195. *The Reaction of Anthracene with Benzyl Radicals.*

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The thermal decomposition of di-*tert.*-butyl peroxide in toluene affords a convenient source of benzyl radicals. These react with anthracene at the *meso*-positions, giving 9 : 10-dibenzylanthracene (VII), 9 : 10-dibenzyl-9 : 10-dihydroanthracene (IV), 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (VI), and 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (II), all of which have been synthesised by independent routes.

Similar products have been isolated after reaction of benzyl chloride with the sodium and lithium adducts of anthracene.

Dehydrogenation of 9-benzyl- and 9 : 10-dibenzyl-9 : 10-dihydroanthracene by 2-cyano-2-propyl radicals, with mercaptoacetic acid as catalyst, has also been examined.

Cumyl radicals, produced from di-*tert.*-butyl peroxide in cumene, do not react with anthracene.

In a previous paper [1] we described the reactions of anthracene with the free radicals produced by thermal decomposition of di-*tert.*-butyl peroxide in chlorobenzene or *o*-dichlorobenzene. In these experiments the isolation of pure compounds was hindered by the presence in the crude reaction product of large amounts of resin, the formation of which was attributed to radical polymerisation initiated by the attack of methyl radicals upon the solvents. In order to study the behaviour of anthracene with a less reactive and more selective reagent we have now conducted the reaction with di-*tert.*-butyl peroxide in toluene and in cumene. In these solvents the resonance-stabilised benzyl and cumyl radicals are readily formed according to the following equations : [2]

$$\mathrm{Bu^tO{\cdot}OBu^t} \longrightarrow \mathrm{2Bu^tO{\cdot}} \tag{1}$$

$$\mathrm{Bu^tO{\cdot}} \longrightarrow \mathrm{COMe_2} + \mathrm{Me{\cdot}} \tag{2}$$

$$\mathrm{PhMe} + \mathrm{Bu^tO{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}} + \mathrm{Bu^tOH} \tag{3}$$

$$\mathrm{PhMe} + \mathrm{Me{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CH_2{\cdot}} + \mathrm{CH_4} \tag{4}$$

$$\mathrm{PhPr^i} + \mathrm{Bu^tO{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CMe_2{\cdot}} + \mathrm{Bu^tOH} \tag{5}$$

$$\mathrm{PhPr^i} + \mathrm{Me{\cdot}} \longrightarrow \mathrm{Ph{\cdot}CMe_2{\cdot}} + \mathrm{CH_4} \tag{6}$$

In cumene solution the cumyl radicals produced by reactions (5) and (6) dimerised to 2 : 3-dimethyl-2 : 3-diphenylbutane and the anthracene was not attacked. However, when the reaction was conducted in toluene solution with 1·7 moles of the peroxide per mole of anthracene all of the hydrocarbon was consumed and there were isolated 9 : 10-dibenzylanthracene (VII), 9 : 10-dibenzyl-9 : 10-dihydroanthracene (IV), 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (VI), and 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (II). Very little tar was formed in the reaction and the total yield of pure products was high.

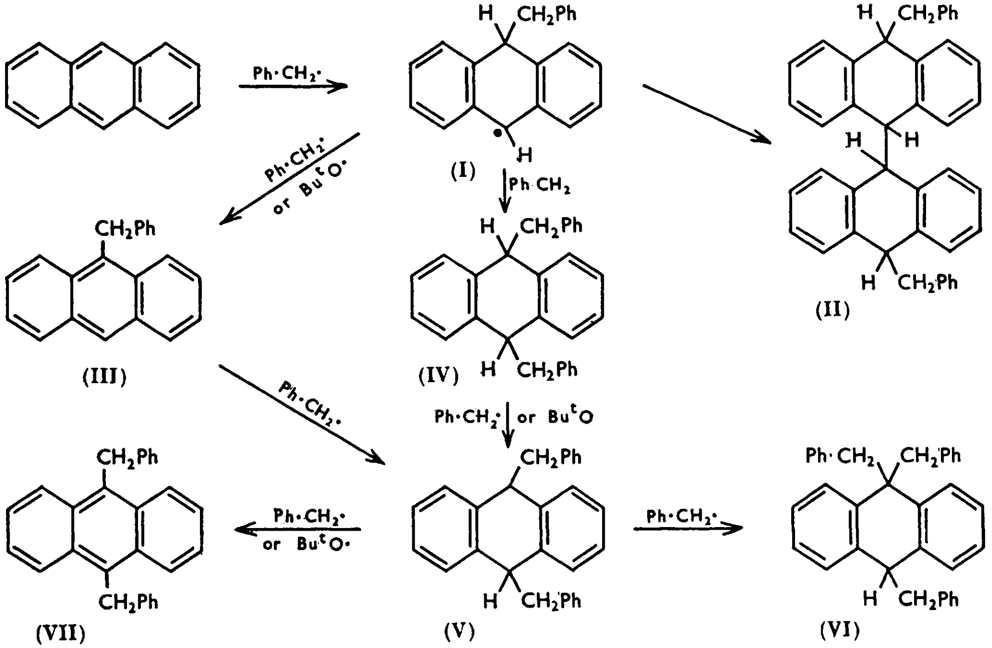
The routes by which the various products were probably formed are indicated in the annexed scheme. Possibly the most interesting feature of the reaction is the simultaneous production of derivatives of both anthracene and 9 : 10-dihydroanthracene. This result supports the view that free-radical addition and substitution of aromatic compounds both proceed by the same initial step, *i.e.*, addition of a radical to a reactive carbon atom in the aromatic molecule. The fate of the radical so formed depends upon the nature of the reagent. With reactive radicals such as methyl the abstraction of hydrogen leads to substitution [1] but with the relatively stable 2-cyano-2-propyl radical only the addition compound is produced.[3]

[1] Beckwith and Waters, *J.*, 1956, 1108.

[2] Raley, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 1336.

[3] Bickel and Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.

The isolation of 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (VI) is of interest as there is no previous account of a trisubstituted compound formed by reaction of anthracene with free radicals although intermediates of this form have been supposed to occur in the oxidation of anthracene by lead tetra-acetate.[4] The diagram shows two ways by which this product (VI) might be formed. Of these, that involving addition of benzyl radicals to 9-benzylanthracene is the more probable for it is known that compounds such as 9 : 10-dibenzyl-9 : 10-dihydroanthracene (IV) are unexpectedly resistant to the abstraction of hydrogen by free radicals.[5] The fact that 9-benzylanthracene could not be isolated does not preclude its participation by this mechanism for it is known that 9-substituted anthracenes are more reactive than the parent compound towards attack by free radicals.[6]



The experiments of Rust, Raley, and Vaughan (*J. Amer. Chem. Soc.*, 1948, **70**, 1336) with di-*tert.*-butyl peroxide in cumene indicate that dehydrogenation by methyl radicals is unlikely to occur under our conditions.

Unlike Bickel and Kooyman [3] who observed both *cis*- and *trans*-addition of 2-cyano-2-propyl radicals to anthracene, we were able to isolate only one form of 9 : 10-dibenzyl-9 : 10-dihydroanthracene.

The structures of all the free-radical products have been confirmed by comparison with specimens synthesised by unequivocal methods. Thus 9 : 10-dibenzyl-9 : 10-dihydroanthracene (IV) was readily obtained by reduction of 9 : 10-dibenzylanthracene with sodium and pentyl alcohol,[7] and 9 : 9 : 10-tribenzyl-9 : 10-dihydro-10-hydroxyanthracene was similarly converted into 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (VI).

In view of the ready production of 9-benzylanthracene by treatment of anthrone with benzylmagnesium chloride it was expected that a similar reaction with dianthron-9-yl would lead to 10 : 10′-dibenzyl-9 : 9′-dianthryl. However, in this case the normal reaction was accompanied by fission of the bond joining the two anthracene nuclei and the only product was 9-benzylanthracene. 10 : 10′-Dibenzyl-9 : 9′-dianthryl was eventually

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[4] Fieser and Putnam, *J. Amer. Chem. Soc.*, 1947, **69**, 1038.

[5] Kooyman and Strang, *Rec. Trav. chim.*, 1953, **72**, 342.

[6] Roitt and Waters, *J.*, 1952, 2695; Farenhorst and Kooyman, *Nature*, 1955, **175**, 598; Greenwood, *ibid.*, 1955, **176**, 1024.

[7] Bergmann and Fujise, *Annalen*, 1930, **480**, 188.

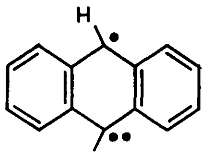
obtained by oxidation with ferric chloride of the Grignard reagent from 9-benzyl-10-bromoanthracene. The reduction of 10 : 10′-dibenzyl-9 : 9′-dianthryl with sodium in boiling pentyl alcohol resulted in fission of the molecule, and the only product was 9-benzyl-9 : 10-dihydroanthracene. When the reaction was repeated at a lower temperature in toluene solution the main product was 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (II) of m. p. 252° but there were also obtained small quantities of 9-benzyl-9 : 10-dihydroanthracene and a stereoisomer of (II) of m. p. 178°. The compound of m. p. 178° was converted into the high-melting form at 200° in a vacuum.

10 : 10′-Dibenzyl-9 : 9′-dianthryl was most easily obtained by a three-stage synthesis from anthrone. When this was treated with benzyl chloride and alcoholic alkali both 10 : 10-dibenzylanthrone and 9-benzyl-10-benzyloxyanthracene were produced. The latter compound was converted by dilute acid into 10-benzylanthrone which was reduced with zinc in hydrochloric acid to 10 : 10′-dibenzyl-9 : 9′-dianthryl.

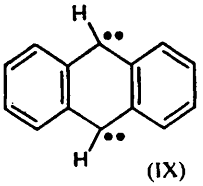
As an alternative approach to the synthesis of benzyl-substituted 9 : 10-dihydroanthracenes we have investigated the reactions of benzyl chloride with the sodium and lithium adducts of anthracene. The structures of these and similar complexes involving other aromatic hydrocarbons have recently been discussed by several groups of workers. Ubbelohde and his colleagues [8] have prepared solid sodium–anthracene complexes and have found them to contain between 1·1 and 2·1 metal atoms per molecule of hydrocarbon. This result accords with the work of Mikhailov and Chernova [9] who estimated the ratio of metal atoms to hydrocarbon molecules in the solid complexes of anthracene with sodium and lithium to be 2 : 1. An analysis of similar complexes in solution has shown that they contain one atom of metal per molecule of hydrocarbon and it has been postulated [10] that complex formation involves the transfer of one electron to the aromatic molecule which thus becomes a radical-ion (VIII). Such a structure is consistent with the results of the investigation of the polarographic half-wave potentials and reduction potentials [11] of aromatic compounds.

Magnetic-susceptibility measurements [12] provide an explanation for the lack of agreement between the analytical results, for it was found that the sodium–anthracene complex, as normally prepared, was paramagnetic, but that prolonged treatment of the adduct with an excess of sodium gave the diamagnetic, bivalent anion (IX).

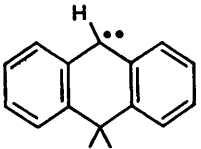
These conclusions are relevant to the interpretation of our results, for we found that the reaction between benzyl chloride and the sodium–anthracene adduct in ether gave anthracene, dibenzyl, 9 : 10-dihydroanthracene, 9-benzyl-9 : 10-dihydroanthracene (XI), and 9 : 10-dibenzyl-9 : 10-dihydroanthracene (IV), the formation of which products is consistent with the scheme proposed [10] for the reactions of radical-ions. However, we could not detect any dianthryl derivatives such as would be expected to result on a free-radical mechanism.



(VIII)



(IX)



(X)

The lithium–anthracene adduct was formed by treatment of 9 : 10-dihydroanthracene

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[8] Holmes-Walker and Ubbelohde, *J.*, 1954, 720; Gracey and Ubbelohde, *J.*, 1955, 4089.

[9] Mikhailov and Chernova, *Doklady Akad. Nauk S.S.S.R.*, 1950, **74**, 939 (*Chem. Abs.*, 1951, **45**, 4698).

[10] Paul, Lipkin, and Weissman, *J. Amer. Chem. Soc.*, 1956, **78**, 116.

[11] Hoijtink, Van Schooten, De Boer, and Aalsbersberg, *Rec. Trav. chim.*, 1954, **73**, 355; Hoijtink, De Boer, Van der Meij, and Wiejland, *ibid.*, 1955, **74**, 277.

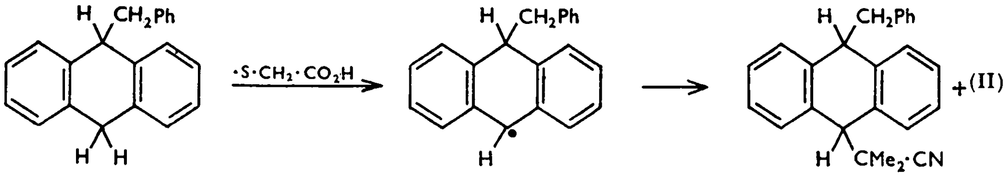
[12] Chu and Yu, *J. Amer. Chem.Soc.*, 1954, **76**, 3367.

with butyl-lithium,[13] a method which should lead to the anions (IX) and (X) rather than to the radical-ion (VIII). However, the nature of the products from the reaction of this adduct with benzyl chloride, which produced the same compounds as were obtained from the sodium adduct plus a small amount of 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (VI), indicates that this reaction must also proceed, to a certain extent, by a free-radical mechanism.

The identification of many of the above-mentioned derivatives of 9 : 10-dihydroanthracene was frequently complicated by the ease with which they were decomposed on attempted dehydrogenation. Thus 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (VI), when heated with sulphur, gave 9 : 10-dibenzylanthracene (VII), and 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (II) was converted into 9-benzylanthracene by treatment with chloranil in boiling phenetole. In an attempt to find a method of dehydrogenation that would proceed at temperatures well below that sufficient to cause homolysis of carbon–carbon bonds we have now investigated the reactions of 9-benzyl- and 9 : 10-dibenzyl-9 : 10-dihydroanthracene with the radicals formed by the decomposition of αα′-azo*iso*butyronitrile in benzene containing mercaptoacetic acid. This reagent was chosen because of the discovery by Bickel and Kooyman[14] that thiyl radicals, produced by the reaction between 2-cyano-2-propyl radicals and thiols, can dehydrogenate 9 : 10-dihydroanthracene although 2-cyano-2-propyl radicals alone are ineffective. Mercaptoacetic acid is a particularly convenient catalyst, for it can easily be removed from the reaction mixture by extraction with alkali.

$$\cdot CMe_2\cdot CN + HS\cdot CH_2\cdot CO_2H \longrightarrow \cdot S\cdot CH_2\cdot CO_2H + CHMe_2\cdot CN$$

(*a*)



(XI) (I) (XII)

$$(b)\quad (IV) \xrightarrow{\cdot S\cdot CH_2\cdot CO_2H} (V) \xrightarrow{\cdot S\cdot CH_2\cdot CO_2H} (VII)$$

When 9-benzyl-9 : 10-dihydroanthracene, αα′-azo*iso*butyronitrile, and mercaptoacetic acid were heated in benzene the products were 9-benzyl-10-(2-cyano-2-propyl)-9 : 10-dihydroanthracene (XII) and two stereoisomers of 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (II). The reaction which must involve the intermediate radical (I) evidently proceeds by the mechanism indicated. When 9 : 10-dibenzyl-9 : 10-dihydroanthracene was similarly treated with thiyl radicals, 9 : 10-dibenzylanthracene (VII) was produced. This result indicates that the intermediate radical (V) is sterically prevented from coupling with another radical and therefore is converted into the fully aromatic compound by loss of a second hydrogen atom.

EXPERIMENTAL

Reaction of Anthracene with Di-tert.-*butyl Peroxide in Cumene.*—(a) *At reflux temperature.* Anthracene (6·0 g.; purified by distillation with ethylene glycol)[15] and di-*tert.*-butyl peroxide (6 g.) were refluxed in purified cumene (100 ml.), under nitrogen, for 24 hr. The mixture was

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[13] Mikhailov and Blokhina, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1949, 279 (*Chem. Abs.*, 1950, **44**, 2963).

[14] Bickel and Kooyman, *Nature*, 1952, **170**, 211.

[15] Fieser, " Experiments in Organic Chemistry," D. C. Heath and Co., 1941, p. 345, footnote.

then fractionally distilled and there was obtained *tert.*-butyl alcohol, b. p. 78—81° (4·1 g.), but neither acetone nor unchanged peroxide. When the temperature of the vapours rose to 120° the remaining solution was cooled and kept overnight at 0°. Anthracene (2·5 g.) was collected and the filtrate was steam-distilled until all the solvent had been removed. The residual oil (9·5 g.), in light petroleum (b. p. 40—60°), was chromatographed on alumina. There were isolated 2 : 3-dimethyl-2 : 3-diphenylbutane (4·1 g.; eluted with light petroleum), m. p. and mixed m. p. 119°, anthracene (2·9 g.; eluted with 4 : 1 light petroleum–benzene), and oils (total 2·1 g.); total recoveries were *tert.*-butyl alcohol 60%, 2 : 3-dimethyl-2 : 3-diphenylbutane 36%, and anthracene 90%.

(*b*) *At* 100°. A solution of anthracene (5·0 g.) and di-*tert.*-butyl peroxide (6 g.) in cumene (50 ml.) was heated on the water-bath for 14 days and the product was then worked up as in (*a*), to give 2 : 3-dimethyl-2 : 3-diphenylbutane (1·2 g.) and anthracene (4·8 g., 96%).

*Reaction of Anthracene with Di-*tert.*-butyl Peroxide in Toluene.*—Anthracene (5·0 g.) and di-*tert.*-butyl peroxide (7 g., 1·7 equivs.) in purified toluene (150 ml.) were refluxed, under nitrogen, for 8 days. An attempt was then made to isolate low-boiling products by fractional distillation but the temperature of the vapour rose immediately to 110°. The solvent was removed under reduced pressure and the oily residue was extracted thrice with hot light petroleum (3 × 100 ml.). The insoluble material (1·8 g.) crystallised from benzene in needles, m. p. 252° (Found: C, 93·45; H, 6·4. $C_{42}H_{34}$ requires C, 93·6; H, 6·4%). When dehydrogenated with chloranil in phenetole it gave 9-benzylanthracene (yield 60%). Comparison with an authentic specimen (see below) identified this compound as 10 : 10′-*dibenzyl*-9 : 9′ : 10 : 10′-*tetrahydro*-9 : 9′-*dianthryl.*

The petroleum-soluble material (9·0 g.) was chromatographed on alumina. Light petroleum eluted dibenzyl (0·2 g.), m. p. 52°, and 6 : 1 light petroleum–benzene eluted an oil which was separated into three crystalline products: (i) Colourless needles (from methanol) of 9 : 10-dibenzyl-9 : 10-dihydroanthracene (2·1 g.), m. p. 119°. (ii) Colourless rods (1·9 g.) (from ethanol), m. p. 175° (Found: C, 92·9; H, 6·8. $C_{35}H_{30}$ requires C, 93·3; H, 6·7%). This compound showed ultraviolet light absorption similar to that of 9 : 10-dibenzyl-9 : 10-dihydroanthracene and was dehydrogenated with sulphur to 9 : 10-dibenzylanthracene; it was not isomerised by treatment with butyl-lithium or sodium hydride; comparison with the synthesised compound showed it to be 9 : 9 : 10-*tribenzyl*-9 : 10-*dihydroanthracene.* (iii) Pale yellow needles (from methyl acetate) of 9 : 10-dibenzylanthracene (0·5 g.), m. p. 248°.

Continued elution of the column yielded 9 : 10-dibenzylanthracene (0·4 g.) and 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl (0·4 g.).

The total yields of products were: dibenzyl, 0·2 g.; 9 : 10-dibenzylanthracene, 0·9 g. (9%); 9 : 10-dibenzyl-9 : 10-dihydroanthracene, 2·1 g. (21%); 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene, 1·9 g. (15%); 10 : 10′-dibenzyl-9 : 9′ : 10 : 10′-tetrahydro-9 : 9′-dianthryl, 2·2 g. (29%).

Preparation of Reference Compounds.—9-*Benzylanthracene.*[16] Anthrone (7·0 g.) in warm benzene (150 ml.) was added, with vigorous stirring, to a solution of benzylmagnesium chloride (from 10 g. of benzyl chloride in 100 ml. of ether), and the mixture was slowly distilled until all of the ether had been removed (1·5 hr.). The mixture was then treated with 20% hydrochloric acid, and the product was isolated in the usual way. 9-Benzylanthracene crystallised from acetone in pale yellow needles (8·6 g., 89%), m. p. 136°. Light absorption in ethanol: max. at 2575 (ε 127,000), 3325 (ε 3000), 3500 (ε 6100), 3650 (ε 8750), and 3850 Å (ε 8600).

9-*Benzyl*-9 : 10-*dihydroanthracene.*[17] 9-Benzylanthracene (3·3 g.) in toluene (30 ml.) and pentyl alcohol (50 ml.) was refluxed with sodium (4·5 g.) until all the metal had dissolved. The product crystallised from methanol in needles (2·6 g., 78%), m. p. 119° (Found: C, 93·0; H, 6·5. Calc. for $C_{21}H_{18}$: C, 93·3; H, 6·7%). Light absorption in ethanol: max. at 2227 (ε 8350), 2524 (ε 1275), 2669 (ε 1500), and 2720 Å (ε 1310).

9 : 10-Dibenzylanthracene, prepared by Barnett and Cook's method,[18] crystallised from benzene in pale yellow needles, m. p. 248°. Light absorption in $CHCl_3$: max. at 2660 (ε 84,000), 3450 (ε 3500), 3600 (ε 7600), 3800 (ε 13,100), and 4000 Å (ε 13,380). Attempts to prepare this compound from anthraquinone by the same method as for 9 : 10-diethylanthracene[1] gave, in one experiment, a yield of 15%.

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[16] Barnett, Cook, and Wiltshire, *J.*, 1927, 1724.
[17] Cook, *J.*, 1926, 2160.
[18] Barnett and Cook, *J.*, 1928, 566.

9 : 10-*Dibenzyl*-9 : 10-*dihydroanthracene*.[7] 9 : 10-Dibenzylanthracene (1·0 g.) was reduced with sodium in pentyl alcohol. The product crystallised from methanol in rods (0·85 g., 85%), m. p. 119° (Found : C, 92·8; H, 6·2. Calc. for $C_{28}H_{24}$: C, 93·3; H, 6·7%). Light absorption in EtOH : max. at 2265 (ε 9350), 2600 (ε 1210), 2655 (ε 1410), and 2720 Å (ε 1070).

The same compound was obtained when 9 : 10-dibenzylanthracene was reduced with sodium in liquid ammonia. It was not isomerised by treatment with sodium hydride or with sodamide. It was dehydrogenated by sulphur at 230° to 9 : 10-dibenzylanthracene.

Benzylation of anthrone. Anthrone (10 g.) and benzyl chloride (20 g.) in methanol (70 ml.) were refluxed under nitrogen while a solution of potassium hydroxide (9·5 g.) in methanol (50 ml.) was added dropwise with stirring. After the addition (30 min.) the mixture was refluxed for 15 min., cooled, and filtered. The residue of 10 : 10-dibenzylanthrone[19] crystallised from benzene in rhombs (12·2 g., 63%), m. p. 229° (Found : C, 90·05; H, 6·1. Calc. for $C_{28}H_{22}O$: C, 89·8; H, 5·9%). Light absorption in $CHCl_3$: max. at 2700 Å (ε 15,900). Reduction of this compound with aluminium amalgam in benzene–ethanol gave a 20% yield of 9 : 9-*dibenzyl*-9 : 10-*dihydro*-10-*hydroxyanthracene* which crystallised from ethanol in pale yellow plates, m. p. 172° (Found : C, 89·4; H, 6·75. $C_{28}H_{24}O$ requires C, 89·3; H, 6·4%). Light absorption in EtOH : max. at 2650 Å (ε 1770).

The filtrate was diluted with water and the precipitate was crystallised from ethanol. 9-*Benzyl*-10-*benzyloxyanthracene* (3·2 g., 16%) formed yellow rods, m. p. 137° (Found : C, 89·7; H, 5·7. $C_{28}H_{22}O$ requires C, 89·8; H, 5·9%). Light absorption in EtOH : max. at 2650 (ε 92,500), 3640 (ε 6800), 3820 (ε 10,600), and 4050 Å (ε 9550).

When the above experiment was conducted with molar equivalents of anthrone (7·0 g.), sodium ethoxide, and benzyl chloride in ethanol there were isolated 10 : 10-dibenzylanthrone (3·3 g., 19%) and 9-benzyl-10-benzyloxyanthracene (1·2 g., 7%).

10-*Benzylanthrone*.[20] 9-Benzyl-10-benzyloxyanthracene (2·5 g.) in acetic acid (30 ml.) was refluxed while concentrated hydrochloric acid (6 ml.) was added dropwise. After the addition (1 hr.) the mixture was refluxed for 1·5 hr., cooled, and poured into iced water. The oil, which solidified on scratching, was crystallised from ether–light petroleum. 10-Benzylanthrone (2·0 g., 85%) formed rods, m. p. 92° (Found : C, 88·35; H, 5·9. Calc. for $C_{21}H_{16}O$: C, 88·7; H, 5·7%). Light absorption in EtOH : max. at 2700 Å (ε 15,000).

9 : 9-Dibenzyl-9 : 10-dihydroanthracene,[7] prepared by the reduction of 10 : 10-dibenzylanthrone with sodium in pentyl alcohol, crystallised from methyl acetate in rods (yield, 82%), m. p. 184° (Found : C, 93·1; H, 6·9%). Light absorption in EtOH : max. at 2670 Å (ε 995).

9 : 9 : 10-Tribenzyl-9 : 10-dihydroanthracene was prepared by reduction of 9 : 9 : 10-tribenzyl-9 : 10-dihydro-10-hydroxyanthracene[18] (1·2 g.) with sodium in pentyl alcohol. It crystallised from acetone in rods (1·0 g., 83%), m. p. 175° (Found : C, 92·9; H, 6·8%). Light absorption in EtOH : max. at 2650 (ε 1450) and 2750 Å (ε 920).

Reaction of dianthron-9-yl with benzylmagnesium chloride. Powdered dianthron-9-yl[21] (1·0 g.) was added to benzylmagnesium chloride solution (prepared from 2·8 g. of benzyl chloride in 100 ml. of ether), and the mixture was refluxed, with stirring, under nitrogen for 2 hr. Benzene (100 ml.) was added and the mixture was slowly distilled until all of the ether had been removed (1·5 hr.). The excess of Grignard reagent was destroyed with dilute acid, and the benzene solution was evaporated to dryness. The products, which were separated chromatographically, were dibenzyl (0·4 g.) and 9-benzylanthracene (0·76 g., 55%).

10 : 10′-*Dibenzyl*-9 : 9′-*dianthryl.* (*a*) 9-Bromo-10-benzylanthracene[17] (5·0 g.), activated magnesium (0·5 g.), and ether (50 ml.) were mixed together under nitrogen. A drop of methyl iodide was added to start the reaction and the mixture was then refluxed, with stirring, for 16 hr. Anhydrous ferric chloride (2·5 g.) was then added and the heating was continued for a further 2 hr. After the addition of an excess of 20% hydrochloric acid, the precipitate was collected, washed with ether, then with methanol, and crystallised from benzene. 10 : 10′-*Dibenzyl*-9 : 9′-*dianthryl* (0·8 g., 21%) formed yellow prisms, m. p. >330° (Found : C, 94·0; H, 5·6. $C_{42}H_{30}$ requires C, 94·35; H, 5·65%). Light absorption in $CHCl_3$: max. at 2530 (ε 148,000), 3450 (ε 5650), 3625 (ε 12,050), 3825 (ε 24,000), and 4050 Å (ε 32,000).

(*b*) 10-Benzylanthrone (1·8 g.) in acetic acid (20 ml.) was refluxed while zinc powder (3 g.) and concentrated hydrochloric acid (4 ml.) were added in small portions. After the addition

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[19] Hallgarten, *Ber.*, 1888, **21**, 2508.

[20] Julian and Magnani, *J. Amer. Chem. Soc.*, 1934, **56**, 2174.

[21] Barnett and Matthews, *J.*, 1923, **123**, 380.

(1 hr.) the mixture was refluxed for 10 min. and then filtered while still hot. The residue, when crystallised from benzene, formed prisms (0·8 g., 47%) identical with the product obtained by method (*a*).

10 : 10'-*Dibenzyl*-9 : 9' : 10 : 10'-*tetrahydro*-9 : 9'-*dianthryl*. Sodium (2 g.) and pentyl alcohol (25 ml.) were added to a suspension of 10 : 10'-dibenzyl-9 : 9'-dianthryl (0·3 g.) in boiling toluene (30 ml.), and the mixture was refluxed until all of the metal had dissolved (2·5 hr.). During this time the dianthryl dissolved and the solution became colourless. After cooling, the mixture was washed with dilute hydrochloric acid, and the solvent was removed under reduced pressure. When the residue was crystallised from benzene–ethanol the tetrahydro-compound was obtained in colourless prisms (0·17 g., 55%), m. p. 252° (Found : C, 93·8; H, 6·2%). Light absorption in EtOH : max. at 2650 A (ε 1400).

Fractional crystallisation of the mother-liquor yielded 9-benzyl-9 : 10-dihydroanthracene (70 mg., 14%), m. p. 119°, and colourless needles (50 mg., 10%), m. p. 178°, of a *stereoisomer* of 10 : 10'-dibenzyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthryl (Found : C, 93·7; H, 6·4%). The latter showed maximum light absorption at 2650 Å (ε 2450). When heated in an evacuated tube at 200° for 5 min. it was converted into the isomer, m. p. 252°.

When 10 : 10'-dibenzyl-9 : 9'-dianthryl was reduced with sodium in boiling pentyl alcohol the only product was 9-benzyl-9 : 10-dihydroanthracene.

Reaction of the Sodium–Anthracene Adduct with Benzyl Chloride.—Anthracene (3·7 g.), sodium (2·0 g., in small pellets), and broken glass were shaken together in ether (50 ml.) under nitrogen. After 70 hr. the blue solution was filtered through glass wool, and benzyl chloride was added dropwise with stirring until the colour changed to yellow. After addition of water the mixture was filtered to remove anthracene (1·1 g.), and the ethereal solution was taken to dryness under reduced pressure. The residual oil was treated with hot light petroleum and, after removal of the insoluble anthracene (0·4 g.), chromatographed on alumina. The following products were obtained : dibenzyl, 1·9 g.; 9-benzyl-9 : 10-dihydroanthracene, 0·9 g. (16%); 9 : 10-dibenzyl-9 : 10-dihydroanthracene, 1·0 g. (13%); 9 : 10-dihydroanthracene, 0·5 g. (14%).

Reaction of the Lithium–Anthracene Adduct with Benzyl Chloride.—9 : 10-Dihydroanthracene [22] (2·0 g.) was added to a filtered solution of butyl-lithium (prepared from 0·7 g. of lithium and 3·9 g. of *n*-butyl chloride in 30 ml. of ether) and shaken at room temperature under nitrogen for 16 hr. Benzyl chloride was then added dropwise with stirring until the colour of the mixture changed to yellow. Water was added and the precipitate of anthracene (0·2 g.) was collected: The ethereal layer was evaporated to dryness and the residue, in light petroleum, was chromatographed on alumina. Light petroleum eluted successively dibenzyl (1·4 g.) and 9 : 10-dihydroanthracene (0·6 g., 30%). 3 : 1 Light petroleum–benzene eluted an oily mixture (1·7 g.) which was re-chromatographed. The fractions obtained were: (*a*) 9-benzyl-9 : 10-dihydroanthracene (0·2 g., 7%), eluted with light petroleum; (*b*) 9 : 10-dibenzyl-9 : 10-dihydroanthracene (0·8 g., 20%); (*c*) 9 : 9 : 10-tribenzyl-9 : 10-dihydroanthracene (0·2 g., 4%), m. p. and mixed m. p. 175°.

Reaction of 9-*Benzyl*-9 : 10-*dihydroanthracene with Mercaptoacetic Acid and* αα'-*Azo*iso*butyronitrile.*—9-Benzyl-9 : 10-dihydroanthracene (1·0 g.), mercaptoacetic acid (1·1 g.), and the azo-compound (0·9 g.) in dry benzene (20 ml.) were refluxed under nitrogen for 4 hr. The mixture was then cooled, extracted with aqueous sodium hydrogen carbonate, and washed with water. After removal of the solvent (vacuum) the crude product was treated with hot methanol. The insoluble material crystallised from benzene in needles, m. p. 252°, of the high-melting isomer of 10 : 10'-dibenzyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthryl (260 mg., 26%).

The methanol-soluble material was chromatographed on alumina. The compounds isolated were : (*a*) 9-benzyl-9 : 10-dihydroanthracene (0·32 g.), eluted with 3 : 1 light petroleum–benzene; (*b*) the stereoisomer, m. p. 178°, of 10 : 10'-dibenzyl-9 : 9' : 10 : 10'-tetrahydro-9 : 9'-dianthryl (40 mg., 4%), eluted with 1 : 1 light petroleum–benzene; (*c*) 9-*benzyl*-10-(2-*cyano*-2-*propyl*)-9 : 10-*dihydroanthracene* which crystallised from ether–light petroleum in colourless needles (180 mg., 14%), m. p. 134° (Found : C, 89·3; H, 7·0; N, 4·05. $C_{25}H_{23}N$ requires C, 89·0; H, 6·9; N, 4·15%). Light absorption in EtOH : max. at 2640 Å (ε 1300). The infrared spectrum showed absorption bands characteristic of the nitrile group.

Reaction of 9 : 10-*Dibenzyl*-9 : 10-*dihydroanthracene with Mercaptoacetic Acid and* αα'-*Azo*iso*butyronitrile.*—9 : 10-Dibenzyl-9 : 10-dihydroanthracene (340 mg.), mercaptoacetic acid (2 g.),

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[22] Bamberger and Lodter, *Ber.*, 1887, **20**, 3073.

and the azo-compound (0·8 g.) in benzene (30 ml.) were refluxed under nitrogen for 5 hr. The products, which were isolated as in the previous experiment, were 9 : 10-dibenzylanthracene (180 mg., 55%), m. p. 248°, and tetramethylsuccinonitrile (80 mg.), m. p. and mixed m. p. 167°.

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