

**231.** *The Reactions of Anthracene and 9-Methylantracene with the Free Radicals derived from Di-tert.-butyl Peroxide.*

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The thermal decomposition of di-*tert.*-butyl peroxide in boiling chlorobenzene or *o*-dichlorobenzene has been used as a source of methyl and *tert.*-butoxy-radicals, and the reactions of these radicals with some polycyclic aromatic hydrocarbons have been investigated. Little significant reaction occurs with chlorobenzene, naphthalene, phenanthrene, or pyrene, but anthracene gives both 9-methylantracene (IV) and 9:9':10:10'-tetrahydro-10:10'-dimethyl-9:9'-dianthryl (III), the formation of the latter being favoured by low temperatures.

9-Methylantracene is more reactive than anthracene. It yields 9:10-dimethylantracene by nuclear substitution, 1:2-di-9'-anthrylethane by dehydrogenation followed by dimerisation, and smaller quantities of 9-ethyl-, 9-ethyl-10-methyl-, and 9:10-diethyl-anthracene, and 1-9'-anthryl-2-(10-methyl-9-anthryl)ethane (XII) by further reactions of the same type.

Since these secondary reactions of anthracene occur so readily, investigations of the initial products of the reaction between anthracene and methyl radicals do not give a correct measure of the ease of this reaction.

SOME years ago it was shown by Roitt and Waters<sup>1</sup> that when certain polycyclic aromatic hydrocarbons such as anthracene, 1:2-benzanthracene, and 3:4-benzopyrene were allowed to react with the homolytic decomposition products of benzoyl peroxide they were substituted in their active *meso*-positions by benzoate groups. In contrast, benzene and many of its less active derivatives are phenylated when subjected to the same reaction.<sup>2</sup>

<sup>1</sup> Roitt and Waters, *J.*, 1952, 2695.

<sup>2</sup> Augood, Hey, and Williams, *J.*, 1952, 2094.

As a continuation of this work we have investigated the reaction between the free radicals formed by the thermal decomposition of di-*tert.*-butyl peroxide,<sup>3</sup> and chlorobenzene, naphthalene, phenanthrene, pyrene, anthracene, and 9-methylanthracene, but only with anthracene and its methyl derivative could we obtain appreciable yields of distinctive reaction products. All the other hydrocarbons were recovered unchanged. This high reactivity of anthracene and its derivatives towards free radicals is in accord with current theories of free valency,<sup>4</sup> and with the analysis by Levy and Szwarc<sup>5</sup> of the gaseous products of reactions between acetyl peroxide and aromatic hydrocarbons.

Our results, which support the widely accepted view that free radicals react first by addition to the carbon atoms of aromatic molecules, indicate that with the radicals  $\text{CH}_3\cdot$  and  $(\text{CH}_3)_2\text{C}\cdot\text{O}$  formed from di-*tert.*-butyl peroxide, the primary aromatic reaction product is certainly equal to, and usually greater than, the starting material in reactivity. Hence a number of secondary free-radical reactions can occur and the percentage yields of the various products actually isolated give little indication of the overall extent of the primary reaction.

The first experiments were conducted in refluxing chlorobenzene which, we had hoped, would prove quite inert to decomposing di-*tert.*-butyl peroxide. However preliminary work showed that this was not so. When chlorobenzene and the peroxide were refluxed together for three days and the volatile products collected, a considerable amount of *tert.*-butanol was obtained, indicating that *tert.*-butoxy-radicals had attacked the liquid mixture. No pure products such as chlorotoluenes or dichlorodiphenyls could be isolated but an appreciable amount of involatile resin was obtained. This residue, which probably resulted from radical polymerisation, greatly increased the difficulty of isolating the crystalline products from later experiments.

When naphthalene was refluxed with di-*tert.*-butyl peroxide in chlorobenzene the yields and relative amounts of volatile products were very similar to those obtained from the experiment with chlorobenzene alone. The naphthalene was recovered in 75% yield after purification but none of its derivatives could be detected. Similarly phenanthrene and pyrene were recovered in yields of 70% and 80% respectively.

However, when the peroxide was refluxed in chlorobenzene with an equimolar amount of anthracene only 40% of the latter could be recovered, and besides the usual tar we were able to isolate pure anthraquinone, 9-methylanthracene (IV), and 9:9':10:10'-tetrahydro-10:10'-dimethyl-9:9'-dianthryl (III). The production of the dianthryl (III) indicates that, as in the work of Bickel and Kooyman<sup>6</sup> with 2-cyano-2-propyl radicals, a methyl radical must first add to the anthracene molecule to give the radical (II) which can then either dimerise to the dianthryl (III) or donate a hydrogen atom to a methyl or *tert.*-butoxy-radical, yielding the methyl derivative (IV). The anthraquinone is probably formed by an oxidation involving substitution by *tert.*-butoxy-radicals rather than by autoxidation, for it is known that alkyloxanthracenes can undergo further oxidation to anthraquinone on purification through active alumina. When this reaction was conducted with an excess of *tert.*-butyl peroxide neither the dianthryl (III) nor 9-methylanthracene (IV) could be isolated, possibly because, after their initial formation, they were involved in further free-radical reactions. Support for this view is provided by the fact that samples of the tarry residues obtained in both reactions with anthracene yielded anthraquinone on chromic acid oxidation. From these oxidations we were unable to isolate any substituted anthraquinones; this indicates that, as expected, radical attack on anthracene is limited to the *meso*-positions.

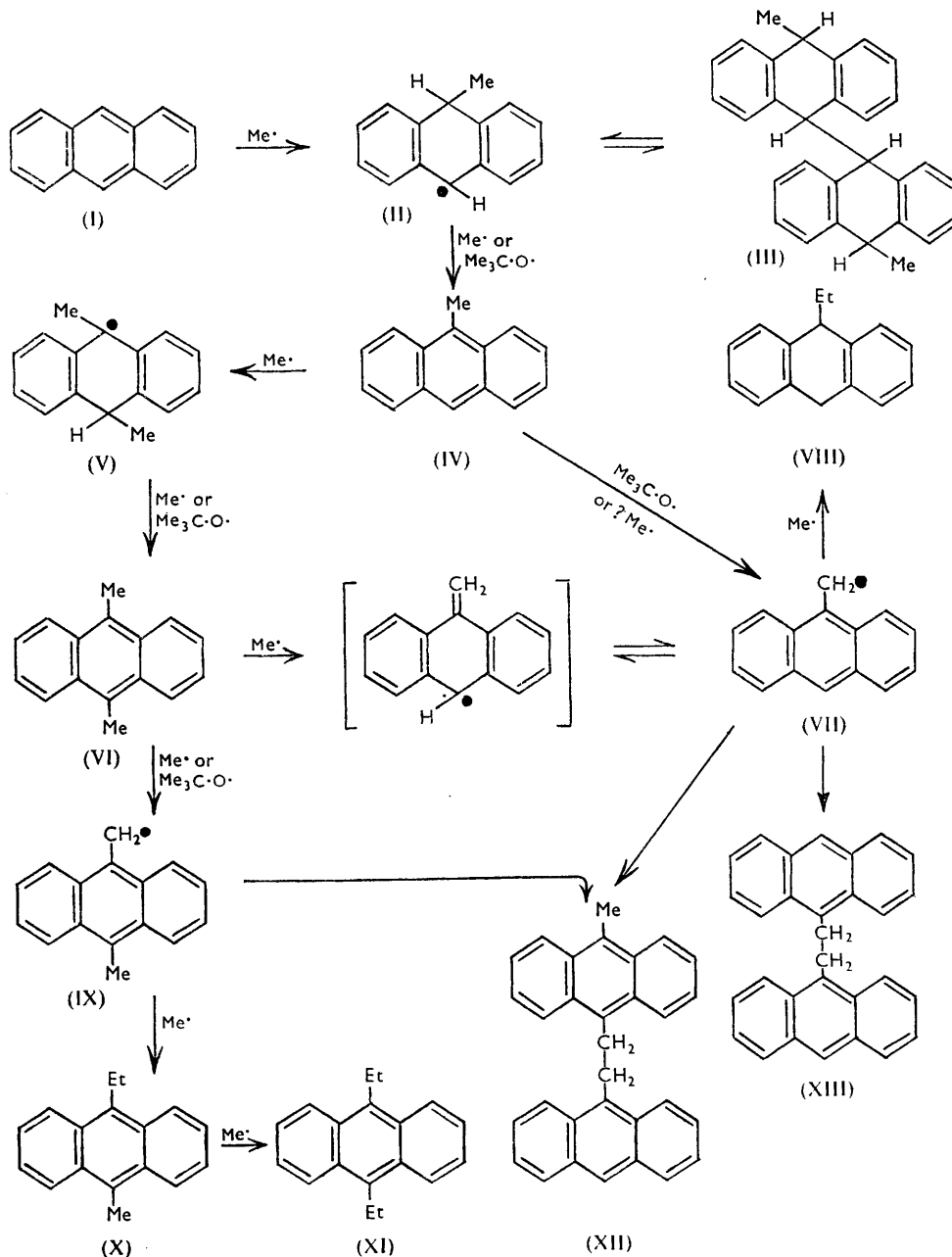
The reaction with equimolar amounts of anthracene and the peroxide was next conducted in refluxing *o*-dichlorobenzene. By removal of the volatile products as they were formed the temperature in the boiling mixture was kept at 155–165°. The reaction was then rapid and gave increased yields of anthraquinone and 9-methylanthracene, but the dimeric product (III) was not isolated. This was probably due to the fact that high

<sup>3</sup> Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88.

<sup>4</sup> Coulson, *J.*, 1955, 1435.

<sup>5</sup> Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.

temperatures favour the reverse reaction (III  $\rightarrow$  II) as shown by the work of Bickel and Kooyman.<sup>6</sup>



A low-temperature experiment was carried out in the absence of a solvent but only unchanged starting material was recovered, probably because of the insolubility of anthracene in the peroxide.

Attention may be drawn to the fact that none of these reactions involving anthracene

<sup>6</sup> Bickel and Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.

led to the formation of 9 : 9'-dianthryl : this indicates that the direct extraction of hydrogen from the anthracene molecule does not occur.

Since in the above experiments there was some evidence of further reaction, to give more highly substituted anthracenes, the thermal decomposition of di-*tert.*-butyl peroxide in the presence of 9-methylanthracene was next examined. Reaction in refluxing chlorobenzene gave, besides unchanged starting material, 1 : 2-di-9'-anthrylethane (XIII) and its polymer (probably identical with that reported by Roitt and Waters<sup>1</sup>), 9 : 10-dimethyl- (VI), 9-ethyl-10-methyl- (X), and 9-ethyl-anthracene (VIII). These substances are probably formed by the routes shown in the annexed scheme. Further information on the mode of reaction was provided by heating the peroxide and 9-methylanthracene without solvent on a bath of boiling toluene. At this lower temperature the hydrocarbon was converted into the coupling product (XIII) and its polymer, and no substitution product was isolated. The only volatile product was *tert.*-butyl alcohol, indicating that under mild conditions the *tert.*-butoxy-radical does not decompose rapidly, and that it is reactive enough to abstract hydrogen from the side chain of 9-methylanthracene. On the other hand, on reaction in boiling *o*-dichlorobenzene there was a notable increase in the amounts of substitution products. This may indicate that at high temperatures the methyl radical is the more important reactant and that methyl rather than *tert.*-butoxy is the radical which easily combines with the anthracene nucleus.

The production of 9 : 10-diethylanthracene (XI) in this high-temperature reaction was unexpected, since the only available route is from 9-methyl-10-ethylanthracene by dehydrogenation and methylation of the 9-methyl group, and it would be expected that the hydrogen atoms on this group would be less reactive than those in the  $\alpha$ -position of the ethyl group. However a model showed that steric hindrance due to the side rings may be a contributing factor in deciding the course of hydrogen abstraction. Another point of interest was that 9-ethyl-10-methylanthracene was formed from the radical (IX) in much higher yield than was 1-9'-anthryl-2-(10-methyl-9-anthryl)ethane (XII), and the dimer, 1 : 2-di-(10-methyl-9-anthryl)ethane was not formed in detectable amount. This indicates that the stationary concentrations in the reaction mixture of the radicals involved in the production of the above compounds were  $\cdot\text{CH}_3 > (\text{VII}) > (\text{IX})$ .

All of the products isolated from these reactions were identified by comparison of melting points and infrared and ultraviolet spectra with those of the authentic materials. In one case 1 : 2-di-(10-methyl-9-anthryl)ethane the compound prepared by us differed considerably from that previously described.<sup>7</sup> We believe that the material described here is the authentic compound since it has the ultraviolet absorption typical of anthracene derivatives, and that the substance obtained by Badger and Pearce<sup>7</sup> was its dihydro-derivative which we have also prepared by another method.

#### EXPERIMENTAL

*Materials.*—Di-*tert.*-butyl peroxide was purified by distilling the commercial material under reduced pressure. The fraction of b. p. 50—52°/90 mm. was collected and used immediately.

Naphthalene, phenanthrene, and pyrene were recrystallised to satisfactory m. p.

Anthracene was purified by two distillations with ethylene glycol.

9-Methylanthracene was first prepared from 9-anthraldehyde<sup>8</sup> by the Huang-Minlon procedure<sup>9</sup> but later experiments showed the following variation of the method of Krollpfeiffer and Bronscheid<sup>10</sup> to be more satisfactory. A suspension of anthrone (16.0 g.) in ether (80 ml.) was added in small portions to a vigorously stirred Grignard solution prepared from methyl iodide (36 g.) and magnesium (6.0 g.) in 60 ml. of ether. After the addition (20 min.) the mixture was refluxed for 2.5 hr. and the excess of reagent was then destroyed by the addition of 15% sulphuric acid. The ether layer was collected and after removal of the solvent the residue was chromatographed on alumina (250 g.; activity I). Elution with 1 : 1 light petroleum-benzene

<sup>7</sup> Badger and Pearce, *J.*, 1950, 2314.

<sup>8</sup> *Org. Synth.*, 1940, 20, 11.

<sup>9</sup> Huang-Minlon, *J. Amer. Chem. Soc.*, 1949, 71, 3301.

<sup>10</sup> Krollpfeiffer and Bronscheid, *Ber.*, 1923, 56, 1617.

gave 9-methylanthracene which crystallised from methanol as very pale yellow plates (13.2 g., 84%), m. p. 80°.

Chromatographic alumina was prepared by washing the commercial product with warm 10% hydrochloric acid, then large amounts of water, and finally methanol. The neutral material was reactivated and standardised by the method of Brockmann and Schodder.<sup>11</sup> The light petroleum used in chromatographic separations had b. p. 40—60°.

*Reactions of Chlorobenzene with Di-tert.-butyl Peroxide.*—A mixture of chlorobenzene (150 ml.) and the peroxide (15.0 g.) was refluxed, away from direct light, for 70 hr. The volatile products were separated by fractional distillation through a helix-packed column. The first fraction (4.1 g.), b. p. 56—60°, proved to be acetone (2 : 4-dinitrophenylhydrazone, m. p. 127°). The second fraction (4.8 g.), b. p. 78—82°, crystallised and was *tert.*-butyl alcohol. No unchanged *di-tert.*-butyl peroxide was recovered. After removal of these low-boiling fractions the solvent was distilled off under reduced pressure, leaving a black tar (4.6 g.) which was chromatographed on alumina (activity II). No crystalline products were obtained. Most of the fractions were oils with strong odours similar to those of the chlorodiphenyls, but there was also eluted an amorphous yellow powder which gave a weak positive test for halogen and slowly sintered when heated.

*Reaction of Naphthalene with Di-tert.-butyl Peroxide in Chlorobenzene.*—*Di-tert.*-butyl peroxide (20 g.) was added slowly to a boiling solution of naphthalene (16.0 g.) in chlorobenzene (250 ml.), and the mixture was refluxed for 70 hr. Separation of the low-boiling fractions by fractional distillation yielded acetone (5.6 g.) and *tert.*-butyl alcohol (5.7 g.). After removal of the solvent (vacuum) the tarry residue was steam-distilled, to give unchanged naphthalene (12.0 g. after crystallisation). The residue (6.4 g.) was chromatographed on alumina (250 g.; activity II) but again only intractable oils and tars, very similar in physical properties to those obtained in the previous experiment, were eluted.

*Reaction of Anthracene with Di-tert.-butyl Peroxide in Chlorobenzene.*—Equimolar quantities of anthracene (18.0 g.) and the peroxide (15.0 g.) were refluxed for 70 hr. in chlorobenzene (250 ml.), and the low-boiling products were removed by fractional distillation. Acetone (4.7 g.) and *tert.*-butyl alcohol (6.9 g.) were obtained. Distillation was continued until 160 ml. of solvent had been collected and the remaining solution was set aside at 0°. Anthracene (3.5 g.), m. p. and mixed m. p. 217°, was precipitated. The mother-liquors were evaporated under reduced pressure, leaving a dark brown oil (15.6 g.). This was refluxed thrice with 150 ml. portions of ethanol which dissolved most of the material, leaving 1.25 g. of colourless powder, m. p. 242°, which, after repeated crystallisation from chloroform was obtained as colourless prisms, m. p. 264° (Found: C, 92.4; H, 6.65%). Comparison of the ultraviolet and infrared spectra showed it to be 9 : 9' : 10 : 10'-tetrahydro-10 : 10'-dimethyl-9 : 9'-dianthryl. Sulphur dehydrogenation at 230° converted it into 9-methylanthracene (70%), m. p. and mixed m. p. 80°. Evaporation of the mother-liquors left 14.0 g. of brown oil which when refluxed with light petroleum (100 ml.) left 1.25 g. of a mixture of anthracene and anthraquinone. Chromatography of the petroleum solution on alumina (activity II) yielded anthracene, 9-methylanthracene, m. p. 79° (partly isolated as the picrate, m. p. and mixed m. p. 137°), anthraquinone, and the above tetrahydrodimethyldianthryl; total yields were: anthracene 7.25 g. (40%); 9 : 9' : 10 : 10'-tetrahydro-10 : 10'-dimethyl-9 : 9'-dianthryl, 1.37 g. (7%); anthraquinone, 0.66 g. (3%); 9-methylanthracene, 1.44 g. (7.5%).

*Reaction of Anthracene with Excess of Peroxide in Chlorobenzene.*—Anthracene and 2 molar proportions of *tert.*-butyl peroxide were refluxed in chlorobenzene under a stream of air for 70 hr. Apparently the low-boiling products were blown through the condenser as no acetone or *tert.*-butyl alcohol was obtained. Removal of the solvent left a dark red viscous oil which was divided into fractions by treatment with hot light petroleum. The petroleum-insoluble fraction, on chromatography, yielded anthraquinone (7%) and various red and yellow oils which, when oxidised with chromic acid in acetic acid solution, all yielded anthraquinone. The petroleum-soluble fraction gave unchanged anthracene (6%) and oils which could not be crystallised.

*Reaction of Anthracene with Di-tert.-butyl Peroxide.*—(a) *In o-dichlorobenzene.* Anthracene (9 g.), the peroxide (9 g.), and *o*-dichlorobenzene (100 ml.) were refluxed in an atmosphere of nitrogen. The reflux condenser was packed with glass helices and surrounded with a jacket of boiling benzene which allowed volatile products to be distilled off as they were formed. By this means the temperature of the reaction mixture was maintained at 155—165°. After 3 hr. the solvent was removed at 100° under reduced pressure, leaving a brown oil (17 g.) which was

<sup>11</sup> Brockman and Schodder, *Ber.*, 1941, **74**, 73.

divided into petroleum-soluble and -insoluble fractions and chromatographically separated in the usual way. The total yields of products were: anthracene, 0.8 g. (9%); 9-methylanthracene, 2.6 g. (27%); anthraquinone, 2.2 g. (21%).

(b) *Without solvent.* When anthracene (5 g.) and di-*tert.*-butyl peroxide (6 g.) were heated together without solvent under nitrogen in a bath of boiling toluene for 5 days, only unchanged anthracene (4.5 g.) was recovered.

*Reaction of 9-Methylanthracene with Di-tert.-butyl Peroxide.*—(a) *In chlorobenzene.* The hydrocarbon (13.6 g.), the peroxide (12.0 g.), and chlorobenzene (90 ml.) were refluxed under nitrogen for 70 hr. Low-boiling products and solvent (total 40 ml.) were distilled off through a fractionating column, and the remaining liquor was set aside overnight at 0°. After separation of the colourless crystalline precipitate (A) (0.84 g.) the solution was taken to dryness (vacuum) under nitrogen. The residue was extracted four times with boiling light petroleum (total 300 ml.) which removed 7.0 g. and left a red oil that was freely soluble in benzene. When cooled, the petroleum extract deposited a yellow amorphous precipitate (0.58 g.), and similar material (0.32 g.) was obtained by concentration of the benzene solution. After repeated crystallisation from toluene this material was identified as 1 : 2-di-9'-anthrylethane.

Product (A), after two recrystallisations from toluene, formed needles, m. p. 310° (Found: C, 93.8; H, 6.0. C<sub>20</sub>H<sub>22</sub> requires C, 94.2; H, 5.8%). Light absorption in CHCl<sub>3</sub> showed a weak maximum at 2725 Å (no absorption between 3000 and 4000 Å). After it had been heated in an evacuated tube at 310–312° until all the material had melted and then cooled, the substance was crystallised from toluene, forming yellow crystals (yield 92%) of 1 : 2-di-9'-anthrylethane (m. p. and mixed m. p. 310°). Substance (A) must therefore be a *polymer* of this hydrocarbon.

The material soluble in light petroleum was separated chromatographically and the successive fractions were further separated by repeated crystallisation from ethanol, methanol, and light petroleum and also by conversion into picrates. There were obtained in this way in all: 9-methylanthracene, 1.7 g. (12.5%) (picrate m. p. 137°); 1 : 2-di-9'-anthrylethane, 1.81 g. (13.5%); polymer of 1 : 2-di-9'-anthrylethane, 2.21 g. (16.5%); 9-ethyl-10-methylanthracene, 55 mg.; 9 : 10-dimethylanthracene, 0.80 g. (5.5%); 9-ethylanthracene, 20 mg.

(b) *Without solvent.* The hydrocarbon (9.8 g.) and the peroxide (11.0 g.) were heated, under reflux, in a bath of boiling toluene. After 5 days a small amount of the solvent was distilled off through a helix-packed column. The temperature of the distilling vapours rose immediately to 80° (b. p. of *tert.*-butyl alcohol), and no acetone was obtained. The mixture was then cooled and diluted with acetone, and its components were separated as described above. It gave: 9-methylanthracene, 4.5 g. (46%); 1 : 2-di-9'-anthrylethane and its polymer, 4.19 g. (42%).

(c) *In o-dichlorobenzene.* 9-Methylanthracene (10.5 g.) and the peroxide (12.0 g.) were refluxed in *o*-dichlorobenzene (90 ml.) under nitrogen. The volatile products were allowed to escape with the nitrogen stream through a fractionating column and by this means the temperature of the reacting mixture was maintained at 150–155°. After 48 hr. the solvent was removed in a vacuum and the residue was separated as described above into: 1 : 2-di-9'-anthrylethane, 0.75 g. (7%); its polymer, 0.95 g. (9%); 9 : 10-dimethylanthracene, 2.15 g. (20%); 9-ethyl-10-methylanthracene, 1.05 g. (9%); 9 : 10-diethylanthracene, 50 mg.; 1-9'-anthryl-2-(10-methyl-9-anthryl)ethane, 45 mg.

*Reaction of Pyrene and of Phenanthrene with Di-tert.-butyl Peroxide.*—When phenanthrene (10 g.) and the peroxide (13 g.) were refluxed in *o*-dichlorobenzene for 3 hr. in the apparatus which allowed the volatile products to escape and the mixture was worked up in the usual way the only pure substance isolated was unchanged phenanthrene (8.6 g.). When pyrene (10 g.) was similarly treated with the peroxide (9 g.), 8.1 g. of unchanged pyrene were recovered.

*Reference Materials.*—(i) 9-Ethylanthracene, prepared from anthrone and ethylmagnesium iodide, crystallised from ethanol in fluorescent plates, m. p. 58° (yield 87%); the dark red picrate had m. p. 120°. (ii) 9-Ethyl-10-methylanthracene, prepared from 10-methylanthrone in 92% yield, crystallised from ethanol in yellow needles, m. p. 144°; the picrate had m. p. 137°. (iii) 9 : 10-Diethylanthracene: a Grignard solution was prepared from ethyl iodide (9.8 g.) and magnesium (1.5 g.) in ether (50 ml.), cooled in ice, and treated, with vigorous stirring, with crystallised anthraquinone (3.0 g.). The stirred mixture was gradually warmed, then refluxed for 2 hr. and eventually decomposed with ammonium chloride solution. There was obtained a solid yellow mixture of crude isomeric forms of 9 : 10-diethyl-9 : 10-dihydro-9 : 10-dihydroxyanthracene. This mixture \* was warmed in acetic acid (30 ml.) with phenylhydrazine (6.0 g.). After the initial vigorous evolution of nitrogen the solution was refluxed for 30 min., cooled, and

\* We thank Dr. K. J. Clark for making available to us the following details.

poured into dilute hydrochloric acid. The precipitate was chromatographed in 1:1 light petroleum-benzene on alumina (150 g.; activity II). The first fraction eluted was 9:10-dimethylanthracene which crystallised from ethanol as pale yellow needles (2.6 g., 77%), m. p. 148° (black picrate, m. p. 130°).

9:9':10:10'-Tetrahydro-10:10'-dimethyl-9:9'-dianthryl. 10:10'-Dimethyl-9:9'-dianthryl (0.50 g.), prepared by the reduction of 10-methylanthrone with zinc dust and ammonia,<sup>12</sup> was gently refluxed in pentyl alcohol (30 ml.) while sodium (2.0 g.) was added in small pieces during 2 hr., then the solution was diluted with methanol, cooled, and poured into water. The precipitate was filtered off and washed with water and thrice with ether. Crystallisation from chloroform gave prisms (180 mg.) of trans-trans-9:9':10:10'-tetrahydro-10:10'-dimethyl-9:9'-dianthryl, m. p. 264° (Found: C, 93.0; H, 6.8. C<sub>30</sub>H<sub>28</sub> requires C, 93.2; H, 6.8%). Light absorption in CHCl<sub>3</sub>: max. at 2650 Å (ε 1750). The ether washings were evaporated to a crystalline mixture (130 mg.), possibly consisting of stereoisomers of the tetrahydro-compound.

1:2-Di-9'-anthrylethane. This was prepared by reduction of 10-methyleneanthrone with zinc and hydrochloric acid in acetic acid;<sup>12,1</sup> it crystallised from toluene as pale yellow needles, m. p. 310°. Light absorption in CHCl<sub>3</sub>: max. at 2550 (ε 22,500), 3400 (ε 439), 3560 (ε 1180), 3750 (ε 2400), and 3980 Å (ε 3050).

2-9'-Anthrylethyl toluene-*p*-sulphonate. To a solution of butyl-lithium [from *n*-butyl chloride (2.5 g.) and lithium (0.40 g.) in ether (50 ml.)] 9-bromoanthracene<sup>13</sup> (5.0 g.) was rapidly added and the solution was stirred at room temperature for 10 min., then treated during 10 min. at <0° with a cooled solution of ethylene oxide (3.0 g.) in ether (20 ml.). Stirring was continued for 30 min. with cooling and 15 min. at the b. p. Water was added, the ether layer was washed and dried, and the solvent was removed under reduced pressure. The residue (3.7 g.), dissolved in dry pyridine (15 ml.), was cooled to 0°. With continued cooling a solution of toluene-*p*-sulphonyl chloride (6.0 g.) in pyridine (10 ml.) was slowly added. After 24 hr. at room temperature the excess of the chloride was destroyed by water (2 ml.) and the mixture was then poured into iced water. The precipitated ester solidified and was washed with dilute acid and water and crystallised from ethanol as fluorescent plates (5.1 g., 69%), m. p. 122° (Found: C, 72.8; H, 5.6; S, 8.7. C<sub>23</sub>H<sub>20</sub>O<sub>3</sub>S requires C, 73.4; H, 5.35; S, 8.5%). Light absorption in EtOH: max. at 3340 (ε 2685), 3500 (ε 5390), 3660 (ε 8100), and 3880 Å (ε 7960).

2-9'-Anthrylethyl iodide. A solution of the foregoing ester (3.6 g.) and dry sodium iodide (3.0 g.) in acetone (30 ml.; freshly distilled from anhydrous copper sulphate) was refluxed for 18 hr., cooled, and poured into water. The oily precipitate was extracted with ether and was washed and dried. After removal of the solvent the residue was chromatographed on alumina (150 g.; activity III). Light petroleum eluted the iodide (3.0 g., 94%) which crystallised from light petroleum or methanol as pale yellow, fluorescent needles, m. p. 112° (Found: C, 57.85; H, 4.15; I, 37.8. C<sub>16</sub>H<sub>13</sub>I requires C, 57.85; H, 3.9; I, 38.2%). Light absorption in EtOH: max. at 2480 (ε 106,500), 2560 (ε 204,000), 3200 (ε 2030), 3350 (ε 4220), 3510 (ε 8750), 3700 (ε 13,500), and 3900 Å (ε 13,380).

1-9'-Anthryl-2-(10-methyl-9-anthryl)ethane. Reaction between the above-mentioned iodide (0.78 g.) in dry ether (20 ml.) with magnesium turnings (60 mg.) was initiated by methyl iodide and iodine and was completed by refluxing for 2 hr. A solution of 10-methylanthrone (0.5 g.) in ether (20 ml.) was added dropwise with stirring and the mixture was refluxed for 1 hr., then cooled and neutralised with dilute hydrochloric acid. The ether was washed and dried and the solvent was removed. The residue was chromatographed on alumina (50 g.; activity I). Light petroleum eluted unchanged iodide (0.41 g.) and 1:1 light petroleum-benzene eluted the required hydrocarbon (0.36 g.) which crystallised from acetone as pale yellow needles, m. p. 236° (Found: C, 93.6; H, 6.3. C<sub>31</sub>H<sub>24</sub> requires C, 93.9; H, 6.1%). Light absorption in CHCl<sub>3</sub>: max. at 2650 (ε 71,000), 3850 (ε 12,600), and 4050 Å (ε 13,100).

9-Iodomethyl-10-methylanthracene. Finely powdered anthraquinone (6.0 g.) was added rapidly to an ice-cold Grignard solution prepared from methyl iodide (18 g.) and magnesium (3.0 g.) in ether (80 ml.). Then the mixture was gently warmed and finally refluxed, with stirring, for 3 hr. The resultant yellow suspension of the magnesium salt of 9:10-dimethyl-9:10-dihydro-9:10-dihydroxyanthracene was converted into the iodomethyl compound by the method of Badger and Pearce.<sup>7</sup> The yield of unstable yellow needles was 7.4 g. (77%).

1:2-Di-(10-methyl-9-anthryl)ethane. Reaction between the above-mentioned iodomethyl compound (1.5 g.) and magnesium (0.12 g.) in benzene (15 ml.) and ether (25 ml.), initiated as above, was completed by refluxing, with stirring, for 30 min. Anhydrous cobalt chloride

<sup>12</sup> Barnett and Matthews, *Ber.*, 1926, 59, 767.

<sup>13</sup> Barnett and Cook, *J.*, 1924, 1084.

(0.6 g.) was added and the mixture was stirred and refluxed for a further hour. After cooling, dilute hydrochloric acid was added and the yellow crystalline precipitate was collected, washed with ether, and crystallised from benzene. 1:2-Di-(10-methyl-9-anthryl)ethane formed bright yellow needles (0.76 g., 82%), m. p. 272° (Found: C, 93.6; H, 6.4.  $C_{32}H_{28}$  requires C, 93.6; H, 6.4%). Light absorption in  $CHCl_3$ : max. at 2650 ( $\epsilon$  49,800), 3500 ( $\epsilon$  2500), 3600 ( $\epsilon$  3945), 3850 ( $\epsilon$  7000), and 4100 Å ( $\epsilon$  10,000).

*Reduction of 1:2-Di-(10-methyl-9-anthryl)ethane.* The hydrocarbon (0.50 g.) was refluxed in butan-1-ol (20 ml.) while sodium (1.0 g.) was added in small pieces. After 30 min. all the sodium and hydrocarbon had dissolved to give a colourless solution, which was cooled and diluted with methanol (20 ml.). The precipitate of the *dihydro-compound* crystallised from benzene-alcohol as cubes (0.43 g.), m. p. 304° (Found: C, 92.9, 39.0; H, 6.7, 6.5.  $C_{32}H_{28}$  requires C, 93.2; H, 6.8%). Light absorption in  $CHCl_3$ : max. at 2650 ( $\epsilon$  1960), 2750 ( $\epsilon$  2460), and 3100 Å ( $\epsilon$  317).

One of us (A. L. J. B.) thanks the Commonwealth Scientific and Industrial Research Organisation of Australia for an Overseas Studentship.

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[Received, September 19th, 1955.]

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