

CCCXVIII.—*Synthesis of Anthracene Homologues.*  
*Part III. 2 : 3 : 6 : 7-Tetramethylantracene.*

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THE least volatile neutral fractions and distillates of low-temperature tar contain a complex mixture of anthracenoid hydrocarbons in which the following individuals have been identified either as such or as their quinones: anthracene,  $\beta$ -methylantracene, 2 : 6- and 2 : 7-dimethylantracenes, and 2 : 3 : 6-trimethylantracene. This mixture also contains a small proportion of a hydrocarbon which we have oxidised to the corresponding quinone, and the properties of these two substances suggest that the former may be a tetramethylantracene.

As the foregoing methyl derivatives of anthracene present in low-temperature tar contain their alkyl groups exclusively in  $\beta$ -positions, it became desirable to synthesise 2 : 3 : 6 : 7-tetramethylantracene and its quinone with the object of comparing them with the two corresponding substances derived from tar.

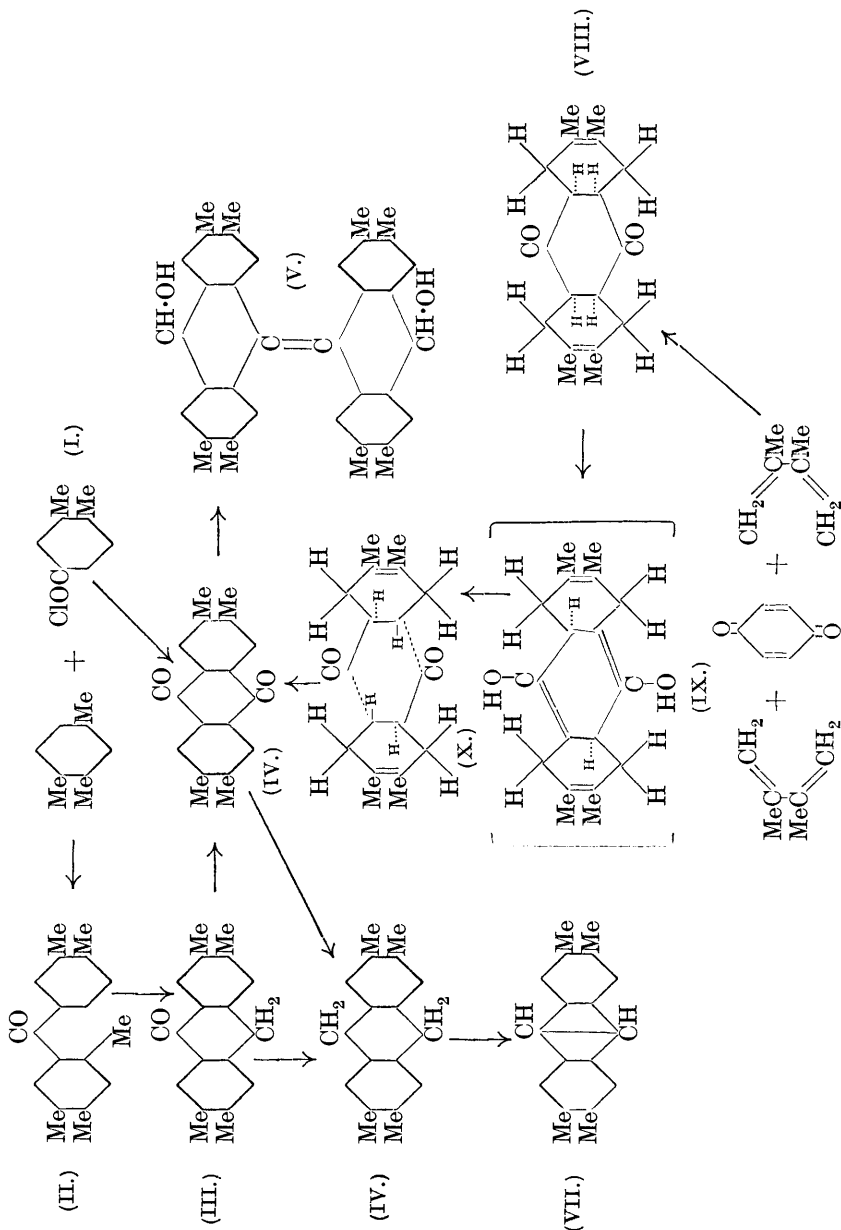
These syntheses have been accomplished by two distinct methods which taken together furnish a complete proof of the chemical constitutions of the hydrocarbon and its quinone.

I. *Pyrolysis of 2 : 4 : 5 : 3' : 4'-Pentamethylbenzophenone.*—In our earlier syntheses of methylated anthracenes (J., 1929, 2204, 2551) we employed Elbs's method of pyrolysing the appropriate *o*-methylbenzophenone, which in the present instance would be 2 : 4 : 5 : 3' : 4'-pentamethylbenzophenone (II), obtainable by condensing either 2 : 4 : 5-trimethylbenzoyl chloride with *o*-xylene or 3 : 4-dimethylbenzoyl chloride (I) with  $\psi$ -cumene: the latter alternative was adopted because of the difficulty of preparing a sufficient amount of trimethylbenzoic acid from  $\psi$ -cumidine. The use of 3 : 4-di-

methylbenzoyl chloride has the further advantage that by condensation under Friedel-Crafts conditions this chloride should itself furnish 2 : 3 : 6 : 7-tetramethylanthraquinone (IV). This anticipation has been realised, although the yield of quinone is only small.

On pyrolysis for short or long periods the appropriate ketone (II) furnishes a good yield of 2 : 3 : 6 : 7-tetramethyl-9-anthrone (III), although the corresponding hydrocarbon cannot be detected. This production of anthrone recalls our experience in the pyrolysis of 2 : 4 : 5 : 4'-tetramethylbenzophenone (*loc. cit.*) in which 2 : 3 : 6-trimethyl-9-anthrone was the initial product whereas 2 : 3 : 6-trimethylanthracene was found among the products of prolonged pyrolysis. These two examples are the only cases in which ring closure proceeds by dehydrogenation rather than by dehydration. It now appears likely in the former case that 2 : 3 : 6-trimethylanthracene is formed from its anthrone by the reducing action of nascent hydrogen generated in the initial reaction. In the present instance the greater resistance to reduction of 2 : 3 : 6 : 7-tetramethylanthrone probably accounts for the non-appearance of the hydrocarbon. 2 : 3 : 6 : 7-Tetramethylanthrone is readily oxidised to give a good yield of 2 : 3 : 6 : 7-tetramethylanthraquinone (IV) identical with the preceding preparation from 3 : 4-dimethylbenzoyl chloride. These modes of formation do not, however, determine indubitably the orientation of the four methyl groups in the foregoing tetramethylanthraquinone, although its melting point (330°) differentiates this quinone from the isomeric 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthraquinones melting respectively at 206° and 300° (Seer, *Monatsh.*, 1912, **33**, 33). There remain the alternative configurations 1 : 2 : 5 : 6-, 1 : 2 : 6 : 7-, 1 : 2 : 6 : 8-, and 1 : 3 : 6 : 7-, but these become excluded by the following supplementary synthesis.

II. *Condensation of p-Benzoquinone and 2 : 3-Dimethyl- $\Delta^{1:3}$ -butadiene.*—The condensation of *p*-benzoquinone with a diolefin, which was first noticed by Euler and Josephson (*Ber.*, 1920, **53**, 822), was applied subsequently by Diels and Alder to the synthesis of derivatives of anthraquinone (*Ber.*, 1929, **62**, 2337; compare E.P. 320,375). For our purpose *p*-benzoquinone was condensed with 2 : 3-dimethyl- $\Delta^{1:3}$ -butadiene to form 2 : 3 : 6 : 7-tetramethyl- $\Delta^{2:6}$ -octahydroanthraquinone (VIII), which readily undergoes isomeric change on fusion, crystallisation from comparatively high boiling solvents such as glacial acetic acid, or by addition to its boiling alcoholic solution of a few drops of alcoholic potash or hydrogen chloride. In this respect the new condensation product resembles its lower homologues prepared by the condensation of *p*-benzoquinone with butadiene and isoprene respectively. Since



the isomeride cannot be acetylated, it can scarcely be regarded as 2 : 3 : 6 : 7-tetramethyl- $\Delta^{2:6}$ -hexahydro-9 : 10-anthrahydroquinone (IX) but rather as the *stereoisomeride* (X), although possibly the intermediate hydroquinone may be a transient phase. This explanation, which has already been adopted by Diels and Alder (*loc. cit.*) in the case of the lower homologues, suggests an analogy with a type of isomerism found among derivatives of tetrahydrobenzene. 2 : 3 : 6 : 7-Tetramethylantraquinone (IV), prepared by a method which determines the position of its methyl groups, is obtained when 2 : 3 : 6 : 7-tetramethyl- $\Delta^{2:6}$ -octahydroantraquinone (VIII) is converted into its isomeride (X) by treatment with boiling alcoholic potash and oxygen is passed through the suspension. This quinone (IV), which is identical with the preparations obtained in the two syntheses from 3 : 4-dimethylbenzoyl chloride, is remarkably resistant to reducing agents; it is unaffected either by zinc dust and aqueous ammonia or by tin and zinc in acid solution. It is reduced by aluminium powder in cold concentrated sulphuric acid to a compound which has the same percentage composition as 2 : 3 : 6 : 7-tetramethylanthrone but is probably the more complex 2 : 3 : 6 : 7 : 2' : 3' : 6' : 7'-octamethyl-10 : 10'-dihydrodianthranol (V) arising by loss of water from two molecules of 2 : 3 : 6 : 7-tetramethyl-9 : 10-dihydroxy-9' : 10'-dihydroanthracene. With a large excess of sodium and boiling amyl alcohol, 2 : 3 : 6 : 7-tetramethylantraquinone is reduced slowly to 2 : 3 : 6 : 7-tetramethyl-9 : 10-dihydroanthracene (VI), a colourless hydrocarbon with an intense blue fluorescence. 2 : 3 : 6 : 7-Tetramethylanthracene (VII) is formed to a small extent when the dihydride is sublimed and dehydrogenation is completed by heating with selenium.

#### EXPERIMENTAL.

3 : 4-Dimethylbenzoyl Chloride (I).—Diphenylcarbonyl chloride (Houben, "Die Methoden . . .," 3rd Edition, Vol. 3, p. 11) (400 g.) was condensed with 350 g. of *o*-xylene by means of 280 g. of aluminium chloride (Lellmann and Bonhoffer, *Ber.*, 1887, **20**, 2119), and the pure 3 : 4-dimethylbenzodiphenylamide obtained (390 g.) was hydrolysed by boiling for 15 minutes with 500 c.c. of concentrated sulphuric acid and 300 c.c. of water. After cooling and dilution, the mixture of diphenylamine and 3 : 4-dimethylbenzoic acid was treated with warm dilute caustic soda solution; the filtered liquid, after being washed with ether, gave pure 3 : 4-dimethylbenzoic acid, m. p. 165—166°, in practically theoretical yield on acidification. The acid was heated for 4 hours under reflux with thionyl chloride (3 parts), the excess of the latter removed, and the residue fractionally distilled under reduced pressure; the *acid chloride*, b. p. 188°/

140 mm. and 185°/126 mm., was then obtained as a colourless liquid with an irritating odour closely resembling that of *p*-toluoyl chloride. The yield (86%) was less when the thionyl chloride was replaced by phosphorus pentachloride in chloroform (Found : Cl, 21.0.  $C_9H_9OCl$  requires Cl, 21.1%). 3:4-Dimethylbenzanilide crystallised from alcohol in colourless elongated plates, m. p. 108° (Found : C, 80.3; H, 6.4.  $C_{15}H_{15}ON$  requires C, 80.0; H, 6.6%).

*Condensation of 3:4-Dimethylbenzoyl Chloride to 2:3:6:7-Tetramethylantraquinone (IV).*—A mixture of the acid chloride (15.0 g.) and aluminium chloride (60 g.) was slowly heated, kept at 130—140° for 3 hours, and cooled. The product was decomposed with water, and the red gummy residue washed with dilute caustic soda solution and purified by crystallisation from acetic acid (with charcoal) and by sublimation. The final product, 2:3:6:7-tetramethylantraquinone (0.2 g.), formed yellow needles, m. p. 330°, identical with specimens prepared by the other synthetic methods.

2:4:5:3':4'-Pentamethylbenzophenone (II).— $\psi$ -Cumidine (48 g.), when diazotised and treated with potassium cuprocyanide, yielded a nitrile which on saponification furnished only 2.0 g. of 2:4:5-trimethylbenzoic acid.

A mixture of  $\psi$ -cumene (30 g.), 3:4-dimethylbenzoyl chloride (42 g.), and aluminium chloride (40 g.) in carbon disulphide was gently warmed and after 2 hours' boiling under reflux the product was decomposed with water. Distillation in steam removed carbon disulphide and the excess of  $\psi$ -cumene. The residual oily ketone was washed in ether with acid, alkali, and finally water, and dried; it solidified when recovered, and fractional distillation then gave 56.3 g., or 89% of the theoretical yield from  $\psi$ -cumene, of 2:4:5:3':4'-pentamethylbenzophenone, b. p. 189—190°/3 mm., m. p. 90°, which was very soluble in all solvents and crystallised from benzene in large colourless prisms (Found : C, 85.6; H, 8.05.  $C_{18}H_{20}O$  requires C, 85.7; H, 7.9%).

*Pyrolysis of 2:4:5:3':4'-Pentamethylbenzophenone: 2:3:6:7-Tetramethyl-9-anthrone (III).*—The ketone (30 g.) was boiled gently under reflux for 3 hours. "Cracking" occurred after about 2 hours, showing that water had been eliminated. On cooling, the residue became solid but no crystals having the characteristic appearance of an anthracene homologue were seen. Unchanged ketone was removed by washing the mixture repeatedly with warm ether and alcohol; from the residue (4 g.), m. p. 266°, after three crystallisations from acetic acid, 2:3:6:7-tetramethyl-9-anthrone was obtained in colourless non-fluorescent needles, m. p. 271—272° (Found : C, 86.6; H, 7.3.  $C_{18}H_{18}O$  requires C, 86.4; H, 7.2%). This compound was slightly soluble in ether or alcohol, soluble in

acetic acid, benzene, or chloroform. It dissolved to a bright yellow solution in warm concentrated alcoholic potash; in concentrated sulphuric acid, its solution was orange-red. It distilled unchanged from zinc dust, was unaffected by zinc dust and ammonia, and was not reduced by boiling with zinc its solution in acetic acid containing hydrochloric acid.

The unchanged ketone from the first pyrolysis was recovered from the ether-alcohol washings and boiled for 12 hours. Fluorescent anthracenoid crystals were then seen in the condenser, but when the product was worked up as before, a further 8.5 g. of crude anthrone were obtained from which no 2 : 3 : 6 : 7-tetramethylantracene could be isolated. The unchanged ketone was recovered again but was very dark-coloured and evidently impure, since it did not crystallise on cooling or after distillation, and was not further pyrolysed.

2 : 3 : 6 : 7-Tetramethyl-9-anthrone was boiled for 8 hours with excess of acetic anhydride and a few drops of pyridine. On cooling, crystals separated which were washed with water and recrystallised from acetic acid. The *substance*, m. p. 233—234°, formed pale cream-yellow rectangular plates which had a greenish fluorescence (also shown by solutions) and was homogeneous when examined microscopically. Analysis showed it to be a complex containing 1 mol. each of 2 : 3 : 6 : 7-tetramethylanthrone and 2 : 3 : 6 : 7-tetramethylanthranyl acetate (Found : C, 84.2; H, 7.1.  $C_{18}H_{18}O, C_{20}H_{20}O_2$  requires C, 84.1; H, 7.0%).

*Oxidation of 2 : 3 : 6 : 7-Tetramethyl-9-anthrone* : 2 : 3 : 6 : 7-Tetramethylantraquinone (IV).—The anthrone (0.3 g.) was dissolved in sufficient boiling acetic acid and oxidised with 0.22 g. of chromic anhydride dissolved in a little water. After 15 minutes' boiling, the green solution was diluted with water, practically pure 2 : 3 : 6 : 7-tetramethylantraquinone (0.3 g.), m. p. 327°, being precipitated; it was recrystallised from glacial acetic acid until the melting point was 330°.

2 : 3 : 6 : 7-Tetramethyl-9 : 10-dihydroanthracene (VI).—Sodium (1 g.) was slowly added to the anthrone (1 g.) suspended in boiling amyl alcohol. The deep red solution obtained gradually became decolorised, but recovered its red colour on exposure to air; sodium was therefore added to the boiling solution until decolorisation was practically complete. The reduction product, precipitated by addition of water, crystallised from acetic acid in large colourless rhombic plates displaying an intense purple fluorescence; m. p. 217—219°, unchanged by further recrystallisation. 2 : 3 : 6 : 7-Tetramethyl-9 : 10-dihydroanthracene was slightly soluble in alcohol, but more so in acetic acid or benzene, it sublimed readily at its m. p. (Found : C, 91.3; H, 8.6.  $C_{18}H_{20}$  requires C, 91.5; H, 8.5%). The

fluorescence shown by the solid dihydride or its solutions was due to a slight trace of some derivative containing unreduced *meso*-ring—in this case 2 : 3 : 6 : 7-tetramethylantracene.

*Condensation of p-Benzoquinone and 2 : 3-Dimethyl- $\Delta^{1:3}$ -butadiene : 2 : 3 : 6 : 7-Tetramethyl- $\Delta^{2:6}$ -octahydroanthraquinone (VIII).—*2 : 3-Dimethylbutadiene (55 g.; 2 mols.), prepared as described by Kyriakides (*J. Amer. Chem. Soc.*, 1914, **36**, 987), and 35 g. of *p*-benzoquinone (1 mol.) were mixed, moistened with alcohol, and heated in a sealed tube at 97° during 5 hours. After cooling, the solid was washed with warm alcohol to remove unchanged reagents, 50 g. of product being obtained, m. p. 202—203° after crystallisation from alcohol. 2 : 3 : 6 : 7-Tetramethyl- $\Delta^{2:6}$ -octahydroanthraquinone formed large, colourless, elongated, rhombic prisms, soluble in acetic acid, less soluble in alcohol (Found : C, 79.3; H, 8.6.  $C_{18}H_{24}O_2$  requires C, 79.4; H, 8.8%). If maintained at its melting point, the material solidifies and melts finally at 304°. Recrystallisation from acetic acid causes the m. p. to be first lowered to 180° and then to rise slowly to 304°, an indication of isomerisation.

When 1 mol. each of dimethylbutadiene and benzoquinone were condensed under the same conditions as above, the same condensation product resulted in smaller yield, but not the 6 : 7-dimethyl-tetrahydro-1 : 4-naphthaquinone which might have been expected.

*Isomerisation of 2 : 3 : 6 : 7-Tetramethyl- $\Delta^{2:6}$ -octahydroanthraquinone (see formulæ IX and X).—*When to a solution of the condensation product, m. p. 200—201°, in sufficient boiling alcohol a few drops of either concentrated hydrochloric acid or 50% caustic potash solution were added, a thick white precipitate separated at once. After 15 minutes' boiling, a quantitative yield of the sparingly soluble *isomeride* of 2 : 3 : 6 : 7-tetramethyl- $\Delta^{2:6}$ -octahydroanthraquinone was obtained; it crystallised from boiling acetic acid in small colourless rhombs, m. p. 307° (Found : C, 79.3; H, 8.6.  $C_{18}H_{24}O_2$  requires C, 79.4; H, 8.8%). When boiled with acetic anhydride and a drop of concentrated sulphuric acid, or with acetic anhydride and pyridine for 16 hours, the substance was unaffected.

2 : 3 : 6 : 7-Tetramethylantracenequinone (IV).—When alcoholic potash (100 c.c.; 5 g. KOH) was added to 10 g. of the condensation product (VIII) in boiling alcohol, the *isomeride* was precipitated in minute crystals. Oxygen was passed during 8 hours through the suspension, boiling under reflux; the colourless crystals slowly dissolved to a deep red solution and yellow crystals began to separate until finally the solution was almost decolorised. 2 : 3 : 6 : 7-Tetramethylantracenequinone, obtained in quantitative yield, crystallised from acetic acid, in which it was only sparingly soluble, in yellow needles or plates, m. p. 330°, which readily sublimed at this temperature (Found : C,

81.6; H, 6.1.  $C_{18}H_{16}O_2$  requires C, 81.8; H, 6.1%). The quinone dissolved in concentrated sulphuric acid to a deep red solution.

*Action of reducing agents on 2 : 3 : 6 : 7-tetramethylantraquinone.* When boiled with zinc dust and concentrated aqueous ammonia, or with amalgamated zinc in concentrated hydrochloric acid, the quinone was quite unaffected. It sublimed unchanged when mixtures with either zinc dust or calcium hydride were heated. When a solution in acetic acid was boiled for 8 hours with zinc and hydrochloric acid, a green deposit of a quinhydrone was formed which dissolved in aqueous potassium hydroxide to a deep red solution of the corresponding anthrahydroquinone. This solution on exposure to air rapidly became colourless with deposition of the anthraquinone.

*2 : 3 : 6 : 7 : 2' : 3' : 6' : 7' - Octamethyl - 10 : 10' - dihydrodianthranol (V).*—Aluminium powder (0.6 g.) was slowly added to 2 g. of 2 : 3 : 6 : 7-tetramethylantraquinone dissolved in 72 c.c. of concentrated sulphuric acid, the temperature being kept just below 40°. When the initial red coloration had almost faded, the mixture was poured on ice, the deposit dissolved in hot benzene to free it from aluminium compounds, and the benzene extract evaporated until the product crystallised in pale yellow octahedra and greenish-yellow flat needles or plates. The former, which predominated, were the less soluble and were obtained pure by recrystallisation from acetic acid. They had m. p. 319° (yield, 0.5 g.). The latter could not be obtained pure owing to a greater solubility in all solvents tried. The *octamethyldihydrodianthranol* was sparingly soluble in acetic acid, benzene, and other solvents; it dissolved slowly in boiling alcoholic potash or in cold concentrated sulphuric acid to yellow solutions (Found: C, 85.9; H, 6.8.  $C_{36}H_{36}O_2$  requires C, 86.4; H, 7.2%). The molecular weight by Rast's method in fused camphor could not be determined owing to the sparing solubility of the product, but its higher melting point and lower solubility differentiated it completely from 2 : 3 : 6 : 7-tetramethylanthrone, even although both substances have the same chemical composition.

*2 : 3 : 6 : 7-Tetramethyl-9 : 10-dihydroanthracene (VI).*—By adding sodium as fast as it dissolved to a solution of 1 g. of 2 : 3 : 6 : 7-tetramethylantraquinone in 200 c.c. of boiling amyl alcohol during 8 hours, the first-formed deep red solution of the sodium derivative of 2 : 3 : 6 : 7-tetramethylantrahydroquinone was finally reduced to a pale amber-coloured solution which did not become coloured when diluted with water or when shaken with air. The product precipitated by water was crystallised from glacial acetic acid; it had m. p. 217—219° and was identical in all respects with 2 : 3 : 6 : 7-tetramethyl-9 : 10-dihydroanthracene prepared from 2 : 3 : 6 : 7-tetramethyl-9-anthrone (yield, 0.5 g.).



*Dehydrogenation of 2:3:6:7-Tetramethyl-9:10-dihydroanthracene: 2:3:6:7-Tetramethylanthracene* (VII).—The dihydride became partly converted into the anthracene when heated to 250°, for the sublimate yielded a small amount of 2:3:6:7-tetramethylanthracene, m. p. 301° after several crystallisations from glacial acetic acid and carbon disulphide. The best method of preparing the aromatic hydrocarbon is by the use of selenium: 2.5 g. of the dihydride were ground with 10 g. of selenium and heated to about 250° in a Hedley sublimator. The first sublimate, colourless with a purple fluorescence, was reheated later with more selenium. Hydrogen selenide was evolved and a sublimate consisting mainly of 2:3:6:7-tetramethylanthracene, yellow with green fluorescence, then appeared, but the greater part of the dehydrogenated product remained in the molten selenium and was obtained, after cooling, by extraction with boiling acetic acid. The crude hydrocarbon, which crystallised from the extract, contained a yellow impurity, insoluble in carbon disulphide, which was removed by extraction with the boiling solvent. The hydrocarbon (1.3 g.) crystallised on cooling in pale yellow, lustrous, thin, crumpled, rhombic plates, m. p. 301° (Found: C, 91.6; H, 7.7. C<sub>18</sub>H<sub>18</sub> requires C, 92.3; H, 7.7%). The hydrocarbon, which was very similar to 2:3:6-trimethylanthracene, sublimed readily when heated to its melting point; it was sparingly soluble in alcohol, more soluble in benzene or glacial acetic acid, and dissolved readily in carbon disulphide.

When added to picric acid in warm dry benzene, the hydrocarbon dissolved easily to a reddish-purple solution, but on cooling, the colour faded somewhat and pure 2:3:6:7-tetramethylanthracene separated. When alcohol was added to the reddish-purple solution, the liquid assumed the yellow tint due to picric acid. There is thus some evidence of the formation of an unstable picrate.

#### *Summary.*

1. 2:3:6:7-Tetramethylanthracene (m. p. 308° corr.) and 2:3:6:7-tetramethylanthraquinone (m. p. 338° corr.) have been synthesised by methods which establish definitely the orientation of the four methyl groups.

2. The heavy neutral oils of low-temperature tar from the carbonisation of bituminous coal contain a complex mixture of anthracenoid hydrocarbons, including 2:3:6:7-tetramethylanthracene, from which 2:3:6:7-tetramethylanthraquinone has been obtained by oxidation.