unite, producing tetrabromo-difluorenylidene, seemed to be greater and the preparation of quaternary ammonium salts was correspondingly more difficult.

Thus, working in benzene, treatment of 2-7-9-tribromofluorene with benzyl-dimethylamine produced only a very small amount of the quaternary salt and on attempting the reaction in nitromethane (cf. Ingold and Jessop[3]; Richardson and Soper[11]) only the red difluorenylidene was produced.

Reasonable yields of the trimethyl salt were obtained, however, by treating tribromofluorene in benzene with an excess of trimethylamine in a tightly stoppered bottle at 100°C. The yield was later improved by working in chlorobenzene.

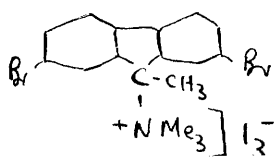
Treatment of this quaternary salt with alkali produced a yellow precipitate which was not the hydroxide, but this could not be freed from alkali and unchanged bromide. Attempts to extract with organic solvents rapidly produced the difluorenylidene compound, releasing trimethylamine. Treatment with silver oxide in aqueous solution (cf. Ingold and Jessop[2]), followed by slow evaporation, gave white crystals of the hydroxide, which on further drying in vacuum gave the yellow compound, but this was again contaminated with the bromide.



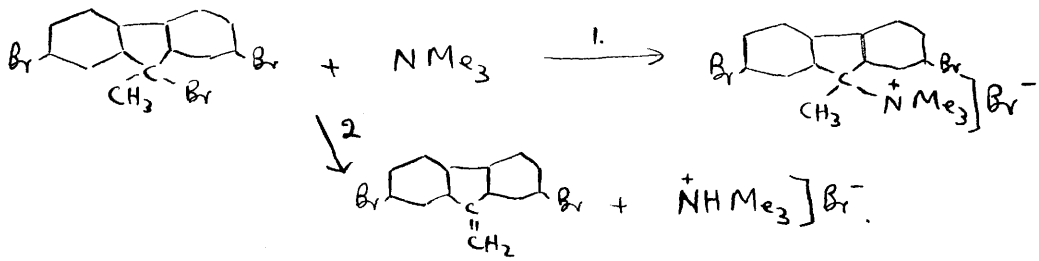
Precipitation of the bromide ion was then carried out by means of an exact equivalent of silver sulphate, followed by a sulphate precipitation with a standard baryta solution. The resultant filtrate was evaporated and dried and a reasonable quantity of the yellow substance was obtained.

The yellow substance was not particularly soluble in water though HBr immediately reproduced the quaternary bromide.

Treatment with methyl iodide gave a water soluble substance giving an iodide precipitate with silver nitrate. It recrystallised from methyl alcohol but appeared to split into two compounds, one of which is almost certainly the periodide



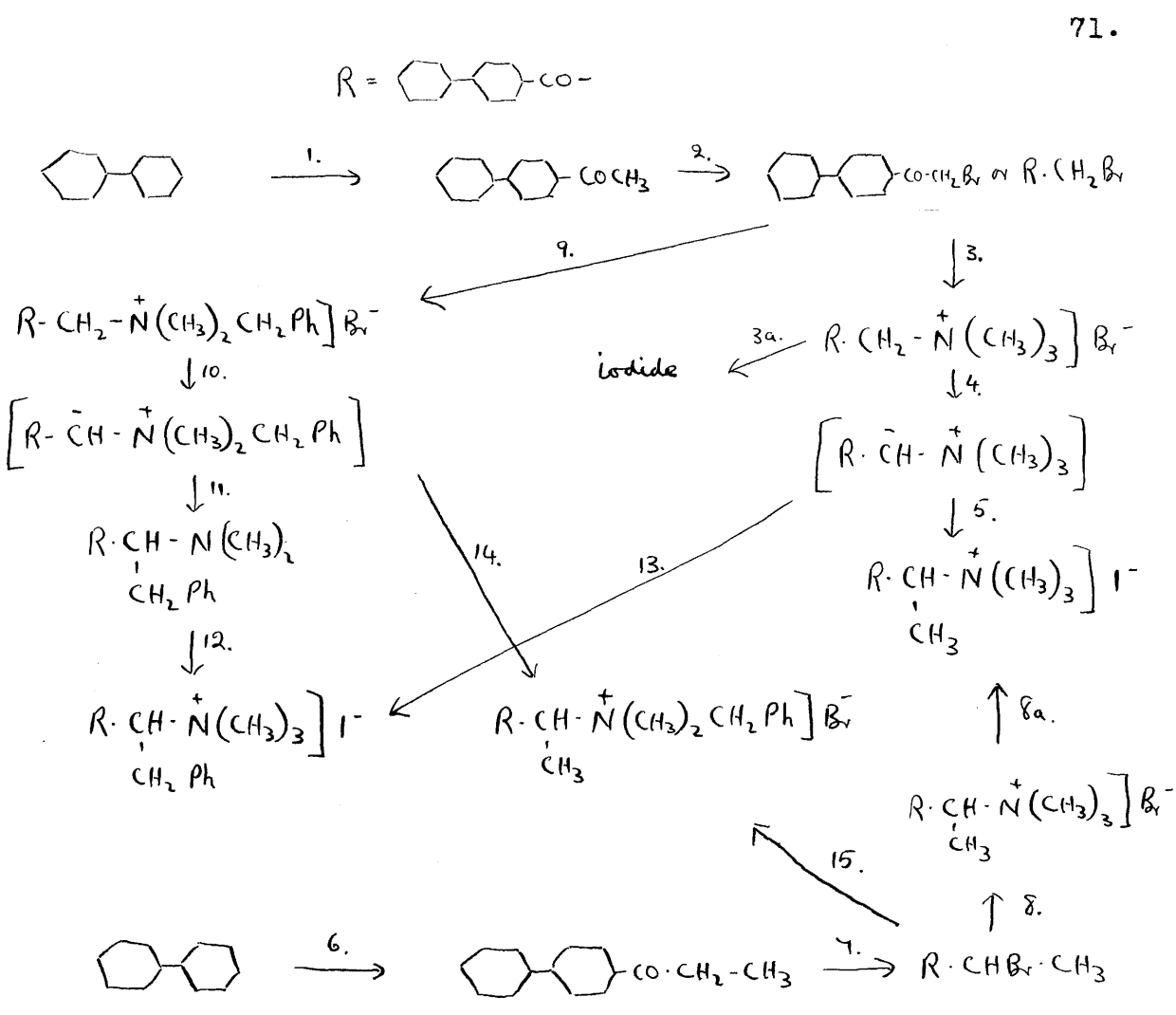
Attempts to synthesise 2-7-dibromo-9-methyl-9-fluorenyl-trimethyl-ammonium bromide or iodide were made through 2-7-9-tribromo-9-methyl-fluorene and 2-7-dibromo-9-methyl-9-iodo-fluorene by treatment with trimethylamine in benzene or chlorobenzene. From the tribromo compound, only crystals of 2-7-dibromo-dibenzfulvene were obtained. The reaction followed course 2 rather than course 1.



With the iodide, crystals of a water soluble substance giving an iodide precipitate with silver nitrate and having a melting point of 96-97°C were obtained. The minute quantity of this substance made further investigation impossible.

P-Phenyl-phenacyl-trialkyl-ammonium Salts.

With the p-phenyl-phenacyl compounds, the object was not so much to isolate the zwitterions (p-phenyl-phenacylides) as to show their existence, by the following scheme:-



Reactions 1 - 3 went smoothly but in reaction 4 the attempt to produce the phenacylide resulted in a red compound which contained no nitrogen. A strong smell of trimethylamine was noticed during the reaction which is probably $2RCH_2\overset{+}{N}(CH_3)_3\ \overset{-}{Br} + 2NaOH \longrightarrow 2NaBr + 2H_2O + 2N(CH_3)_3 + R.CH{=}CH.R$, the red compound being a p-p'diphenyl-diphenacylidene. The trans form of this compound has been prepared by Oddy[12] and is yellow with a melting point of 248°C. The red compound

obtained was obviously impure and may be a mixture of isomers.

Carrying out the alkali treatment in presence of excess methyl iodide (reaction 5), in the hope that the -ve carbon of the zwitterion would react with the methyl group, was no more successful, the only product obtained being the p-phenyl-phenacyl-trimethyl-ammonium iodide, as obtained from reaction 3a. This is apparently produced as follows:-

$$CH_3ONa + CH_3I \longrightarrow CH_3OCH_3 + NaI$$

$$R.CH_2.\overset{+}{N}(CH_3)_3\ \overset{-}{Br} + NaI \longrightarrow R.CH_2\overset{+}{N}(CH_3)_3\ \overset{-}{I} + NaBr$$

A combination of reactions 4 and 13 was also unsuccessful, yielding no workable products.

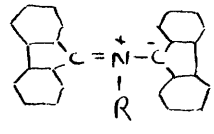
Reactions 6,7,8 and 8a were carried out with difficulty, though some discrepancies in the melting points given in the literature for both p-phenyl-propiophenone and the -bromo compound (see experimental p.89/90) were discovered. Reaction 15 likewise presented little difficulty.

The preparation of p-phenyl-phenacyl-benzyl-dimethyl-ammonium bromide and its subsequent rearrangement (reactions 9-11) was then carried out. The rearrangement product reacted readily with methyl iodide (reaction 12), the same product being obtained when the rearrangement was carried out in presence of methyl iodide. Several attempts were

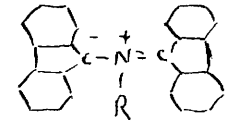
made to methylate the carbon atom of the phenacyl group, but the alkaline condensing agents necessary always promoted the rearrangement of the extremely mobile benzyl group and reaction 14 was unsuccessful.

2-7-Dibromo-fluorenyl-trialkyl-ammonium Salts.

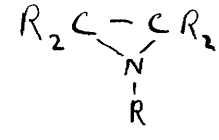
Since our attempts to isolate the dibromofluorenylide zwitterion were inconclusive, and since it does not seem possible to hold up the rearrangement of benzyl-dimethyl quaternary salts or the degradation of trimethyl salts sufficiently to allow the zwitterion to react with alkyl halides, it was thought that if an alternative seat could be found for the -ve charge on the carbon atom, a more stable resonance structure could be obtained. Thus the decomposition of fluorenylidene-9-fluorenyl-alkyl-ammonium halides might give rise to zwitterions resonating between the two structures



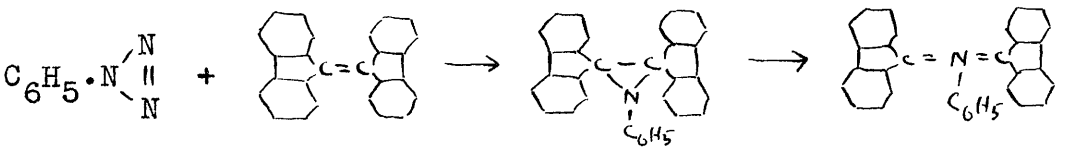
and



Such semi-polar double bonds as are used in these formulae are assumed to exist in the amine oxides, and the "nitrenes" of Staudinger[13] could also be formulated thus:- $R_2\bar{C} - \underset{R}{\overset{+}{N}} = CR_2$, though Taylor Owen and Whittaker[14] give evidence for the cyclic structure

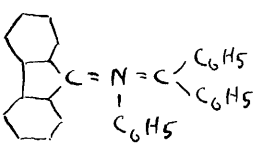


In a footnote in his original paper, Staudinger mentions a green compound corresponding to a nitrene which he obtained by treatment of "Graebe's Hydrocarbon", difluorenylidene with phenylazide.

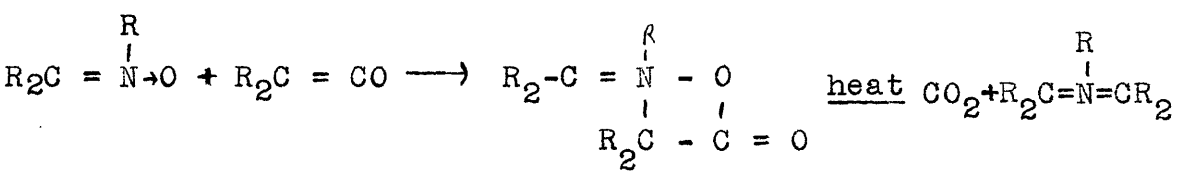


The last formula with a pentavalent nitrogen atom is Staudinger's own formulation, while the intermediate cyclic structure corresponds to those suggested by Taylor & Co.

Staudinger also prepared the nitrene which he calls diphenylene-diphenyl-N-phenyl-nitrene and on this basis, the compound obtained from the difluorenylidene would presumably be called di-diphenylene-N-phenyl-nitrene. The use of the term fluorenylidene seems to be more desirable, the last mentioned compound thus becoming di-fluorenylidene-N-phenyl-nitrene.



So far the preparation of nitrenes as carried out by Staudinger and repeated by Taylor & Co. has been by heating the addition product obtained between a ketene and a nitrone.

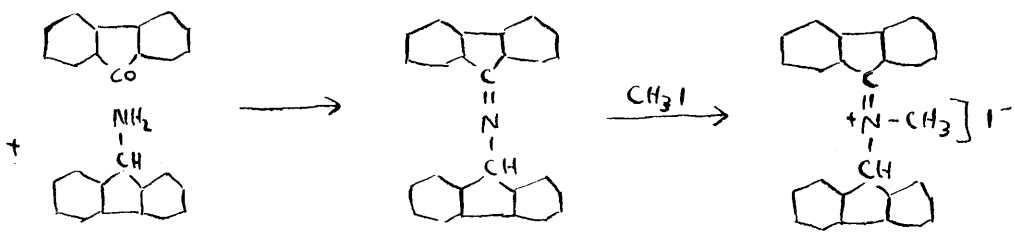


The decomposition of quaternary ammonium salts is therefore a new and interesting approach to the problem.

The only quaternary salt of the type required which could be found in the literature is the benzylidene-p-tolyl-methyl-ammonium iodide of Decker and Becker[15], prepared from benzal-p-toluidene and methyl iodide.

Attempts were therefore made to prepare the following quaternary salts by the route shown.

1. Fluorenylidene-9-fluorenyl-methyl-ammonium iodide



2. Fluorenylidene-9-fluorenyl-methyl-ammonium methosulphate. (As above using dimethyl sulphate instead of methyl iodide).
3. Fluorenylidene-9-fluorenyl-allyl-ammonium iodide, using allyl iodide.

The two methods used by Ingold and Wilson[16] for the condensation of fluorenone with 9-fluorenylamine to fluorenylidene-9-fluorenylamine gave very poor yields and the use of zinc chloride as a condensing agent did not improve matters. (See Reddelien's prep. of anils[17]).

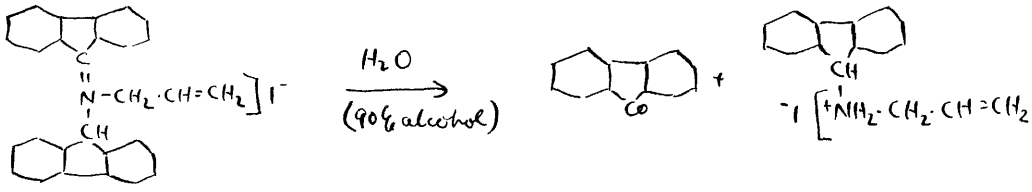
Working with the hydrochloride of the amine and an equivalent quantity of sodium ethoxide in a perfectly dry

alcoholic solution, improved yields were obtained.

The first attempt to produce a quaternary salt yielded only a small amount of an unidentified iodide, after working with methyl iodide in a sealed tube. Further investigation of this reaction was therefore considered impracticable.

None of the methyl-ammonium methosulphate was obtained at all.

The allyl salt has however been obtained and its structure proved by hydrolysis to fluorenone and 9-fluorenyl-allylamine hydriodide.



The quantity of fluorenylidene-9-fluorenyl-allyl-ammonium iodide obtained was not sufficient to study the alkaline degradation and as I had already commenced work on "Aromatic Hydrocarbons", it was not possible to prepare further quantities of the allyl salt. In view of the very strong tendency of these salts to undergo hydrolysis (cf. Decker and Becker[15] and experimental, p. 103), any degradation would need to be carried out with a non-hydroxylic reagent such as sodamide or silver oxide.

In the attempts to prepare fluorenylidene-9-fluorenyl-methyl-ammonium methosulphate no reaction took place on refluxing fluorenylidene-fluorenylamine with dimethyl sulphate in benzene. On analogy with Ingold and Jessop's preparation of fluorenyl-9-dimethyl-sulphonium bromide[3], it was decided to try the use of nitromethane as a solvent (see also Richardson & Soper[11]).

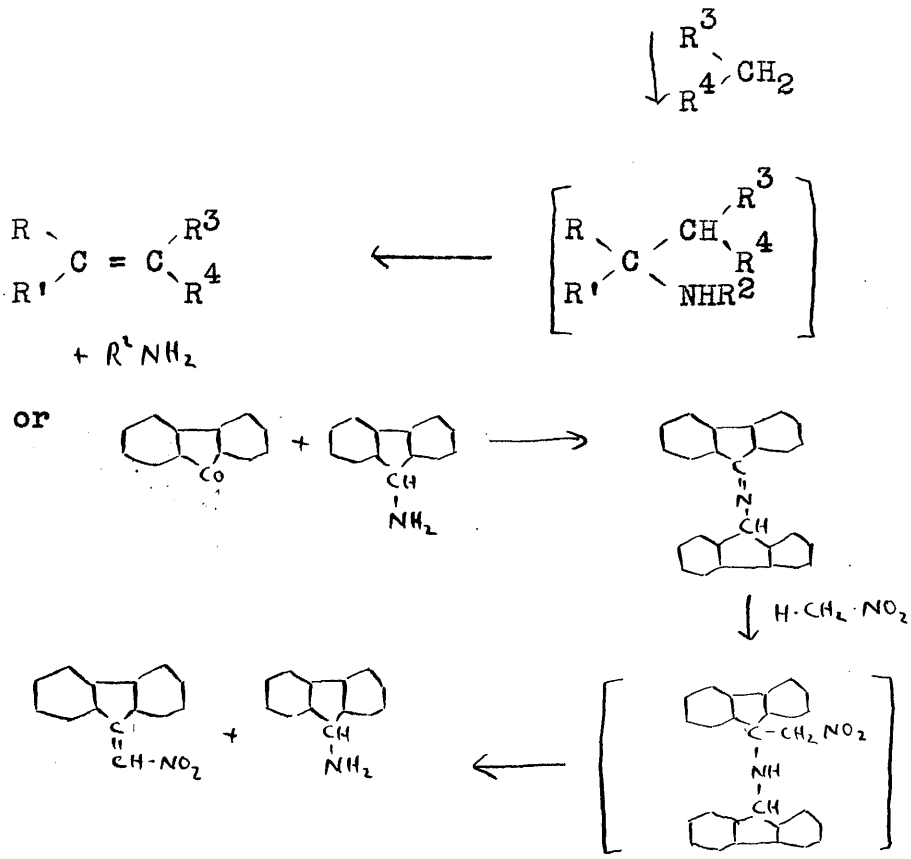
The resulting products, however, were fluorenylidene-nitromethane and 9-fluorenyl-methylamine hydromethosulphate. Fluorenylidene-nitromethane was also obtained by treatment of fluorenylidene-fluorenylamine with nitromethane alone and a trace is believed to have been obtained by treatment of fluorenone-anil with nitromethane. It was not, however, produced from fluorenone and nitromethane in the presence of sodium methoxide or zinc chloride.

This seems to furnish proof that the basic catalyst in the Knoevenagel condensation first combines with the ketonic component before the latter condenses with the methylenic component.

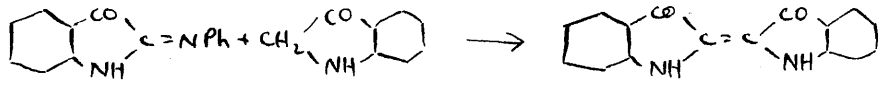
Thus with a primary amine where R^3 or R^4 or both are activating groups:-

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!CO + R^2NH_2 \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!C\!<\!\begin{matrix} OH \\ NHR^2 \end{matrix} \qquad \text{or} \qquad \begin{matrix} R \\ R' \end{matrix}\!\!>\!C = NR^2$$

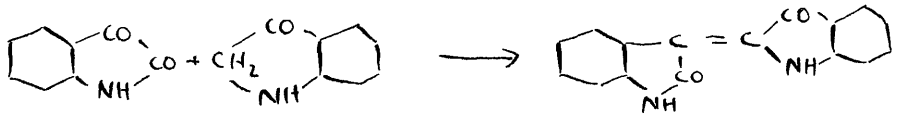
↓
See over



The reactivity of C = N- is shown by the following



whereas



Experimental.

Preparation of 2-7-Dibromofluorenyl Derivatives.

Fluorene ——→ Fluorenone

See Graebe & Rateanu[18], also Huntress, Herschberg & Cliff[19].

The method of Graebe & Rateanu was less troublesome and gave a better yield.

Fluorenone ——→ Fluorenol

Bachmann[20].

Fluorenol ——→ 9-Bromofluorene

Ingold & Jessop[2].

9-Bromofluorene was later prepared direct from fluorene with N-bromo-succinimide[5].

9-Bromofluorene ——→ 2-7-9-Tribromofluorene

Cf. Hodgkinson & Matthews[21].

9-Bromofluorene was dissolved in warm chloroform and treated with an equivalent quantity of bromine. The reaction was fairly violent and great clouds of HBr were given off.

Tribromofluorene recrystallises in cream coloured needles from chloroform and melts at 196-197°C.

Analysis:

C	38.73		C	38.71
H	1.99	$C_{13}H_7Br_3$ requires	H	1.74
Br	59.89		Br	59.55

Attempt to prepare 2-7-dibromofluorenyl-benzyl-dimethyl-ammonium Bromide.

(a) In Benzene.

1 gm. of 2-7-9-tribromofluorene was dissolved in boiling benzene and .33 gm. of benzyl-dimethylamine added. The mixture was refluxed for about two hours, when on cooling small colourless flakes crystallised out. These were filtered and recrystallised from alcohol with the addition of a little ether. They were water soluble giving a precipitate with silver nitrate. M.P. 142°C.

The yield was very small and most of the tribromo-fluorene was recovered from the mother liquors.

(b) In Nitromethane.

Equimolecular proportions of tribromofluorene and benzyl-dimethylamine were refluxed in a solution of nitro-methane. Almost immediately the colour darkened and as the tribromofluorene dissolved an orange/red precipitate was formed. This substance gave no melting point below 250° and was found to be mainly the tetrabromo-difluorenylidene.

2-7-9-tribromofluorene ⟶ 2-7-dibromofluorenyltrimethyl ammonium bromide.

This reaction was brought about by heating the tri-bromofluorene at 100° with slight excess of trimethylamine in a benzene solution in a tightly stoppered bottle. A

precipitate of the quaternary salt was gradually deposited as the reaction proceeded.

Better yields were later obtained using chlorobenzene as a solvent.

The quaternary salt crystallises from boiling water in two forms:-

(a) Prisms

Analysis

C	41.04		C	41.56
H	3.70	$C_{16}H_{16}NBr_3$	H	3.47
N	3.24	requires	N	3.03
Br	52.38		Br	51.95

(b) Needles

C	39.53		C	40.00
H	3.78	$C_{16}H_{16}NBr_3 \cdot H_2O$	H	3.75
N			N	2.92
Br	50.10	requires	Br	50.00
O			O	3.33

Attempt to prepare <u>Trimethyl ammonium 9-(2-7-dibromo)-fluorenylide.</u>

This was done by treating the quaternary bromide with an equivalent quantity of silver sulphate and heating on the water bath till no further precipitate was obtained with either $AgNO_3$ or HCl. The solution was then treated with an equivalent quantity of baryta solution. The solution was filtered and placed in a vac. desiccator over NaOH sticks. A white precipitate first formed which was probably the quaternary hydroxide. On further standing in the desiccator

it became yellow, probably being converted to the fluorenylide.

Attempts to recrystallise the yellow compound generally led to the rapid formation of the difluorylidene compound and the splitting off of trimethylamine. It appeared to recrystallise from methyl alcohol but on further investigation it was found that NMe_3 had again split off, the remainder of the molecule being oxidised to dibromofluorenone.

Some of the freshly prepared yellow compound was then treated with water and was found to be only slightly soluble. On addition of HBr, however, the quaternary bromide was immediately reproduced, m.p. 213°. On keeping in a corked bottle for a period of time the supposed fluorenylide appeared to gradually oxidise to dibromofluorenone, again splitting off NMe_3 (recognised by smell).

Attempts to prepare 9-(2-7-dibromo-9-methyl)fluorenyl-trimethyl ammonium iodide.

(a) From the fluorenylide.

A solution of fluorenyltrimethylammonium bromide in MeOH was treated with some solid NaOH, when a yellow precipitate was obtained (as in water). A slight excess of MeI was added and the tube corked and left overnight at ca. 40°. The orange precipitate formed was soluble in water giving a yellow precipitate with $AgNO_3$. It did not melt below 250° though a slight reddening took place at 190°.

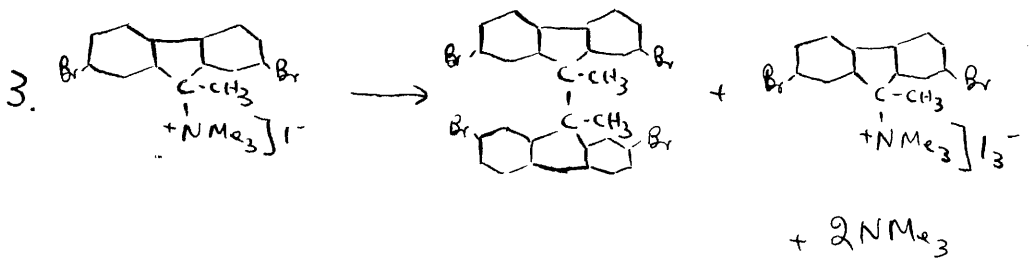
On attempting the same reaction using MeONa instead of NaOH the same compound was obtained along with a quantity of tetrabromodifluorylidine.

The yellow compound was washed quickly with a very dilute HCl solution to remove any free NMe_3. It was then left standing with excess methyl iodide for a few days, when water was added and the excess MeI steam distilled off. A large quantity of the red tetrabromo-difluorenylidene was filtered off and the aqueous solution evaporated down in a vac. desiccator. Crystals were obtained which were pale yellow in colour and after recrystallisation from methyl alcohol/ether gave a melting point of 150° dec.

The mother liquors from the recrystallisation gave a further yellow precipitate on standing as well as some dark brown crystals, M.P. 158°, mixed M.P. 140-150°. Analysis of these brown crystals indicates the periodide, the high value for carbon being due to contamination products.

Found:	C 28.77%	$C_{17}H_{18}NBr_2I_3$	C 26.25%
	H 2.44%	requires	H 2.32%.

The yellow precipitate from the mother liquors contained no nitrogen and may be a difluorenyl compound, the following decomposition being possible:



(b) Direct synthesis.

Fluorene ——→ Dibromofluorene

Hogdkinson & Matthews[21]

2-7-Dibromofluorene ——→ 2-7-dibromofluorenone

as for fluorenone prep. Cf. (18).

Recrystallised from glacial acetic acid, m.p. 200°.

2-7-Dibromofluorenone ——→ 2-7-dibromo-9-methyl-fluorenol.

Sieglitz & Jassoy[22].

Prep. of 2-7-dibromo-9-methyl-9-chlorofluorene

2-7-9-tribromo-9-methylfluorene

and 2-7-dibromo-9-methyl-9-iodofluorene.

Chloro compound prepared as by Sieglitz & Jassoy[22].

Bromo and iodo compounds prepared in a similar manner using HBr and HI solutions.

Chloro compound, m.p. 180°

Bromo compound, m.p. 190-191° (from chloroform)

Iodo compound, m.p. 167° (from alcohol).

Analysis of Bromo compound:

C 40.49		C 40.29
H 2.28	$C_{14}H_9Br_3$ requires	H 2.13
Br 57.40		Br 57.55.

2-7-Dibromo-9-methyl-9-iodofluorene ——→ 9-(2-7-dibromo-9-methylfluoryl)trimethyl ammonium iodide.

A small quantity of the iodo compound was dissolved in benzene and treated with a slight excess of a benzene

solution of trimethylamine.

A white precipitate was produced on standing overnight which was soluble in water giving a yellow precipitate with $AgNO_3$.

It melted at 96-97°.

9-(2-7-dibromo-9-methylfluoryl)trimethyl ammonium bromide.

Some of the 9-methyl-2-7-9-tribromofluorene was dissolved in chlorobenzene and treated with NMe_3 in a sealed tube at 100° for four hours. Some brownish crystals were obtained on cooling, which were partially soluble in water giving a precipitate with $AgNO_3$. They melted slowly between 205° and 220°.

This pale brown substance recrystallised from benzene in pale yellow needles of M.P. 205°. These were insoluble in water and contained no nitrogen.

Some 2-7-dibromo-dibenz-fuluene was prepared as by Sieglitz and Jassoy[22], M.P. 205°, mixed M.P. with above substance 205°.

P-Phenyl-Phenacyl Derivatives.

Reaction nos. refer to table on p. 71.

Reaction 1.

Diphenyl ⟶ Diphenylmethylketone or paraphenyl-acetophenone

Cf. Drake & Bronitsky[23],

Ferris & Turner[24].

This reaction was carried out in CS_2 with anhydrous $AlCl_3$ and acetic anhydride. After hydrolysis the product was filtered from the CS_2 and water, but was found to be still contaminated with the addition compound. The CS_2 was steam distilled off from the filtrate and hydrolysis completed by re-adding the product to the warm water. After refiltering it was dried and excess diphenyl extracted with 40-60 petroleum ether, according to the method of Ferris & Turner (above).

The final product was recrystallised from boiling absolute alcohol with addition of a little charcoal, M.P.120°.

Reaction 2.

p-Phenylacetophenone ⟶ bromo p-phenylacetophenone Carpenter & Turner[25].

This method seemed simpler than that of Drake & Bronitsky[23].

Reaction 3.

α-bromo-p-phenyl-acetophenone ⟶ p-phenylphenacyl trimethyl ammonium bromide.

1 gm. α-bromo-p-phenyl-acetophenone was placed in a stoppered bottle with a little benzene and .25 gm. of trimethylamine (2 cc. of .137 gm./cc. benzene solution) added. On standing at normal temperature for a few hours a white

powder was obtained which was soluble in hot water giving a precipitate with $AgNO_3$ in HNO_3. It did not melt sharply but became discoloured at 190° and finally melted at 216°, turning to a dark red liquid.

Recrystallised from methyl alcohol, M.P. 230°.

The picrate was prepared by treating the compound with an equivalent of picric acid in MeOH. M.P. 178°.

Analysis of Bromide:

Found:

C	61.04		C	61.08
H	5.82	$C_{17}H_{20}ONBr$	H	5.99
N	4.25	requires	N	4.19
Br	23.83		Br	23.95
O			O	4.79

Analysis of Picrate:

Found:

C	57.43		C	57.27
H	4.52	$C_{23}H_{22}O_8N_4$	H	4.56
N	11.50	requires	N	11.62
O			O	26.56

3a. p-Phenyl-phenacyl-trimethylammonium iodide.

An aqueous solution of the bromide was treated with excess of a warm aqueous KI solution. There was an immediate precipitation of a pure white substance of M.P. 215°. Recrystallisation from MeOH gave M.P. 227°. It was only very slightly soluble in water, giving a yellow precipitate with $AgNO_3$ and was much less soluble in MeOH than the corresponding bromide.

Reaction 4. Attempt to isolate trimethylammonium p-phenyl phenacylide.

An aqueous solution of the quaternary bromide was treated with a slight excess of 2N NaOH as for the re-arrangement (Reactions 10 & 11). On gentle heating the solution turned deep red. The water was allowed to evaporate slowly, when a red solid was left in the flask. This turned out to be mainly unchanged bromide though, obviously, other ions were present, the red coloration being almost certainly due to the presence of the phenacylide ion.

The above reaction was repeated and after evaporation the red substance was washed several times with hot water until there was no trace of bromide in the filtrate. A strongish smell of trimethylamine was noticed during the reaction and the remaining substance was found to contain no nitrogen and melted at 142°. It changed colour from dark red to brown when left in daylight, and is possibly a mixture of cis and trans isomers of p-p'-diphenyl-diphenacylidene.

A few white crystals obtained from the hot filtrate on cooling proved to be the unchanged quaternary bromide.

Reactions 4, 5 & 13.

-Methyl-p-phenyl-phenacyl trimethyl ammonium iodide

or -Benzyl-p-phenyl-phenacyl trimethyl ammonium iodide.

Reaction 4 was repeated in MeOH using a slight excess of MeONa and a slight excess of MeI. The solution had

turned red slowly before the MeI was added and the whole was then refluxed slowly for several hours. The solution was then cooled slightly and an equal volume of ether added, when a pink precipitate was produced. This was filtered and thoroughly washed with water, MeOH and ether, but the pink colour persisted. It was recrystallised from MeOH in which it was sparingly soluble and came out in pale pink plates, M.P. 222°d. These were soluble in hot water and gave a definite iodide precipitate with $AgNO_3$ in HNO_3.

Mixtures with the products of the reactions 8a and 3a both melted ca. 222° and were inconclusive.

The picrate prepared melted at 178° and was identical with that from 3 and 3a and not with that from 8a.

A similar reaction carried out in presence of benzyl iodide instead of methyl iodide yielded no workable products.

Reaction 6.

Diphenyl ⟶ p-phenylpropiophenone

Long & Henze[26].

As in the preparation of the methyl ketone, it was found necessary to warm the ice mixture to complete the hydrolysis of the addition compound. Crystallisation from benzene (hot filtration) and from alcohol gave a product of M.P. 96-97°.

N.B. Long & Henze (above) and Willgerodt & Scholtze[27] give M.P. as 89°.

Campbell & Chattaway[28] give M.P. as 98°.

Reaction 7.

Paraphenylpropiophenone ⟶ ∝-bromo-p-phenylpropiophenone.

This was carried out as for the preparation of the corresponding acetophenone compound according to the method of Carpenter & Turner[25]. Slight excess of bromine being added to an acetic acid solution of the ketone at about 50°, the compound which crystallised out on cooling had a M.P. of 101-102° (mixed M.P. with the unbrominated ketone is 88-90°). On recrystallisation from alcohol gave white plates, M.P. 102-103°.

Collet[29] gives M.P. as 79-80°.

Analysis:

Found:

C 61.66	$C_{15}H_{13}OBr$	C 62.29
H 4.42	requires	H 4.30
Br 27.55		Br 27.68

Though analysis and melting point of this compound might leave some doubt as to its constitution, subsequent reactions 8 and 8a indicate that it is indeed ∝-bromo-p-phenyl-propiophenone.

The following method of preparation gives further evidence that the p-phenyl propiophenone has been brominated in the ∝-position.

N-bromo-succinimide is known to brominate unsaturated compounds in the allyl position.
(Ziegler, Späth, Schaf, Schumann and Winkleman[30], Ruzicka et al[31]).

We have also used it to brominate fluorene in the 9-position (p. 79). (Wittig and Felletschin[5]).

The method of bromination is generally to reflux the compound to be brominated with the N-bromo-succinimide in carbon tetrachloride. p-Phenyl propiophenone was recovered unchanged under these conditions, so the following method was employed.

2 gm. of p-phenyl-propiophenone was mixed with an equivalent quantity of N-bromosuccinimide and the two substances fused together on an oil bath at 130°. Crystals of succinimide soon appeared on the cool neck of the flask. After a few hours' heating α-bromo-p-phenyl-propiophenone was extracted with CCl_4 and recrystallised from alcohol. M.P. 101-102° (as before).

A mixed M.P. with the substance obtained by direct bromination was also 101-102°.

Reaction 8.

α-Bromo-p-phenylpropiophenone ⟶ α-methyl-p-phenyl phenacyltrimethyl ammonium bromide.

1 gm. of the bromo ketone was treated with 50% excess of NMe_3 in benzene solution (3 cc. of .104 gm/cc.

solution). The solution was sealed in a stoppered bottle and heated on the water bath for about an hour and the white precipitate filtered and washed with a little clear benzene. It looked very pure and had a M.P. of 204°d.

Recrystallised from MeOH/ether in beautiful white needles, M.P. 218°d.

Reaction 8a.

Bromide of (8) ⟶ iodide.

An aqueous solution of the bromide was treated with excess KI solution, when a white precipitate was obtained, M.P. 214°. Recryst. MeOH/ether, M.P. 219°. It was fairly soluble in water and gave a definite iodide precipitate with $AgNO_3$.

Picrate prepared as for (3) and (3a), M.P. 186°.

Analysis:

Found:

C	58.25	$C_{24}H_{24}O_8N_4$	C	58.06
H	4.86	requires	H	4.84
N	11.16		N	11.29
O			O	25.80.

Reaction 9.

α-bromo-p-phenylacetophenone ⟶ p-phenyl-phenacylbenzyl dimethyl ammonium bromide.

(Cf. Carpenter & Turner[25]).

1 gm. of α-bromo-p-phenylacetophenone was dissolved in warm benzene and .5 gm. of benzyldimethylamine added.

An immediate vigorous reaction took place and a white substance separated out which was soluble in hot water, giving a bromide precipitate with $AgNO_3$, M.P. 196-197°d. Recrystallised from MeOH/ether, M.P. 207°d.

Analysis:

Found	C	67.49	$C_{23}H_{24}ONBr$	C	67.32
	H	5.69		H	5.85
	N		requires	N	3.41
	Br	19.41		Br	19.51
	O			O	3.90

Reactions 10 & 11.

Rearrangement of p-phenyl-phenacylbenzyl-dimethyl ammonium bromide to p-phenyl-α-benzyl-α-dimethylamine acetophenone. (Cf. Stevens[1]).

1 gm. of the quaternary bromide was dissolved in hot water and a slight excess of aqueous 2N.NaOH solution added. A reaction immediately took place and a yellow oil separated from the aqueous layer. This became semi-solid on cooling, was filtered and recrystallised from aqueous MeOH. M.P. 103-104°.

These yellow crystals had a pleasant honey-like odour.

Analysis:

Found:	C	83.91	$C_{23}H_{23}ON$	C	83.89
	H	6.83		H	6.99
	N	4.21	requires	N	4.26
	O			O	4.86

The above experiment was then repeated using MeONa (2N solution) in MeOH. On adding the methoxide in the cold

no visible reaction took place, but on gradually heating the flask to 100° on the water bath the solution gradually became yellow and then red. On cooling orange red crystals were deposited. M.P. 103°.

(Yield about .7 gm. from 1 gm. of salt).

Reaction 12.

p-Phenyl-α-benzyl-α-dimethylaminoacetophenone ⟶

α-(p-phenyl-α-benzyl)phenacyltrimethylammonium iodide.

About .6 gm. of the rearrangement product was dissolved in MeOH and a slight excess of MeI added and the mixture gradually warmed to boiling until all the excess MeI had boiled off. Ether was then added to the MeOH solution till the precipitate just remained permanent. Pale yellow flakes crystallised out on cooling. M.P. 194°d.

The compound was soluble in water and gave an iodide precipitate with $AgNO_3$.

Analysis:

Found:	C	61.10	$C_{24}H_{26}ONI$	C	61.15
	H	5.40		H	5.52
	N		requires	N	2.97
	I	26.94		I	26.97
	O			O	3.40

Attempt at Reaction 14.

α-Methyl-p-phenyl-phenacyl-benzyl-dimethyl ammonium iodide.

Reaction 10 was repeated in methyl alcoholic solution as above with the addition of a slight excess of

methyl iodide. On heating the mixture slowly on a water bath the same colour changes took place as in the absence of the MeI. On cooling, however, no precipitate was obtained and the solution gradually changed from red to yellow. On heating and addition of ether pale yellow flakes were obtained, M.P. 190°.

Recrystallised from MeOH/ether, M.P. 194-195°d.

Mixed M.P. with product of reaction 12, 194-195°d.

It is therefore obvious that the rearrangement (reaction 11) has again taken place in preference to reaction 14.

A further attempt to introduce a methyl group in the position of the phenacyl radicle was made using ethyl alcoholic sodium ethoxide as condensing agent. The rearrangement again took place, however, and the final products were the iodide of reaction 12 and the unchanged bromide.

Reaction 15.

α-Bromo-p-phenyl-propiophenone ⟶ α-methyl-p-phenyl-phenacyl-benzyl-dimethyl-ammonium bromide.

1 gm. of the bromo ketone was dissolved in methyl alcohol and about ½ gm. of benzyl-dimethylamine added and the solution heated for a short time. Crystals which were obtained on cooling were found to be mainly unchanged bromo-ketone.

The experiment was repeated using benzene as a solvent. On heating on the water bath the solution gradually turned red and a few colourless crystals were deposited on cooling. These were soluble in water and gave a bromide precipitate with silver nitrate. Much of the solvent was evaporated off and on standing for several days quite a reasonable quantity of brownish crystals was obtained. Recrystallisation from methyl alcohol/ether gave white flakes, M.P. 192-193° dec.

Fluorenylidene-9-fluorenyl Derivatives.

Fluorenone ⟶ Fluorenone Oxime.

This was carried out according to the methods used for the general preparation of oximes.

Hydroxylamine hydrochloride was dissolved in a minimum quantity of water and an equivalent quantity of fluorenone was added followed by an equivalent of NaOH also dissolved in a minimum quantity of water. Sufficient alcohol was then added to just dissolve the fluorenone on heating. The solution was allowed to reflux on the water bath for about 4 hours. The oxime crystallised out in good yield on cooling and was in a reasonably pure state.

It was recrystallised from a very large quantity of benzene or from acetic acid. M.P. 193-194°.

Fluorenone oxime ⟶ 9-Fluorylamine.
(Cf. Ingold & Wilson[16]).

The yield of the free amine obtained by this method was poor and recrystallisation difficult, apparently due to carbonate formation.

A good yield of the hydrochloride was obtained, however, and was found to crystallise well from hot water. It was also found to be more suitable for the next experiment than the free amine.

Preparation of Fluorenylidene-9-fluorylamine.
(Cf. Ingold & Wilson[16]).

Attempts were made as suggested by Ingold & Wilson to condense the ketone and amine

(a) by heating together at 100° for 4 hours,
and (b) by heating in boiling alcohol for 7 hours.

Yields from both of these methods were very poor, being in the region of 7%.

A further attempt was made using zinc chloride as a condensing agent but there was no improvement in the yield. (Cf. Reddelien[17]).

The following method gave a slightly improved yield.

.5 gm. of sodium was dissolved in about 100 cc. of absolutely dry alcohol (dried over lime and distilled from sodium). 5 gm. of fluorylamine hydrochloride and 4.13 gm.

fluorenone were added (theoretical quantities). The solution was then refluxed on the water bath for 6-7 hours, a deep green colour developing in the heat but fading to a pale primrose yellow on cooling. The solution was filtered hot and on cooling the filtrate pale yellow crystals of fluorenylidene-9-fluorylamine crystallised out, M.P. 178°d. (Ingold & Wilson[16] give M.P. as 175°d).

The yield was about 1 gm., but further quantities of the compound were obtained by evaporating the alcohol from the final filtrate or by further extracting the residue from the hot filtration with benzene or petroleum ether and recrystallising from benzene.

The final residues were then oxidised back to fluorenone by treatment with $Na_2Cr_2O_7$ in glacial acetic acid.

Attempt to prepare 9-fluorylidene-9-fluoryl-methyl-ammonium iodide.

(Cf. Decker & Becker[15]).

Preparation of benzylidene-p-tolyl-methyl-ammonium iodide.

N.B. In this and subsequent experiments great care had to be taken to have reagents and solvents thoroughly dry as any hydroxylic substance tends to decompose the quaternary salt.

Fluorenylidene-9-fluorylamine was found to be readily soluble in methyl iodide and several attempts were made to

cause the two substances to react by heating the former with a large excess of the latter. Fluorenylidene-fluorylamine was returned unchanged, however.

Similar results were obtained by refluxing the two substances in benzene for several hours although on carrying out the experiment in benzene solution in a tightly stoppered bottle a very small amount of a substance crystallising in short yellow needles was obtained among the hexagonal plates of fluorenylidene-fluorylamine.

The needles were soluble in water and gave a definite iodide precipitate with $AgNO_3$.

This experiment was therefore repeated in a sealed glass tube which was heated at 100° for about 3 hours. A very small amount of a reddish product was obtained which reacted with water to give an iodide precipitate and had a M.P. of 160°.

The yield, however, was too small to be of any practical value.

Attempt to prepare Fluorenylidene-9-fluoryl methyl-ammonium methosulphate.

(1) In benzene. Fluorenylidene-fluorylamine was refluxed in benzene for several hours with dimethyl sulphate, the mixture being kept vigorously stirred. Some slight reaction took place but generally speaking, the fluorenylidene-fluorylamine was recovered unchanged.

(2) In nitromethane. The above experiment was repeated using nitro methane as a solvent, the mixture being stirred and heated on an oil bath between 110° and 130° for several hours. The solution became very dark and a dark brown gummy substance was obtained which on drying gave a M.P. of 205-210°. Other lighter crystals which settled out on the side of the flask gave a M.P. of 215-225°. This substance gave a positive sulphur test and on fusion with NaOH gave off either ammonia or methylamine.

The nitromethane in the filtrate was then evaporated down under reduced pressure and on cooling some well formed very dark crystals were obtained, M.P. 133°.

These recrystallised from nitromethane in dark prisms. M.P. 133-134°.

Recrystallised from benzene in less intensely coloured brown needles, M.P. 133-134°.

An attempt to hydrolise this product with 95% alcohol (according to the method of Decker & Becker[15]) on the assumption that it was the required salt, simply yielded beautiful brown needles, M.P. and mixed M.P. 133°.

The analysis of this brown compound suggested that fluorenylidene-nitromethane had been formed.

Analysis:

Found	C	75.93	$C_{14}H_9NO_2$ requires	C	75.34
	H	4.14		H	4.04
	N	5.90		N	6.27

The same brown crystals (M.P. 133°) were obtained by heating fluorenylidene-9-fluorylamine in CH_3NO_2 without the methyl sulphate.

Further attempts to establish the constitution of the brown crystals ($C_{14}H_9NO_2$?) as <u>fluorenylidene-nitromethane</u>.

Attempts were made to condense fluorenone with nitromethane, (a) alone, (b) using sodium methoxide, and (c) zinc chloride as condensing agents.

(a) and (b) were unsuccessful and (c) yielded primarily a red compound which was inorganic and was probably the fluorenone-zinc chloride complex. It decomposed on standing in CH_3NO_2.

Some fluorenone anil was then treated with nitromethane, being refluxed in it for several hours. No crystals could be obtained on evaporating off the excess CH_3NO_2, but on treatment of the tar with dilute HCl a solution of aniline hydrochloride was obtained. (Diazotised and coupled with naphthol).

The residue left after the HCl extraction was mainly fluorenone and not fluorylidene-nitromethane. The dark colour of the impure product, however, indicated the presence of a small amount of a substance similar to that obtained from the fluorenylidene-fluorylamine nitro-methane experiment.

Attempt to prepare Fluorenylidene-9-fluoryl-allyl-ammonium iodide.

A small quantity of fluorenylidene-fluorylamine was heated on an oil bath with an excess of allyl iodide for several hours, the excess allyl iodide being finally distilled off under reduced pressure. A dark tarry substance was obtained which, after washing with ether, hardened into an apparently crystalline product which, however, gave no definite melting point.

Attempts to recrystallise the product from benzene, carbon tetrachloride, etc., were unsuccessful.

Hydrolysis with 95% alcohol seemed to indicate decomposition into fluorenone and 9-fluoryl-allyl-amine-hydriodide.

The reaction between fluorenylidene-fluorylamine was then attempted in xylene which had been carefully dried and distilled from sodium.

The mixture was refluxed on an oil bath at about 140° for several hours and the xylene and slight excess of allyl iodide distilled off under reduced pressure. The resulting black tar was washed with dry benzene and a brown microcrystalline substance was obtained. M.P. 210-215°d.

Recrystallised from nitromethane, M.P. 228°.

The picrate was prepared by treatment with an equivalent quantity of picric acid in methyl alcohol. M.P. 233°

(Mixed M.P. with iodide 180°).

Analysis:

Awaiting Results. (See P. 104 footnote)

Hydrolysis of Fluorenylidene-9-fluoryl allyl ammonium iodide.

A small amount of the salt was refluxed in aqueous ethyl alcohol. It did not appear to hydrolyse so rapidly as Decker & Becker's benzylidene-p-tolyl-methyl ammonium iodide, but after several hours' refluxing a yellow solution was obtained; the original solution being dark brown. On addition of a small quantity of water a white precipitate was obtained which redissolved on heating and recrystallised out as fluorenone. (Identified by M.P. and mixed M.P.).

After precipitating all the fluorenone by further addition of water the remaining solution was evaporated down under reduced pressure, when a very small quantity of a water soluble iodide was obtained.

A further quantity of this iodide was obtained by boiling the fluorenylidene salt with water, filtering off the insoluble fluorenone and evaporating down the aqueous solution.

The iodide gave no definite M.P. below 350°.

The picrate was prepared by treatment with an equivalent of picric acid in methyl alcohol. M.P. 172°.

A further quantity of the iodide was then prepared directly to identify the hydrolysis product.

Preparation of 9-Fluoryl-allyl-amine-hydriodide.

Equivalent quantities of 9-fluorylamine and allyl iodide were refluxed together in alcohol for several hours.

No solid was obtained on cooling, so excess alcohol was removed under reduced pressure.

The gummy material left was washed with benzene, when a good yield of a microcrystalline solid was obtained.

It was very soluble in water, giving iodide reactions, but gave no definite M.P. below 360°.

9-Fluoryl-allylamine.

On addition of ammonia to an aqueous solution of the hydriodide a precipitate of the amine was obtained. M.P. 44°.

Picrate of 9-Fluoryl-allylamine.

The picrate was prepared by treating the hydriodide with picric acid in methyl alcohol. Recrystallised from methyl alcohol, M.P. 175°. Being analysed. (see footnote)

A mixed melting point was then taken of the picrate (above) and the picrate prepared from the hydrolisis product and was found to be 173-174°.

The analysis of these picrates was unsatisfactory possibly due to reduction by the HI set free during the picrate formation.

PART II.

BIBLIOGRAPHY.

(1)	Stevens	J.C.S. 1930, 2107
(2)	Ingold & Jessop	" 1929, 2357
(3)	" "	" 1930, 713
(4)	Marrian & Stevens	Private Communication
(5)	Wittig & Felletschin	Ann. 1944, 555, 133
(6)	Pinck & Hilbert	J.A.C.S. 1946, 68, 751
(7)	" "	" " " 2011
(8)	" "	" 1947, 69, 723
(9)	" "	" 1932, 54, 710
(10)	Thomson & Stevens	J.C.S. 1932, 55
	Dunn & Stevens	" " 1926
(11)	Richardson & Soper	" 1929, 1873
(12)	Oddy	J.A.C.S. 1923, 45, 2156
(13)	Staudinger & Miescher	Helv.Chim.Acta, 1919, 2, 554
(14)	Taylor, Owen & Whittaker	J.C.S. 1938, 206
(15)	Decker & Becker	Ann. 1912, 395, 370
(16)	Ingold & Wilson	J.C.S. 1933, 1499
(17)	Reddelien	Ber. 1909, 42, 4760
		1910, 43, 2476
(18)	Graebe & Rateanu	Ann. 1894, 279, 258
(19)	Huntress, Hershberg & Cliff	J.A.C.S. 1931, 53, 2721
(20)	Bachmann	" 1933, 55, 770
(21)	Hodgkinson & Matthews	J.C.S. 1883, 164
(22)	Sieglitz & Jassoy	Ber. 1922, 55, 2037
(23)	Drake & Bronitsky	J.A.C.S. 1930, 52, 3718
(24)	Ferris & Turner	J.C.S. 1920, 1147
(25)	Carpenter & Turner	" 1934, 870
(26)	Long & Henze	J.A.C.S. 1941, 63, 1939
(27)	Willgerodt & Scholtze	J.Pr.Ch. 1910, 81, 396
(28)	Campbell & Chattaway	Proc.Roy.Soc. 1942, B130, 440
(29)	Collet	Compt.rend. 1897, 125, 306
(30)	Siegler et al.	Ann. 1942, 551, 80
(31)	Ruzicka et al.	Helv.Chim.Acta, 1943, 26, 1235.

A P P E N D I X.

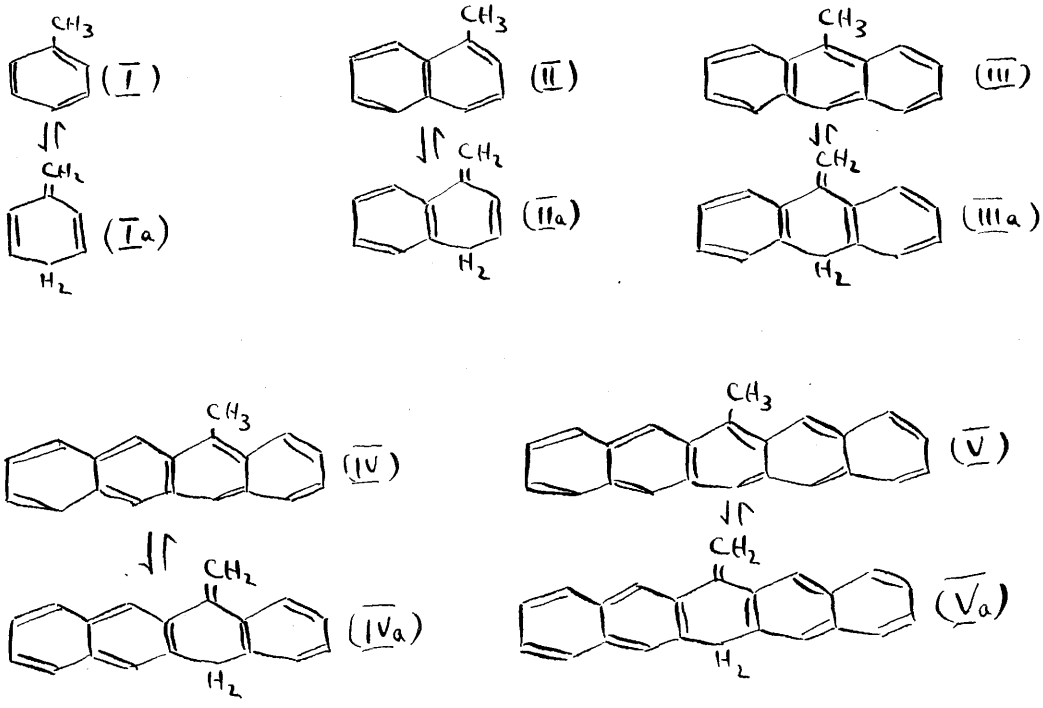
(1) On p.22 the possibility of the formation of a molecular compound of 7-8-benzterrylene and anthracene is mentioned.

It seems likely that similar compounds may have been formed with tetracene and 1-2-5-6-dibenzperylene or with tetracene and naphtho-(2'-3'-1-2)-perylene (pp.14 and 46). This would account for the difficulty of separating the tetracene from the perylene derivatives and for the fact that it is found so widely spread on the alumina column.

Copy of Letter to "Nature" submitted November, 1948.

The Equilibrium between Methyl-acenes and Methylene-dihydroacenes.

Tautomerism between methyl-acenes (I, II, III, IV, V) and methylene-dihydroacenes (Ia, IIa, IIIa, IVa, Va, respectively) has often been postulated to explain side-chain reactivity of aromatic compounds, but hitherto no methylene-dihydroacene has been isolated. This weakness in the hypothesis has now been removed by the synthesis of pure 6-methylene-6:13-dihydropentacene (Va). The "anellation principle"[1] requires a gradual transition in properties in the acene series and it may be inferred therefore that (IV), (III), (II) and (I) will also contain the corresponding methylene forms, but in decreasing proportions.



This view is supported by study of the absorption spectra of the hydrocarbons (see figure). The spectrum of 9-methyl-anthracene (III) resembles very closely that of anthracene, but does not exclude the presence of a small proportion of the methylene form (IIIa) which would have only feeble absorption. The orange 5-methyltetracene (IV) shows an absorption similar to that of tetracene, but the intensity of the bands is considerably lower than in the case of tetracene, whereas with 9-methylanthracene and anthracene the reverse relationship holds. This suggests the presence in (IV) of an appreciable proportion of a weakly absorbing methylene form (IVa). When we come to the pentacene series we find that the spectrum of the pale yellow methylene dihydropentacene (Va) shows no resemblance to that to be expected from methylpentacene (V), which may be calculated by application of the anellation principle[1]. If the pale yellow solution of (Va) in 1-methylnaphthalene is heated with exclusion of air to 200°, the solution becomes violet-red and shows the first three bands calculated for methylpentacene (V). The colour fades slowly on cooling.

The fact that methylpentacene exists at room temperature almost entirely in the methylene form (Va) is important from the standpoint of resonance in aromatic compounds. As each member of the pairs of structures formulated above

contains the same number of double bonds as the other member, the energy-difference between the methyl form and the methylene form must consist of the difference in resonance energy. Wave mechanical treatment predicts a decreasing difference in resonance energy of these pairs of hydrocarbons with increasing numbers of rings, until the difference becomes zero with an infinite number of rings[2]. Hence the ratio between methyl and methylene forms should never exceed 1:1. This prediction has thus been shown to be entirely erroneous, and the evidence now adduced may perhaps provide a new basis for the calculation of the decreasing energy per ring in the higher acenes.

9-Methylanthracene (III) was prepared as described by Sieglitz and Marx[3]. 5-Methyltetracene (IV) was obtained by dehydration of the crude carbinol formed by interaction of methylmagnesium iodide with tetracenone, prepared by reduction of 5:12-tetracenequinone[4] with alkaline sodium hydrosulphite solution. It formed orange-red prisms (from benzene), m.p. 160°, and gave a bright green solution in sulphuric acid (found: C, 94.2; H, 5.7. $C_{19}H_{14}$ requires C, 94.2; H, 5.8%).

6-Methyl-6:13-dihydropentacene (V) was similarly prepared from pentacenone[5] and formed pale yellow needles (from xylene), which dissolved in sulphuric acid to give a blue solution which afterwards turned to brown (found:

C, 94.4; H, 5.65. $C_{23}H_{16}$ requires C, 94.5; H, 5.5%). The m.p. was between 244° and 254°, and in an evacuated capillary the melt was deep red. Oxidation with selenium dioxide in boiling nitrobenzene gave pentacene-5:13-quinone. A sparingly soluble by-product from the Grignard condensation formed colourless crystals, m.p. 420°(decomp.) which gave a greenish-yellow solution in sulphuric acid (found: C, 94.2; H, 5.8. $C_{46}H_{30}$ requires C, 94.5; H, 5.5%).

We thank the D.S.I.R. for a grant which enabled one of us (J.W.W.) to participate in the experimental section of this investigation.

E.Clar
(I.C.I. Research Fellow),

J.W. Wright.

Chemistry Department,

University of Glasgow.

[1] E.Clar, Aromatische Kohlenwasserstoffe, Springer-Verlag 1941, p.20.

[2] J.K. Sirkin and M.E. Diatkina, Bull.Acad.Sci.U.R.S.S., Cl. Sci.Chim., 1946, 153. Brit.Abstr., 1946, AI, 365. The view of these authors was supported, and in some cases, an even greater stability of the higher methyl-acenes was predicted, in private communications from leading authorities in this field.

[3] B. 56, 1619 (1923).

[4] E.Clar, Ber. 75, 1271 (1942). Compare L.F. Fieser: Am. Soc., 53, 2329 (1931).

[5] Ch.Marschalk, Bull.Soc.Chim. (5), 4, 1549 (1937).

N.B. The figure referred to is identical to Fig.4, p.7a of this thesis. J.W.W.