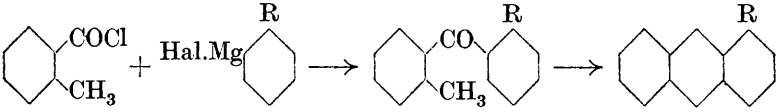
CXXXVII.—*Polycyclic Aromatic Hydrocarbons. Part I. 1- and 2-Phenylanthracenes and Derivatives of 1 : 2-Benzanthracene.*

By James Wilfred Cook.

The substance responsible for the cancer-producing properties of tars and mineral oils is probably a polycyclic aromatic hydrocarbon of very high boiling point, and the hydrocarbons to be described in this and subsequent communications have been prepared in the course of a search for an active carcinogenic substance of known structure. The correlated experiments on animals are being conducted by E. L. Kennaway and the fluorescence spectra of the pure hydrocarbons have been examined by I. Hieger for comparison with the characteristic banded spectrum of tars and other cancer-producing mixtures (for example, the products of the action of aluminium chloride upon 1 : 2 : 3 : 4-tetrahydronaphthalene). The results of Kennaway and Hieger are published elsewhere (*Biochem. J.*, in the press).

Of the three possible structural isomerides of monophenylanthracene only the *meso*-compound has hitherto been described. 1- and 2-*Phenylanthracenes* have now been prepared, the former by pyrolysis of 2-o-*toluoyldiphenyl* (I; R = Ph) obtained from magnesium 2-diphenylyl iodide and *o*-toluoyl chloride, and the latter by reduction of 2-phenyl-9-anthrone :

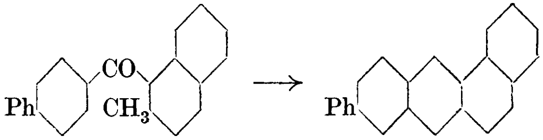


(I.) (R = Ph or Me)

1-Phenylanthracene resembles 1-methylanthracene in its ready solubility and fusibility, whereas 2-phenylanthracene, like the 2-methyl compound, is sparingly soluble and high-melting. When *di*-o-*tolyl ketone* (I; R = CH_3), prepared from magnesium *o*-tolyl bromide and *o*-toluoyl chloride, was boiled for a long time, it underwent the condensation of an *o*-methyl benzophenone derivative to an anthracene derivative discovered by Elbs (*Ber.*, 1884, **17**, 2848; 1886, **19**, 408; *J. pr. Chem.*, 1886, **33**, 185; 1887, **35**, 471; 1890, **41**, 1) and recently extended by Morgan and Coulson (J., 1929, 2203, 2551) and by Clar and his co-workers (*Ber.*, 1929, **62**, 351, 940, 951, 1574, 3021). The product was not 1-methylanthracene, however, but anthracene itself, one methyl group being eliminated from the ketone. This observation emphasises the need for confirmation of structures assigned to α-alkylanthracenes obtained by pyrogenic means. For instance, H. Meyer and Bernhauer (*Monatsh.*, 1929, **53** and **54**, 731) obtained an anthracene hydrocarbon, m. p. 199°, by distillation of benzyl-*o*-xylene, but were in error in regarding their product as 1-methylanthracene, which has been shown by several investigators to melt at 86° (*e.g.*, von Braun and Bayer, *Ber.*, 1926, **59**, 916). The formation of 1 : 3-dimethylanthracene by pyrolysis of benzylmesitylene (Louïse, *Ann. Chim.*, 1885, **6**, 185) shows that this loss of α-methyl groups is not universal. 2-Methylanthracene and its derivatives have frequently been obtained by pyrogenic methods (*e.g.*, *Eng. Pats.* 251,270; 253,911; Elbs, *loc. cit.*; Morgan and Coulson, *loc. cit.*), but no case of loss of a β-methyl group appears to have been recorded.

6-*Phenyl*-1 : 2-*benzanthracene* (III) was formed by pyrolysis of 1-p-*phenylbenzoyl*-2-*methylnaphthalene* (II), obtained from 2-methylnaphthalene and *p*-phenylbenzoyl chloride :

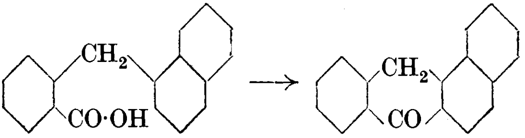
(II.)



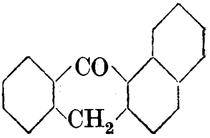
(III.)

Reduction of 3-methyl-1 : 2-benzanthraquinone (Scholl and Tritsch, *Monatsh.*, 1911, **32**, 997) with zinc dust and potassium hydroxide, although slow and incomplete, led to 3-*methyl*-1 : 2-*benzanthracene*. 1 : 2-Benzanthraquinone reacted normally with magnesium phenyl bromide to give 9 : 10-*diphenyl*-9 : 10-*dihydro*-1 : 2-*benzanthraquinol*, which was reduced by zinc dust in boiling acetic acid to 9 : 10-*diphenyl*-1 : 2-*benzanthracene*. Subsequent to this preparation these two compounds were described by Clar (*Ber.*, 1930, **63**, 118).

1 : 2-Benz-10-anthrone (IV), formed by dehydration of 1-naphthylphenylmethane-2′-carboxylic acid, was converted by benzoic anhydride in pyridine solution into 1 : 2-benzanthranyl 10-benzoate, m. p. 171°, whereas reduction of 1 : 2-benzanthraquinone with aluminium powder and concentrated sulphuric acid led to an anthrone (V), which gave the isomeric 1 : 2-benzanthranyl 9-benzoate, m. p. 202—203°. These two benzoates were obtained by Barnett and Matthews (*Chem. News*, 1925, **130**, 339) from the mixture of anthrones obtained by reduction of benzanthraquinone with tin and hydrochloric acid and the methods of preparation now given require transposition of the orientations suggested by these authors.



(IV.)

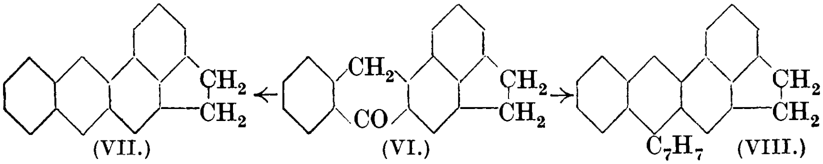


(V.)

1 : 2-Benz-10-anthrone reacted normally with magnesium benzyl chloride. The resulting 10-*hydroxy*-10-*benzyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene* was dehydrated to 10-*benzyl*-1 : 2-*benzanthracene*, and the same hydrocarbon was also formed in small yield when 1 : 2-benzanthracene was heated with benzyl chloride and zinc dust in carbon disulphide solution (compare Lippmann and Fritsch, *Monatsh.*, 1904, **25**, 793). Treatment of 1 : 2-benz-10-anthrone with magnesium methyl iodide yielded only resinous products, and the same remark applies to the action of magnesium benzyl chloride on 1 : 2-benz-9-anthrone.

With the object of obtaining intermediate compounds from which 9 : 10-dibenzyl-1 : 2-benzanthracene might be prepared by a method analogous to that previously used for dibenzylanthracene (Barnett and Cook, J., 1928, 567), 1 : 2-benz-9-anthrone and 1 : 2-benz-10-anthrone were heated with benzyl chloride and potassium hydroxide solution. Both anthrones yielded only resinous products. When 1 : 2-benzanthraquinone was heated with benzyl chloride and alkali in presence of sodium hydrosulphite, similar resinous products were formed, together with a small amount of a substance which had the composition and properties of a *benzyloxybenzanthracene.* Such a compound might conceivably be formed by monobenzylation and reduction of 1 : 2-benzanthraquinol. The anticipated benzylhydroxybenzanthrone was not isolated.

3-Acenaphthylphenylmethane-2′-carboxylic acid was completely sulphonated in 2 hours by concentrated sulphuric acid at room temperature, but was dehydrated by zinc chloride to acenaphthanthrone (VI), not obtained pure but characterised as the acetate of its enol. This anthrone was reduced by zinc dust and sodium hydroxide to *acenaphthanthracene* (VII) and was converted by magnesium benzyl chloride into an unstable dihydroanthranol which passed into *benzylacenaphthanthracene* (VIII) :



(VII.) (VI.) (VIII.)

An attempt to condense acenaphthylene with phthalic anhydride was unsuccessful, the acenaphthylene being polymerised by aluminium chloride to the polyacenaphthylene, m. p. 345—350°, described by Dziewoński and Leyko (*Ber.*, 1914, **47**, 1685).

Experiments are in progress which have as their object the preparation of derivatives of chrysene and other condensed 4-ring hydrocarbons together with more highly condensed compounds. It is probable that 3 : 4-benzphenanthrene has not yet been prepared, since the compound so described by Weitzenböck and Lieb (*Monatsh.*, 1912, **33**, 564) may equally well be 1 : 2-benzanthracene, which has more recently been shown to have the same m. p. as their hydrocarbon.

EXPERIMENTAL.

Phenylanthracenes.

o-*Iododiphenyl.*—This compound was mentioned by Bachmann and Clarke (*J. Amer. Chem. Soc.*, 1927, **49**, 2049), who gave no description of its preparation. It was readily obtained in 70% yield by the addition of a concentrated aqueous solution of potassium iodide to a diazotised solution of *o*-aminodiphenyl * in dilute sulphuric acid. The crude *iodo*-compound was twice distilled in a vacuum and then formed a colourless viscous oil, b. p. 140°/3—4 mm. (Found : C, 53·2; H, 3·5. $C_{12}H_9I$ requires C, 51·4; H, 3·2%). The high figure obtained for carbon was probably due to the presence of diphenyl, but the substance was sufficiently pure for the subsequent experiments.

2-o-*Toluoyldiphenyl* (I; R = Ph).—A Grignard solution prepared from *o*-iododiphenyl (20 g.), magnesium turnings (1·7 g.), and ether (45 c.c.) was added slowly, with agitation, to *o*-toluoyl chloride (10 c.c.) diluted with ether (30 c.c.) and cooled to −10°. After ¼ hour at − 10°, the solution was allowed to warm slowly and then boiled for an hour. The product was decomposed with ice and hydrochloric acid, and the crude ketone freed from unchanged acid chloride by passing steam into its alkaline suspension for ½ hour. It was then dried in ethereal solution with sodium sulphate and distilled in a vacuum. The chief fraction was collected at 190—192°/3—4 mm. The distillate, a yellowish syrup, was obtained in 55% yield as a colourless crystalline powder, m. p. 66—67°, by crystallisation from light petroleum (Found : C, 88·3; H, 5·95. $C_{20}H_{16}O$ requires C, 88·2; H, 5·9%). This *ketone* gave a yellow solution in concentrated sulphuric acid.

1-*Phenylanthracene*.—The aforesaid ketone (5 g.) was boiled gently for 7½ hours, and the product distilled. The red wax-like distillate was triturated with acetic acid and the solid in suspension was collected after 2 days and recrystallised from alcohol. The *product* (0·85 g.) was obtained pure by recrystallisation from ligroin and then twice from alcohol. It formed small, pale yellow prisms, m. p. 110—112°, readily soluble in the usual media (Found : C, 94·1; H, 5·6. $C_{20}H_{14}$ requires C, 94·5; H, 5·5%).

2-*Phenylanthracene*.—2-Phenyl-9-anthrone (5 g.) (Scholl and Neovius, *Ber.*, 1911, **44**, 1078) was reduced with zinc dust (15 g.) activated with copper, and 2*N*-sodium hydroxide solution (100 c.c.). The product, after extraction of the zinc with hydrochloric acid, was recrystallised from methyl ethyl ketone and then from ethyl acetate. 2-*Phenylanthracene* formed small, pale yellow leaflets, m. p. 207—207·5°, sparingly soluble in most media (Found : C, 94·2; H, 5·4%).

Di-o-*tolyl Ketone*.

A Grignard solution prepared from *o*-bromotoluene (36·5 g.), magnesium turnings (5·1 g.), and ether (100 c.c.) was added slowly, with agitation, to *o*-toluoyl chloride (30 c.c.) diluted with ether (100

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* The author is indebted to Professor G. T. Morgan, F.R.S., for a gift of the *o*-aminodiphenyl used in this experiment.

c.c.) at — 10°. After ½ hour the solution was allowed to warm and then boiled for an hour. The product was decomposed with ice and hydrochloric acid, and the crude *ketone* freed from unchanged *o*-toluoyl chloride and distilled (b. p. 307—308°). The solid distillate was recrystallised from methyl alcohol (yield, 25 g.) and then formed colourless needles, m. p. 64—67° (Found: C, 85·6; H, 6·5. $C_{15}H_{14}O$ requires C, 85·7; H, 6·7%).

Pyrolysis. Di-*o*-tolyl ketone (5 g.) was boiled gently for 24 hours, and the product distilled. The distillate was diluted with alcohol and the resulting crystals were collected and recrystallised from ethyl acetate, forming colourless plates, shown by the method of mixed melting points to consist of pure anthracene. After removal of the solvents from the mother-liquor, oxidation of the residue with chromic acid in glacial acetic acid yielded anthraquinone but no anthraquinonecarboxylic acid.

Derivatives of 1 : 2-*Benzanthracene.*

6-*Phenyl*-1 : 2-*benzanthracene.*—(i) Anhydrous aluminium chloride (11·5 g.) was slowly added to 9·4 g. of *p*-phenylbenzoyl chloride * (Scholl and Seer, *Annalen*, 1912, **394**, 148; Wieland and others, *ibid.*, 1927, **452**, 7) and 2-methylnaphthalene (6·5 g.) in carbon disulphide (50 c.c.). After 3 hours, the reaction was completed by ½ hours' heating on the water-bath. The product was decomposed with ice and hydrochloric acid, the carbon disulphide distilled off, and the steam-volatile by-products removed. The residue was dried and distilled in a vacuum (b. p. 265°/4—5 mm.). The distillate, an amber-coloured resin, was dissolved in hot ligroin, and the solution cooled. The resulting crystalline solid was obtained analytically pure by two recrystallisations from methyl alcohol. 1-p-*Phenylbenzoyl*-2-*methylnaphthalene* (II) formed colourless needles, m. p. 109—110° (Found: C, 89·4; H, 5·6. $C_{24}H_{18}O$ requires C, 89·4; H, 5·6%). The solution in sulphuric acid was cherry-red.

(ii) 1-*p*-Phenylbenzoyl-2-methylnaphthalene (4 g.) was boiled gently for ½ hour, and the dark-coloured residue distilled. The distillate was recrystallised from benzene (yield, 0·3 g.) and then from ethyl acetate. 6-*Phenyl*-1 : 2-*benzanthracene* (III) formed pale yellow leaflets, m. p. 240—241° (Found: C, 94·4; H, 5·3. $C_{24}H_{16}$ requires C, 94·7; H, 5·3%). This compound gave a crimson solution with a yellowish-green fluorescence in concentrated sulphuric acid. On gentle warming, the colour became purple and then

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* *p*-Phenylbenzoic acid was obtained in good yield by oxidation of 4-acetyldiphenyl (Adam, *Ann. Chim.*, 1888, **15**, 255) with boiling alkaline potassium permanganate.

intensely blue. This colour reaction is shown by 1 : 2-benzanthracene itself and also by all its hydrocarbon derivatives so far examined with the exception of the 9 : 10-diphenyl derivative.

3-*Methyl*-1 : 2-*benzanthracene*.—3-Methyl-1 : 2-benzanthraquinone (5 g.), mixed with zinc dust (15 g.), was heated on the water-bath with concentrated aqueous ammonia (50 c.c.) diluted with water (25 c.c.). After 3 hours, the initial blood-red colour had faded to pale yellow but was restored by the addition of 50% potassium hydroxide solution (25 c.c.). After boiling for 20 hours, the solution was treated with a further 5 g. of zinc dust and then boiled for 50 hours. Reduction was still incomplete, but the product was collected and zinc removed by hydrochloric acid and unchanged quinone by boiling alkaline sodium hydrosulphite solution. The residue was recrystallised from pyridine and alcohol, glacial acetic acid, and benzene–light petroleum. 3-*Methyl*-1 : 2-*benzanthracene* formed almost colourless plates, m. p. 153—154° (Found : C, 94·1; H, 5·8. $C_{19}H_{14}$ requires C, 94·2; H, 5·8%).

1 : 2-*Benz*-10-*anthrone* (IV).—Twenty g. of 1-naphthylphenylmethane-2′-carboxylic acid (Scholl, Seer, and Zinke, *Monatsh.*, 1920, **41**, 601) were intimately mixed with anhydrous zinc chloride (60 g.) and heated at 180° for 20 minutes. The molten mass was cooled and extracted with water and then with dilute sodium carbonate solution, the latter treatment removing a small amount of unchanged acid. Purification of the crude anthrone (16 g.) was not feasible on account of its instability. This method of preparation gave much better results than dehydration of the acid with concentrated sulphuric acid, which led to considerable oxidation and sulphonation.

1 : 2-*Benzanthranyl* 10-*benzoate* was formed when the anthrone was treated with benzoic anhydride and pyridine at 100°. It melted at 171—172°, in agreement with the figure given by Barnett and Matthews (*loc. cit.*) for the compound which they suggested was the 9-benzoate.

1 : 2-*Benzanthranyl* 10-*acetate* was obtained when the above anthrone (3 g.) was treated at 100° for an hour with acetic anhydride (5 c.c.) and pyridine (20 c.c.). It formed straw-coloured needles, from benzene and alcohol, which melted at 156° to a cloudy liquid, becoming clear at 163° (Found: C, 83·7; H, 4·85. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%).

10-*Hydroxy*-10-*benzyl*-9 : 10-*dihydro*-1 : 2-*benzanthracene*. — To a Grignard solution prepared from benzyl chloride (6 c.c.) and magnesium powder (1·5 g.), cooled in a freezing mixture, was added finely powdered 1 : 2-benz-10-anthrone (IV; 5 g.). After 2 hours, the product was allowed to warm to room temperature, kept overnight, and decomposed with ice and ammonium chloride. The washed ethereal solution was evaporated, and the residual oil mixed with 2 volumes of hot alcohol. The crystalline solid obtained by cooling was recrystallised from benzene–light petroleum (Found: C, 89·2; H, 5·9. $C_{25}H_{20}O$ requires C, 89·3; H, 5·95%). This *dihydroanthranol* formed a colourless crystalline powder, m. p. 153—153·5°. Treatment of its solution in boiling alcohol with a few drops of hydrochloric acid resulted in separation of a thick meal of crystals of 10-*benzyl*-1 : 2-*benzanthracene*, yellowish leaflets (from benzene), m. p. 195—196°, intensely fluorescent in solution (Found: C, 94·1; H, 5·6. $C_{25}H_{18}$ requires C, 94·3; H, 5·7%). The same compound was also obtained in small yield when 1 : 2-benzanthracene (6·4 g.), benzyl chloride (6·75 c.c.), and zinc dust (0·5 g.) were heated together in carbon disulphide (50 c.c.) for 16 hours. After removal of the solvent from the filtered solution a viscous oil remained. Its ethereal solution slowly deposited the 10-benzyl-1 : 2-benzanthracene.

1 : 2-*Benz*-9-*anthrone* (V).—This was obtained when aluminium powder (12·5 g.) was slowly added with occasional cooling to a solution of 1 : 2-benzanthraquinone (50 g.) in concentrated sulphuric acid (500 c.c.). After 3 hours, the orange-yellow solution was poured into ice and water, and the precipitate collected and dried in a vacuum desiccator. The resulting brown powder was recrystallised from chloroform, in which it was extremely easily soluble. It could not be obtained analytically pure on account of its instability, but was converted by benzoic anhydride in pyridine into the benzoate, m. p. 201—202°, described by Barnett and Matthews (*loc. cit.*). This benzoate, which depressed the m. p. of the 10-benzoate, is clearly 1 : 2-benzanthranyl 9-benzoate.

Benzylation of Benzanthraquinol.—A boiling suspension of 1 : 2-benzanthraquinone (5·2 g.) in 10% potassium hydroxide solution (100 c.c.) was treated with excess of sodium hydrosulphite and then with benzyl chloride (4·6 c.c.). After 2 hours' boiling, addition of more potassium hydroxide solution (20 c.c.) and benzyl chloride (1 c.c.) resulted in rapid fading of the red colour of the solution. Steam-volatile products were removed and the residual resin was dissolved in hot alcohol. The solution yielded, on cooling, a small amount of crystalline material, which was recrystallised from benzene and alcohol. The substance, probably 10-*benzyloxy*-1 : 2-*benzanthracene,* formed colourless needles, m. p. 178—179°. Its solutions in benzene and in sulphuric acid were fluorescent, and alcoholic alkali produced no " anthranol colour " (Found: C, 90·1; H, 5·6. $C_{25}H_{18}O$ requires C, 89·8; H, 5·4%).

Acenaphthanthrone (VI).—3-Acenaphthylphenylmethane-2′-carboxylic acid (12 g.), prepared by reduction of the corresponding ketoacid with zinc and sodium hydroxide (compare Lorriman, *J. Amer. Chem. Soc.*, 1925, **47**, 215), was dehydrated with zinc chloride (36 g.) in the manner described for the preparation of 1 : 2-benz-10-anthrone. The acenaphthanthrone, obtained in good yield, had little power of crystallisation and was characterised as the *acenaphthanthranyl acetate*, obtained with acetic anhydride and pyridine at 100° and recrystallised from xylene. This acetate formed straw-coloured needles, m. p. 229—230° (Found : C, 84·5; H, 5·15. $C_{22}H_{16}O_2$ requires C, 84·6; H, 5·1%).

Acenaphthanthracene (VII).—The aforesaid anthrone (from 12 g. of acid) was reduced by boiling for 16 hours with zinc dust (35 g.) and 2*N*-sodium hydroxide solution (200 c.c.). The product, after extraction of zinc with hydrochloric acid, was crystallised from acetic acid (yield, 4 g.) and obtained analytically pure by recrystallising it twice from xylene and twice from benzene. This *hydrocarbon* formed yellow plates, m. p. 192°, and gave the usual benzanthracene colour reaction with sulphuric acid (Found : C, 94·5; H, 5·5. $C_{20}H_{14}$ requires C, 94·5; H, 5·5%).

10-*Benzylacenaphthanthracene* (VIII).—Acenaphthanthrone (VI; 1 mol.) was treated with magnesium benzyl chloride (3 mols.) as described in the case of 1 : 2-benz-10-anthrone. The intermediate dihydroanthranol was unstable and partly dehydrated to the hydrocarbon even by boiling alcohol. Conversion was completed by crystallisation from glacial acetic acid and the product was finally recrystallised twice from ethyl acetate. 10-*Benzylacenaphthanthracene* formed pale yellow needles, m. p. 199—200° (Found : C, 93·9; H, 5·8. $C_{27}H_{20}$ requires C, 94·2; H, 5·8%).

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