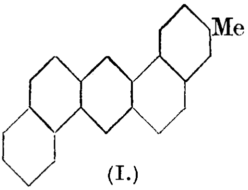
LXVI.—*Polycyclic Aromatic Hydrocarbons. Part III. Derivatives of* 1 : 2 : 5 : 6-*Dibenzanthracene.*

By James Wilfred Cook.

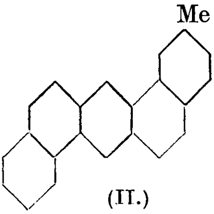
Hieger (*Biochem. J.*, 1930, **24**, 505) has shown that many cancer-producing mixtures, such as the products of the action of aluminium chloride on tetralin, show a characteristic banded fluorescence spectrum which is very similar to that of 1 : 2-benzanthracene except that the bands in the former lie nearer the visible region, and several hydrocarbons derived from benzanthracene were prepared (J., 1930, 1087) with the object of obtaining a pure compound which would reproduce the spectrum associated with cancer-producing mixtures. It was found that the introduction of alkyl groups into the benzanthracene molecule produced a shift of the spectrum in the desired direction, but in none of the cases examined was the shift sufficiently large. Hieger further showed that the more highly condensed 1 : 2 : 5 : 6-dibenzanthracene (compare preceding paper) gives a very similar spectrum which lies midway between those of 1 : 2-benzanthracene and of aluminium chloride-treated tetralin. It thus seemed possible that a compound having the desired spectrum would be found among the homologues of this dibenzanthracene and to this end several of its derivatives have been prepared, which are now described. The additional observation of Kennaway and Hieger (*Brit. Med. J.*, 1930, I, 1044) that 1 : 2 : 5 : 6-dibenzanthracene has carcinogenic properties has given further stimulus to the examination of its derivatives from the standpoint of constitutional influences on the carcinogenic activity.

Fieser and Dietz (*Ber.*, 1929, **62**, 1827) obtained 3′-methyl-1 : 2 : 5 : 6-dibenzanthracene (I) by pyrolysis of the monoketone obtained from 2 : 6-dimethylnaphthalene and β-naphthoyl chloride by the Friedel–Crafts reaction, and the same hydrocarbon has now been formed by isomerisation and dehydration of 2 : 6-*dimethyl*-1 : 1′-*dinaphthyl ketone* (from 2 : 6-dimethylnaphthalene and α-naphthoyl chloride). In an analogous way 2 : 7-dimethylnaphthalene has been condensed with α- and β-naphthoyl chlorides to yield 2 : 7-*dimethyl*-1 : 1′-*dinaphthyl ketone* and 2 : 7-*dimethyl*-1 : 2′-*di*-

naphthyl ketone respectively. Both ketones were converted by pyrolysis into 2′-*methyl*-1 : 2 : 5 : 6-*dibenzanthracene* (II):



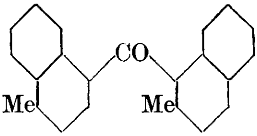
(I.)

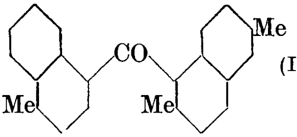


(II.)

2 : 4′-*Dimethyl*-1 : 1′-*dinaphthyl ketone* (III), from 2-methylnaphthalene and 4-methyl-1-naphthoyl chloride, lost one of its methyl groups when it was heated for a short time at 450°, since the product was 1 : 2 : 5 : 6-dibenzanthracene and not its 3-methyl derivative. Similar loss of a methyl group occurred in the ketones prepared from 2 : 6-dimethylnaphthalene and 4-methyl-1-naphthoyl chloride (IV), 2 : 7-dimethylnaphthalene and 4-methyl-1-naphthoyl chloride (V), and 1 : 6-dimethylnaphthalene and 2-methyl-1-naphthoyl chloride (VI):

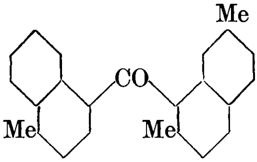
(III.)

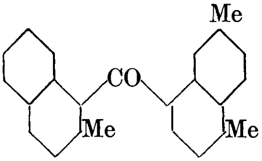




(IV.)

(V.)





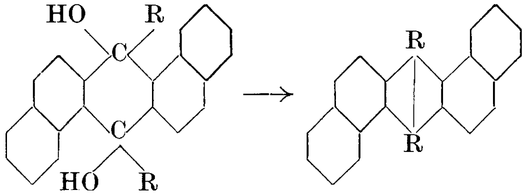
(VI.)

The methyl group which was eliminated was always the one which was in the α-position to a condensed ring (compare Part I, J., 1930, 1088); moreover, dehydration was in each case preceded by isomerisation to the corresponding trimethyl derivative of 1 : 2′-dinaphthyl ketone, since (IV) gave 3′-methyl-1 : 2 : 5 : 6-dibenzanthracene, and (V) and (VI) both yielded 2′-methyl-1 : 2 : 5 : 6-dibenzanthracene. The preparation of 3-alkyl derivatives of 1 : 2 : 5 : 6-dibenzanthracene by non-pyrogenic methods is being attempted.

The structures assigned to the aforementioned ketones have not been rigidly established, but a consideration of all the facts leaves little doubt as to their correctness. For instance, α-naphthoyl chloride must condense with 2 : 6-dimethylnaphthalene in position 1 or 3, since a methyl group *ortho* to carbonyl is required for the formation of the new ring; on general grounds, condensation at position 3 is unlikely. Furthermore, migration of methyl groups under the influence of aluminium chloride is rendered improbable by the fact that different products are formed when 2 : 7-dimethylnaphthalene is used. In the case of 1 : 6-dimethylnaphthalene, in which positions 4 and 5 might be reactive, it is apparent that condensation actually occurs in position 4, since no appreciable amounts of anthracene hydrocarbons were formed by the pyrolysis of the ketones resulting from the action of benzoyl chloride or α-naphthoyl chloride, whereas when 2-methyl-1-naphthoyl chloride was used the resulting ketone (VI) readily yielded such a hydrocarbon.

9 : 10-Dialkyl derivatives (VIII) of 1 : 2 : 5 : 6-dibenzanthracene were formed by reduction of the diols (VII) resulting from 1 : 2 : 5 : 6-dibenzanthraquinone by treatment with Grignard solutions and in two cases (R = Me and Bu^a) the experiment was performed both with the quinone obtained by oxidation of the hydrocarbon formed by pyrolysis of 2-methyl-1 : 2′-dinaphthyl ketone and also with the quinone obtained from the pyrolysis product of 2-methyl-1 : 1′-dinaphthyl ketone and erroneously described by Clar as 1 : 2 : 7 : 8-dibenzanthraquinone (preceding paper). The fact that both quinones yielded the same products is regarded as final proof of their identity.

(VII.)

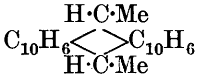


(VIII.)

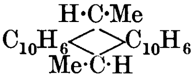
(R = Me, Bu^a, or CH_2Ph)

The fluorescence spectra of these hydrocarbons (VIII) are somewhat anomalous, but it may be stated that the spectrum of the benzyl compound (R = CH_2Ph) is almost indistinguishable from that of the cancer-producing mixtures to which reference has been made. When the diol (VII; R = Me) obtained with magnesium methyl iodide was reduced with hydriodic acid and phosphorus in boiling glacial acetic acid solution, it was converted into a mixture of two compounds which, from their composition and properties, appeared to be geometrically isomeric 9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracenes* (IX and X) :

(IX.)



$$C_{10}H_6\genfrac{}{}{0pt}{}{<\overset{\text{H·C·Me}}{}}{}\!\!\!\!\begin{matrix}\text{H·C·Me}\\ \diamond\\ \text{H·C·Me}\end{matrix}C_{10}H_6$$



$$C_{10}H_6\begin{matrix}\text{H·C·Me}\\ \diamond\\ \text{Me·C·H}\end{matrix}C_{10}H_6$$

(X.)

1 : 2 : 5 : 6-Dibenzanthracene is not reduced by hydriodic acid

under the same conditions, but is reduced to an *octahydro*-compound by sodium and boiling amyl alcohol.

The spectroscopic examination of these new hydrocarbons and their use in animal experiments will be reported elsewhere in due course.

EXPERIMENTAL.

Condensation of Methylnaphthalenes with Acid Chlorides.

The general conditions were as follows : A solution (or suspension) of the hydrocarbon (1 part) and the acid chloride (1 part) in carbon disulphide (3 parts) was cooled in ice and treated slowly, with agitation, with finely powdered anhydrous aluminium chloride (1 part). After being kept in ice for 3—6 hours with occasional shaking, the product was decomposed with ice and hydrochloric acid and the solvent and excess of hydrocarbon were removed with steam. The residue was again submitted to steam distillation in the presence of sodium hydroxide, and the residual ketone purified by recrystallisation.

2 : 6-*Dimethyl*-1 : 1′-*dinaphthyl Ketone* (from 2 : 6-dimethylnaphthalene and α-naphthoyl chloride).—The crude ketone was recrystallised from glacial acetic acid (yield, 50%), methyl ethyl ketone, and finally alcohol (Found : C, 88·7; H, 5·8. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%). This *ketone* formed a yellowish crystalline powder, m. p. 162—163°.

2 : 7-*Dimethyl*-1 : 1′-*dinaphthyl Ketone* (from 2 : 7-dimethylnaphthalene and α-naphthoyl chloride).—The crude ketone was twice recrystallised from acetic acid (yield, 70%), a sample for analysis being further recrystallised from toluene (Found : C, 88·8; H, 5·8. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%). This *ketone* formed tufts of colourless needles, m. p. 161—162°, depressed by admixture with the 2 : 6-dimethyl compound.

2 : 7-*Dimethyl*-1 : 2′-*dinaphthyl Ketone* (from 2 : 7-dimethylnaphthalene and β-naphthoyl chloride).—The crude product was recrystallised from acetic acid (yield, 40%), then from alcohol, and, for analysis, twice from *cyclo*hexane. Almost colourless needles were obtained, m. p. 113·5—114·5° (Found : C, 88·8; H, 5·7. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%).

4-*Benzoyl*-1 : 6-*dimethylnaphthalene*.—The crude product from 1 : 6-dimethylnaphthalene (15·6 g.), benzoyl chloride (14 g.), and anhydrous aluminium chloride (15 g.) in carbon disulphide (50 c.c.) was distilled in a vacuum, the chief fraction being collected at 220—230°/5 mm. It formed a viscous oil which solidified after several weeks (yield, 21 g.) and was then triturated with light petroleum and recrystallised from methyl alcohol. This *ketone* formed colourless rhombs, m. p. 77—78°, and was scarcely attacked when its suspension in alkaline potassium permanganate was boiled for 10 hours (Found : C, 87·4; H, 5·85. $C_{19}H_{16}O$ requires C, 87·7; H, 6·15%).

α-Naphthoyl chloride reacted readily with 1 : 6-dimethylnaphthalene under the usual conditions, but the resulting ketone could not be freed from resinous impurities.

2 : 4′-*Dimethyl*-1 : 1′-*dinaphthyl Ketone* (III; from 2-methylnaphthalene and 4-methyl-1-naphthoyl chloride).—The 2-methyl- and 4-methyl-naphthoyl chlorides used in this and subsequent experiments were obtained by the action of thionyl chloride on the corresponding acids, prepared from 2-methylnaphthalene and 1-methylnaphthalene respectively by the method of Mayer and Sieglitz (*Ber.*, 1922, **55**, 1839).

A solution of the crude *ketone* in glacial acetic acid deposited crystals after several days. These were recrystallised from acetic acid, methyl alcohol, and then from *cyclo*hexane and formed almost colourless needles, m. p. 120—121°. This figure was only obtained after drying in a vacuum desiccator over paraffin wax and phosphoric oxide. The yield was poor (Found : C, 88·7; H, 6·0. $C_{23}H_{18}O$ requires C, 89·0; H, 5·8%).

2 : 7 : 4′-*Trimethyl*-1 : 1′-*dinaphthyl Ketone* (V; from 2 : 7-dimethylnaphthalene and 4-methyl-1-naphthoyl chloride).—The crude product was recrystallised twice from acetic acid (yield, 45%) and then, for analysis, from alcohol and *cyclo*hexane. The pure *ketone* was an almost colourless, crystalline powder, m. p. 140° (Found : C, 88·9; H, 6·0. $C_{24}H_{20}O$ requires C, 88·9; H, 6·2%).

Pyrolysis of the Ketones.

The appropriate ketone was heated in a small Pyrex glass retort in a metal-bath at 440—450° until water was no longer liberated (about $\frac{3}{4}$—$1\frac{1}{2}$ hours); the residue was rapidly distilled over a free flame, the crystalline distillate being purified by recrystallisation.

1 : 2 : 5 : 6-*Dibenzanthracene*.—The crude distillate from 2 : 4′-dimethyl-1 : 1′-dinaphthyl ketone (III) was recrystallised twice from xylene and then from benzene. The resulting yellow leaflets were shown by the method of mixed melting points to consist of 1 : 2 : 5 : 6-dibenzanthracene, the methyl group in position 4′ being eliminated from the ketone. In order to show that this elimination was not due entirely to the high temperature required for distillation of the hydrocarbon, a little of the crude residue in the retort, obtained by heating the ketone at 450°, was sublimed at 230°/5—6 mm. 1 : 2 : 5 : 6-Dibenzanthracene was isolated from the sublimate; the elimination of methyl was, however, probably less complete, as the hydrocarbon was only obtained pure after repeated recrystallisation.

3′-*Methyl*-1 : 2 : 5 : 6-*dibenzanthracene* (I).—(i) The crude distillate from 2 : 6-dimethyl-1 : 1′-dinaphthyl ketone (11 g.) was recrystallised from xylene, the product (2·6 g.) dissolved in toluene (350 c.c.), and the cold solution shaken 5 or 6 times with concentrated sulphuric acid (portions of 10 c.c.).* This treatment removed most of the colour, and the purified hydrocarbon, obtained by concentration of the washed and dried solution, was recrystallised three times from benzene and then formed almost colourless leaflets, m. p. 245°, alone or mixed with the 3′-methyl-1 : 2 : 5 : 6-dibenzanthracene obtained by the method of Fieser and Dietz (*loc. cit.*) from 2 : 6-dimethyl-1 : 2′-dinaphthyl ketone (Found : C, 94·2; H, 5·4. Calc.: C, 94·5; H, 5·5%). The m. p. was depressed by admixture with 1 : 2 : 5 : 6-dibenzanthracene, or its 2′-methyl derivative.

(ii) The crude ketone from 2 : 6-dimethylnaphthalene and 4-methyl-1-naphthoyl chloride (IV) could not be obtained crystalline and was therefore pyrolysed in the usual manner. The product, after purification, was identified as 3′-methyl-1 : 2 : 5 : 6-dibenzanthracene.

2′-*Methyl*-1 : 2 : 5 : 6-*dibenzanthracene* (II).—(i) The crude distillate from 2 : 7-dimethyl-1 : 2′-dinaphthyl ketone (10 g.) was recrystallised from xylene, the deep yellow crystals (3·15 g.) shaken in toluene solution with sulphuric acid, and the purified hydrocarbon again recrystallised from xylene. 2′-*Methyl*-1 : 2 : 5 : 6-*dibenzanthracene* formed almost colourless nodules, m. p. 256—257·5°, depressed by admixture with 1 : 2 : 5 : 6-dibenzanthracene (Found : C, 94·1; H, 5·6. $C_{23}H_{16}$ requires C, 94·5; H, 5·5%).

(ii) The crude distillate from 2 : 7-dimethyl-1 : 1′-dinaphthyl ketone (10 g.) was recrystallised from benzene (yield, 2 g.), and the product further purified as described under (i). It was found to be identical with the above 2′-methyl-1 : 2 : 5 : 6-dibenzanthracene.

(iii) The crude ketone (VI) prepared from 1 : 6-dimethylnaphthalene and 2-methyl-1-naphthoyl chloride could not be obtained crystalline and was therefore submitted to pyrolysis. The distillate was purified as described under (i) and yielded 2′-methyl-1 : 2 : 5 : 6-dibenzanthracene.

(iv) 2 : 7 : 4′-Trimethyl-1 : 1′-dinaphthyl ketone (V) also yielded

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* 1 : 2 : 5 : 6-Dibenzanthracene is always contaminated with a yellow impurity which cannot be removed by recrystallisation or sublimation, but is removed by this treatment with sulphuric acid. The purified hydrocarbon forms colourless plates which have a violet luminescence in the ultra-violet light of a mercury vapour lamp (compare Clar, *Ber.*, 1929, **62**, 352). The yellow 1 : 2-benzanthracene of Barnett and Matthews (*Chem. News*, 1925, **130**, 339) was also rendered colourless by sulphuric acid treatment. The melting points were unaltered.

2′-methyl-1 : 2 : 5 : 6-dibenzanthracene by purification of the products of its pyrolysis.

Dialkyl Derivatives of 1 : 2 : 5 : 6-*Dibenzanthracene.*

9 : 10-*Dihydroxy*-9 : 10-*dimethyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracene* (VII; R = Me).—A Grignard solution was prepared from methyl iodide (10·5 c.c.) and magnesium turnings (4 g.), the ether removed on the water-bath, and the residue dissolved in dry benzene (50 c.c.). The resulting solution, cooled in ice, was treated slowly, with agitation, with a suspension of 1 : 2 : 5 : 6-dibenzanthraquinone (Clar, *Ber.*, 1929, **62**, 357) (10·5 g.) in benzene (50 c.c.). The whole was boiled for 3 hours, and the resulting gelatinous mass decomposed with ice and ammonium chloride. The solid in suspension (8·3 g.) was collected and dried, a further crop of crystals (1·9 g.) being obtained from the benzene liquor by concentration. The substance was recrystallised from xylene and from toluene as a colourless crystalline powder, m. p. 245—250° (Found: C, 84·9; H, 5·9. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%). This *diol* gave an intense cornflower-blue solution in concentrated sulphuric acid.

Reduction experiments. (i) Reduction with zinc dust and acetic acid yielded resinous substances from which no crystalline material could be isolated.

(ii) 9 : 10-*Dimethyl*-1 : 2 : 5 : 6-*dibenzanthracene* (VIII; R = Me). Hydriodic acid (*d* 1·9; 2 c.c.) was added to a boiling solution of the diol (2 g.) in glacial acetic acid (50 c.c.). After boiling for 5 minutes, the solution was rapidly cooled, and the crystals which separated were collected, washed, and recrystallised from xylene and then twice from benzene. This *hydrocarbon* formed yellowish needles, m. p. 205·5—206·5°, and gave an intense violet solution in concentrated sulphuric acid (Found: C, 94·0; H, 5·9. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%).

The same dimethyl compound was obtained when the above experiments were repeated with the quinone prepared by oxidation of the hydrocarbon formed by pyrolysis of 2-methyl-1 : 1′-dinaphthyl ketone (Clar, *loc. cit.*) and regarded by him as 1 : 2 : 7 : 8-dibenzanthraquinone (see preceding paper).

(iii) cis- *and* trans-9 : 10-*Dimethyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracenes* (IX and X). Red phosphorus (1·5 g.) and hydriodic acid (*d* 1·9; 5 c.c.) were added to a boiling solution of the diol (3 g.) from magnesium methyl iodide and 1 : 2 : 5 : 6-dibenzanthraquinone in glacial acetic acid (100 c.c.). The whole was boiled for 1½ hours and poured into water, and the precipitate collected and dried. The solid was extracted with benzene, and the filtered solution concentrated and treated with *cyclo*hexane. The crystals which separated were recrystallised from benzene and then fractionally crystallised from xylene. The less soluble fraction was recrystallised from ethyl acetate and formed a colourless crystalline powder, m. p. 277—278° (Found: C, 93·4; H, 6·6. $C_{24}H_{20}$ requires C, 93·5; H, 6·5%). This *dihydro*-compound (X) probably had the *trans*-configuration, since it was less soluble than its isomeride and had a higher m. p. (compare Barnett, Cook, and Matthews, *Rec. trav. chim.*, 1925, **44**, 728). Its solutions were non-fluorescent.

The xylene liquors, on standing, yielded a substance which, recrystallised twice from *cyclo*hexane, formed a colourless microcrystalline powder, m. p. 207—209°, the m. p. being depressed by admixture with 9 : 10-dimethyl-1 : 2 : 5 : 6-dibenzanthracene (Found: C, 93·4; H, 6·55. $C_{24}H_{20}$ requires C, 93·5; H, 6·5%). This *dihydro*-compound (IX), probably the *cis*-isomeride, gave solutions which had a feeble fluorescence in ultra-violet light.

Neither dihydro-compound gave a colour with concentrated sulphuric acid.

9 : 10-*Dihydroxy*-9 : 10-*di*-n-*butyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracene* (VII; R = Bu^a).—A Grignard solution was prepared from *n*-butyl bromide (24 g.) and magnesium turnings (3·5 g.), the ether removed, and the residue dissolved in dry benzene (50 c.c.). The resulting solution was treated gradually with a suspension of 1 : 2 : 5 : 6-dibenzanthraquinone (10·5 g.) in dry benzene (50 c.c.), kept at room temperature for an hour, and then boiled for 1½ hours. The product was decomposed with ice and ammonium chloride, the benzene layer separated (more benzene was necessary to give a clear solution) and washed, and the solvent removed under diminished pressure. The residue was treated with light petroleum and the crystalline product was collected, extracted several times with boiling alkaline sodium hydrosulphite to remove unchanged quinone, and then recrystallised twice from benzene. This *diol* formed colourless needles, m. p. 214—215° (yield, 5·9 g.), and gave an intense cornflower-blue solution in concentrated sulphuric acid (Found: C, 84·9; H, 7·5. $C_{30}H_{32}O_2$ requires C, 84·9; H, 7·55%).

In another preparation hydrochloric acid was used instead of ammonium chloride for decomposition of the magnesium compound. The product, after purification in the manner described, formed colourless needles, m. p. 225—226°, and depressed the m. p. of the above diol, m. p. 214—215°. The high figure obtained for hydrogen suggested that a third *n*-butyl group had entered the molecule, so the higher-melting substance is probably a *mono*-n-*butyl ether* of the diol (Found: C, 85·0; H, 8·3. $C_{34}H_{40}O_2$ requires C, 85·0; H, 8·3%). It was not further examined.

9 : 10-*Di*-n-*butyl*-1 : 2 : 5 : 6-*dibenzanthracene* (VIII; R = Bu^{a}).—A solution of the diol (3 g.) in glacial acetic acid (75 c.c.) was boiled for 2 hours with zinc filings (7·5 g.). The hot solution was decanted into a large volume of cold water and the precipitate was collected, dried in a vacuum desiccator, and recrystallised from alcohol. The product (1·1 g.) formed small yellowish crystals, m. p. 143·5—144·5°, and the m. p. was not changed by recrystallisation from benzene–light petroleum (Found: C, 92·7; H, 7·4. $C_{30}H_{30}$ requires C, 92·3; H, 7·7%). This *hydrocarbon* dissolved in warm concentrated sulphuric acid, yielding a purple solution with a dark red fluorescence.

The same di-*n*-butyl compound was obtained when the above experiments were repeated with the alleged 1 : 2 : 7 : 8-dibenzanthraquinone of Clar.

9 : 10-*Dihydroxy*-9 : 10-*dibenzyl*-9 : 10-*dihydro*-1 : 2 : 5 : 6-*dibenzanthracene* (VII; R = CH_2Ph).—A Grignard solution was prepared from benzyl chloride (23 c.c.), magnesium turnings (5 g.), and dry benzene (65 c.c.) in the same way as the methyl compound, cooled in ice, and slowly treated with a suspension of 1 : 2 : 5 : 6-dibenzanthraquinone (15·4 g.) in dry benzene (65 c.c.). After addition of the quinone, the suspension was boiled for 1½ hours, kept at room temperature over-night, and decomposed with ice and ammonium chloride. The filtered benzene solution was evaporated on the water-bath, and the residual oil treated with alcohol (100 c.c.). The resulting crystals were collected, extracted several times with boiling alkaline sodium hydrosulphite, and recrystallised from benzene (yield, 2·9 g.). For analysis, the *diol* was crystallised from ethyl acetate–alcohol, forming colourless needles, m. p. 249—251° (Found: C, 87·6; H, 5·6; *M*, cryoscopic in benzene, 472. $C_{36}H_{28}O_2$ requires C, 87·8; H, 5·7%; *M*, 492). The solution in concentrated sulphuric acid was orange-red.

9 : 10-*Dibenzyl*-1 : 2 : 5 : 6-*dibenzanthracene* (VIII; R = CH_2Ph).—A solution of the above diol (2 g.) in glacial acetic acid (50 c.c.) was boiled for 2 hours with zinc dust (5 g.). The solution was poured into water, and the precipitate collected and dried. The resinous product could not be obtained crystalline from any of the usual media, but was purified by addition of picric acid (2 g.) to its solution in acetone (20 c.c.). The red crystalline picrate was collected, washed, and decomposed with ammonium hydroxide, and the hydrocarbon recrystallised from benzene–light petroleum (Found: C, 94·1; H, 5·6. $C_{36}H_{26}$ requires C, 94·3; H, 5·7%). 9 : 10-*Dibenzyl*-1 : 2 : 5 : 6-*dibenzanthracene* formed almost colourless needles, m. p. 195—201° (decomp.).

Reduction of 1 : 2 : 5 : 6-*Dibenzanthracene.*

Sodium (2 g.) was added gradually to a boiling suspension of 1 : 2 : 5 : 6-dibenzanthracene (2 g.) in amyl alcohol (50 c.c.). The resulting clear solution was poured into water while hot, the amyl alcohol removed with steam, and the residual solid collected and dried. The crude product had m. p. 167—170° and this was only raised to the highest figure obtained by repeated recrystallisation from ethyl acetate. Analysis of three different samples gave figures indicating the formation of an octahydro-compound, although on theoretical grounds a decahydro-compound is more probable (Found: C, 92·2; H, 7·8. $C_{22}H_{22}$ requires C, 92·3; H, 7·7%). *Octahydro*-1 : 2 : 5 : 6-*dibenzanthracene* forms colourless plates, m. p. 188—190°. The same compound was formed by reduction of the hydrocarbon which Clar supposed was 1 : 2 : 7 : 8-dibenzanthracene (preceding paper).

The author wishes to record his indebtedness to Mr. F. Goulden for the preparation of the whole of the methylnaphthoyl chlorides and 1 : 2 : 5 : 6-dibenzanthracene used in this investigation.

Appendix on the High-boiling Constituents of Coal Tar.

Concurrently with the synthetic work described in this series of papers, an attempt is being made to isolate the carcinogenic constituent of coal tar. The tar used in these preliminary experiments was formed by carbonising coal in horizontal retorts, the fraction boiling above 400° was diluted with acetic acid, and the solid was filtered off and washed free from tar oils with acetic acid and alcohol. The resulting yellow crystals yielded almost pure chrysene after two recrystallisations from xylene. The solid obtained from the xylene liquors was submitted to a long series of fractional crystallisations, both alone and also in conjunction with picric acid. One of the fractions, m. p. 153—156°, appeared to consist chiefly of one substance; this substance was not pyrene. Its solutions had a very intense violet fluorescence and the fluorescence spectrum had bands which coincided with those in the spectrum of the complex carcinogenic mixture obtained from tetralin by the action of aluminium chloride (Kennaway and Hieger, *loc. cit.*). The properties of this fraction do not agree with those of any constituent of coal tar so far described. Oxidation with chromic acid yielded a mixture of quinones from which *o*-quinones, such as chrysenequinone, were completely removed by treatment with sodium bisulphite and alcohol. The residual quinones were extracted with boiling alkaline sodium hydrosulphite, and the quinones regenerated from the deep red filtered solution by atmospheric oxidation. No constituent of constant m. p. has yet been isolated from these quinones, which form orange-brown needles, and appear to be more highly condensed derivatives of anthraquinone. Further chemical examination is postponed pending the results of animal experiments with the hydrocarbons.

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