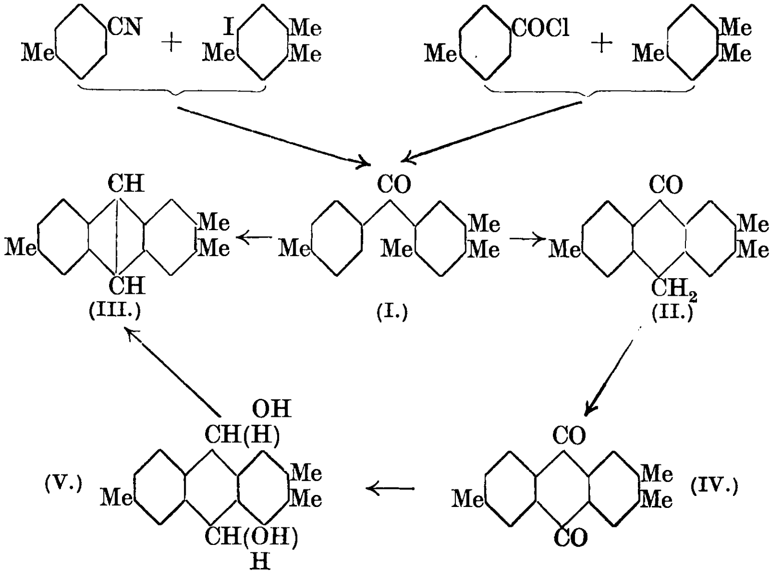
CCCXLI.—*Synthesis of Anthracene Homologues. Part II. 2 : 3 : 6-Trimethylanthracene.*

By Gilbert T. Morgan and Edward Auty Coulson.

In continuation of our researches on the chemical constituents of low-temperature tar we have isolated from the anthracene fraction of certain tar distillates a hydrocarbon melting at 245° (corr.), giving analytical numbers corresponding with either a di- or a tri-methylanthracene and yielding on oxidation a quinone melting at 240° (corr.). These melting points are close to those of 2 : 6-dimethylanthracene and its quinone respectively, but the two hydrocarbons are not identical and as so far only anthracene homologues with β-methyl groups have been isolated from such tar fractions it seemed probable that the new hydrocarbon might be 2 : 3 : 6-trimethylanthracene. Accordingly this hydrocarbon has been synthesised, because the hitherto known trimethylanthracenes do not resemble our product from low-temperature tar (compare Gresly, *Annalen*, 1886, **234**, 239, 241; Elbs, *J. pr. Chem.*, 1887, **35**, 482; 1890, **41**, 123, 143; Elbs and Olberg, *Ber.*, 1886, **19**, 410; Wende, *Ber.*, 1887, **20**, 868).

I. *Synthesis of* 2 : 3 : 6-*Trimethylanthracene.*—2 : 4 : 5 : 4′-*Tetramethylbenzophenone* (I) was produced through the intermediate ketimine by the action of the Grignard compound of 5-iodo-ψ-cumene on *p*-toluonitrile, a method of formation which establishes



the constitution of the ketone, and it was also prepared in quantity by condensation of *p*-toluoyl chloride with ψ-cumene in presence of aluminium chloride.

When the ketone (I) was boiled for 8 hours as in the condensation described in Part I (this vol., p. 2203), very little water was eliminated; the solid product gave analytical numbers for 2 : 3 : 6-*trimethyl*-9-*anthrone* (II) and was oxidisable to 2 : 3 : 6-*trimethylanthraquinone* (IV). This dehydrogenation of an *o*-methylbenzophenone is novel, although many examples are known of dehydration (compare this vol., p. 2209) and Elbs (*loc. cit.*) records two cases of aerial oxidation to anthraquinones.

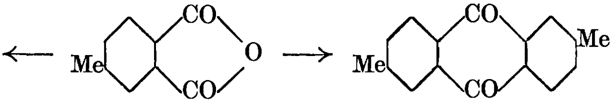
Continuous boiling of the ketone for 5 days had the effect of inducing the more usual condensation, for water was disengaged and a considerable amount of 2 : 3 : 6-*trimethylanthracene* (III) accumulated, accompanied by ill-defined products intermediate in composition between the hydrocarbon and the anthrone (II). The crude product of long boiling is preferably oxidised forthwith to 2 : 3 : 6-trimethylanthraquinone, which is then reduced to 2 : 3 : 6-trimethylanthracene, this procedure being the most effective mode of conducting the synthesis of the hydrocarbon.

II. *Synthesis of* 2 : 3 : 6-*Trimethylanthraquinone.*—A more direct synthesis of this quinone has been accomplished by using the little-known 4-methylphthalic anhydride (VI), which for this purpose was prepared from 3-nitro-4-aminotoluene (Fast Red Base GL) kindly supplied by the British Alizarine Company.

When condensed with *o*-xylene in presence of aluminium chloride, 4-methylphthalic anhydride yields an intermediate acidic product, probably 3 : 4 : 3′-*trimethylbenzophenone*-6′-*carboxylic acid*, which by loss of water and ring closure is transformed into 2 : 3 : 6-trimethylanthraquinone (IV).

On comparing the two synthetic preparations of 2 : 3 : 6-trimethylanthraquinone with the quinone obtained by oxidising the hydrocarbon from low-temperature tar, the identity of these quinones was established. Hence the coal tar hydrocarbon melting at 245° is mainly 2 : 3 : 6-trimethylanthracene, which when pure melts at 255° (corr.). The impurity in the coal tar product is probably 2 : 7-dimethylanthracene.

(IV.)



(VI.) (VII.)

III. *Synthesis of* 2 : 6-*Dimethylanthraquinone.*—When 4-methylphthalic anhydride (VI) was condensed with toluene, an intermediate acidic product was obtained, probably 3 : 4′-*dimethylbenzophenone*-6-*carboxylic acid*, which loses water and passes by ring closure into 2 : 6-dimethylanthraquinone (VII), thus affording a supplementary synthesis of this quinone.

EXPERIMENTAL.

5-Iodo-ψ-cumene was prepared from ψ-cumidine by Kurzel (*Ber.*, 1889, **22**, 1586), but no details are recorded. The finely ground base (67·5 g.), suspended in 100 g. of concentrated sulphuric acid diluted with 450 c.c. of water, was diazotised below 5° with 35 g. of sodium nitrite in 100 c.c. of water. The diazo-solution was stirred into a cooled solution of 84 g. of potassium iodide in 100 c.c. of water; a crystalline paste separated and the mixture was warmed until the crude oily iodo-compound separated. After addition of sodium bisulphite, the iodo-compound was extracted with ether, and the washed ethereal solution dried over calcium chloride. After the ether had been removed, the oil was distilled from solid caustic potash, the fraction, b. p. 240—260°, being collected and redistilled; 56 g. of iodo-compound, b. p. 250—255°, were obtained which solidified to pale yellow crystals, m. p. 37°.

ψ-Cumene.—The process employed differed from that outlined by Haller (*Ber.*, 1885, **18**, 93). Powdered ψ-cumidine (81 g.) was added to 210 c.c. of concentrated hydrochloric acid; the suspended hydrochloride, cooled to 0°, was diazotised below 5° with 50 g. of sodium nitrite in 114 c.c. of water. The filtered diazo-solution was stirred into sodium bisulphite solution, made by passing sulphur dioxide into 135 g. of caustic soda in 900 c.c. of cold water until the solution was neutral to phenolphthalein. When the pale yellow diazo-solution was poured into the bisulphite solution at 0°, a red coloration developed which rapidly faded to orange, and after addition of about half the diazo-solution a canary-yellow pulp separated. The mixture was warmed; the precipitated diazonium sulphite then dissolved and was succeeded by yellow hydrazinesulphonate, which redissolved on being warmed to 60°. Crystallised sodium acetate (200 g.) was then added and the sodium salt of the hydrazinesulphonate separated on cooling in yellow flakes. This salt was boiled with 200 c.c. of hydrochloric acid in 800 c.c. of water. A heavy oily by-product (crude ψ-cumenol) was removed and the cooled solution was rendered alkaline to precipitate the ψ-cumylhydrazine in colourless needles, which, being unstable, was at once dissolved in acetic acid and added gradually to 20% copper sulphate solution heated in a reflux apparatus. The cooled copper sulphate solution was extracted with ether, and the ethereal extract washed with dilute aqueous caustic soda to remove ψ-cumenol and dried over calcium chloride. After ether had been removed, the crude ψ-cumene was fractionated under ordinary pressure, 14—15 g. being obtained as a colourless limpid liquid, b. p. 169—172°. It appeared to be impossible by altering the conditions of hydrolysis to prevent ψ-cumylhydrazinesulphonate from decomposing largely into ψ-cumenol.

Trimellitic Acid.—ψ-Cumene prepared by the foregoing process gave on oxidation by the method of Schültze (*Ber.*, 1909, **42**, 3604) a good yield of trimellitic acid, m. p. 238°. This melting point is higher than the recorded values; Schültze gives m. p. 219° and Perkin and Stone (J., 1925, **127**, 2297) give m. p. 226—227° (Found : C, 51·0; H, 2·9. Calc. for $C_9H_6O_6$: C, 51·4; H, 2·9%).

2 : 4 : 5 : 4′-*Tetramethylbenzophenone* (I).—(a) *By the Friedel–Crafts reaction.* The preparation was carried out with equivalent weights of ψ-cumene (26·5 g.) and *p*-toluoyl chloride (34·0 g.) in dry carbon disulphide and aluminium chloride (34·0 g.) by the method used in the preparation of 2 : 4 : 4′-trimethylbenzophenone (this vol., p. 2208), the ketone (46·0 g.) being obtained as a viscid colourless oil, b. p. 220°/22 mm.

(b) *By the Grignard reaction.* 5-Iodo-ψ-cumene (50·0 g.) was dissolved in dry ether and 5·0 g. of magnesium turnings were added with a crystal of iodine. A brisk reaction set in, but the metal did not entirely dissolve. The mixture was boiled for 1 hour, *p*-toluonitrile (23·0 g.) dissolved in dry ether was added, and the whole boiled and poured into cold dilute sulphuric acid. The ketone was extracted with ether and isolated as before (yield, 3 g. of correct b. p.).

2 : 4 : 5 : 4′-*Tetramethylbenzophenone* is a colourless oil which does not solidify at the ordinary temperature (Found : C, 85·5; H, 7·3. $C_{17}H_{18}O$ requires C, 85·7; H, 7·6%). The ketone was shaken for a fortnight with excess of hydroxylamine hydrochloride and sodium acetate in aqueous-alcoholic solution. On dilution with water a crude *oxime* separated; after three crystallisations from alcohol with charcoal, it was obtained in colourless rhombs, m. p. 151° (Found : N, 5·7. $C_{17}H_{19}ON$ requires N, 5·5%).

2 : 3 : 6-*Trimethyl*-9-*anthrone* (II).—2 : 4 : 5 : 4′-Tetramethylbenzophenone (30 g.) was boiled under reflux during 8 hours. On cooling, 2·5 g. of practically pure anthrone separated, which was washed with ether; the washings contained unchanged ketone, which was recovered and added to the filtrate. The solid, crystallised successively from carbon disulphide and acetic acid, formed colourless flat needles or rhombic plates displaying no fluorescence and melting constantly at 196° (corr.) (Found : C, 86·5; H, 6·7. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%). When dissolved in boiling alcoholic potash, the anthrone developed a bright orange coloration.

2 : 3 : 6-*Trimethylanthracene* (III).—The ketone recovered from the preparation of the anthrone was boiled under reflux for 6 days; on cooling, 20 g. of crude product separated, which was washed with ether, the residual ketone being somewhat charred. This solid (2 g.) was heated in a Hedley sublimator at 170—220° and the sublimate (1 g.) was crystallised twice from boiling acetic acid. The 2 : 3 : 6-*trimethylanthracene* obtained had m. p. 255° (corr.).

The ketone prepared by the foregoing Grignard reaction, when boiled for 2½ days, yielded the same 2 : 3 : 6-trimethylanthracene.

Three g. of the condensation product were extracted with hot acetic acid and the undissolved residue was crystallised from more boiling acetic acid; 1 g. of 2 : 3 : 6-trimethylanthracene was then obtained. After further crystallisation (charcoal) the hydrocarbon melted constantly at 255° (corr.). It formed pale yellow flakes with a strong bluish fluorescence and was indistinguishable in appearance from 2 : 6- and 2 : 7-dimethylanthracenes, which it also resembled in solubility. It formed no stable solid picrate, although a solution in benzene containing picric acid was deep blood-red (Found : C, 92·7; H, 7·0. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%).

The material extracted by hot acetic acid was precipitated by water and again extracted with acetic acid, leaving a small residue of the trimethylanthracene. The cooled extract deposited almost colourless, ill-defined needles melting after further crystallisations at 170—175°, which, although giving a golden-orange coloration with boiling alcoholic potash, did not readily yield pure trimethylanthrone but on oxidation gave 2 : 3 : 6-trimethylanthraquinone.

2 : 3 : 6-*Trimethylanthraquinone* (IV).—The condensation product from the ketone (11·0 g.) was dissolved in boiling acetic acid and chromic anhydride (13·7 g.) dissolved in water was slowly added. The solution was poured into water and the precipitated quinone was boiled with dilute aqueous caustic soda to dissolve an acidic by-product. When crystallised from boiling acetic acid the residue yielded 10·5 g. of 2 : 3 : 6-*trimethylanthraquinone* in very pale yellow needles, m. p. 240° (corr.) (Found : C, 81·3; H, 5·6. $C_{17}H_{14}O_2$ requires C, 81·6; H, 5·6%).

2 : 3 : 6-Trimethyl-9-anthrone (1·1 g.), when similarly oxidised with chromic anhydride (1·37 g.) in boiling acetic acid, yielded 2 : 3 : 6-trimethylanthraquinone (0·9 g., m. p. 240°), as did also the purified trimethylanthracenes from specimens of the ketone made by both methods (a) and (b).

Reduction of 2 : 3 : 6-*Trimethylanthraquinone*.—(a) *To* 2 : 3 : 6-*trimethylanthracene*. Powdered 2 : 3 : 6-trimethylanthraquinone (4·0 g.) was suspended in 50 c.c. of aqueous ammonia (*d* 0·880) and

50 c.c. of water. Zinc dust was introduced and the mixture was gently warmed, with further additions of zinc dust and concentrated aqueous ammonia. After 2 days the initial red colour had been entirely discharged. The undissolved material was treated with warm dilute hydrochloric acid; the residue, when crystallised from acetic acid, yielded 3 g. of trimethylanthracene. The ammoniacal filtrate had a purplish fluorescence, and ether extraction furnished a small amount of the dihydroanthranol derivative (V), which on crystallisation from acetic acid passed into trimethylanthracene.

(b) *To* 2 : 3 : 6-*trimethyl*-9-*anthrone.* No heat was generated when aluminium powder was added to a solution of the anthraquinone in concentrated sulphuric acid. As the anthraquinone did not appear to be reducible to anthrone by this method, 2·0 g. of tin and 5 c.c. of concentrated hydrochloric acid were added slowly to 1·0 g. of the trimethylanthraquinone dissolved in 20 c.c. of boiling acetic acid. The filtrate on cooling deposited colourless crystals (0·5 g.), which after several crystallisations melted at 193° and underwent no depression of melting point in admixture with pure 2 : 3 : 6-trimethyl-9-anthrone. The material is probably this anthrone contaminated with isomeric 2 : 3 : 6-trimethyl-10-anthrone.

Oxidation of 2 : 3 : 6-*Trimethylanthraquinone.*—The trimethylanthraquinone (2·5 g.) was dissolved in 100 c.c. of acetic acid boiling under reflux, and 10·0 g. of chromic anhydride solution were slowly added. Acetic acid was then distilled off and the residue poured into water to precipitate the crude oxidation product, which was extracted with boiling dilute aqueous caustic soda and precipitated with acid. The crude product crystallised from acetic acid as an ill-defined, cream-coloured substance (0·2 g.), readily electrified on being touched and giving a blood-red vat with zinc dust and ammonia. It had no melting point and decomposed above 300° (Found: C, 66·6; H, 3·5. $C_{17}H_{10}O_6$ requires C, 65·8; H, 3·2%). It is probably either 2-methyl-3 : 6-dicarboxy- or 3-methyl-2 : 6-dicarboxy-anthraquinone, or a mixture of the two.

4-*Methylphthalic Anhydride* (VI).—Scanty details for the conversion of 3-nitro-4-aminotoluene into 4-cyano-3-nitrotoluene are given by Niematowski (*Ber.*, 1888, **21**, 1535). The following conditions are suitable for large batches: 60 g. of the base were dissolved in 100 c.c. of acetic acid and a mixture of 96 c.c. of concentrated hydrochloric acid and 96 c.c. of water was stirred in rapidly to produce fine crystals. This paste at −10° was diazotised by one addition of 30 g. of sodium nitrite in 80 c.c. of water, the temperature remaining below 10°. The filtered diazo-solution was poured into a Sandmeyer reagent at 50° consisting of 120 g. of potassium cyanide dissolved in 200 c.c. of water with addition of

108 g. of copper sulphate crystals in 400 c.c. of water. A brown solid separated which, on heating, decomposed into crude oily nitrile; this crystallised on cooling and was extracted with benzene (yield, 35 g. of 4-cyano-3-nitrotoluene).

The reduction of this nitro-compound to 4-cyano-3-aminotoluene had been effected by Glock (*Ber.*, 1888, **21**, 2662), using stannous chloride in hydrochloric acid, but by his method our yield was unsatisfactory. Niematowski (*loc. cit.*) used tin and hydrochloric acid, but gave no details. We found that the temperature of reduction must be controlled if hydrolysis of the nitrile group is to be avoided. The following method was suitable and gave yields approaching 90% of the theoretical. A solution of 100 g. of the nitro-compound in 100 c.c. of warm acetic acid was cooled to obtain suitably small crystals. Concentrated hydrochloric acid (450 c.c.) was added and 200 g. of tin were introduced slowly, the temperature being maintained at 55—60°. When the nitro-compound and nearly all the tin had dissolved, the solution was filtered, diluted with water, cooled, and neutralised with concentrated caustic soda solution. The precipitated crude base was extracted with ether in a Soxhlet apparatus, practically pure 4-cyano-3-aminotoluene, m. p. 90°, being obtained; a further quantity was recovered by ethereal extraction of the neutralised filtrate. If during reduction the temperature rose above 60°, 2-amino-*p*-toluamide, m. p. 147°, was largely formed.

The conversion of 4-cyano-3-aminotoluene into the dinitrile of 4-methylphthalic acid was not described in detail by Glock (*loc. cit.*), but the procedure employed by Findeklee (*Ber.*, 1905, **38**, 3543) for 3-cyano-4-aminotoluene was applicable to the present isomeric base, the yield of dinitrile being 25—30 g. from 50 g. of amine.

The dinitrile yielded 4-methylphthalic acid (m. p. 150·5°) in colourless needles or thin prisms. On distillation under ordinary pressure it passed quantitatively into the corresponding anhydride (b. p. 299°, m. p. 93°).

Condensations with 4-Methylphthalic Anhydride.—(1) 2 : 3 : 6-*Trimethylanthraquinone.* Powdered aluminium chloride (7·0 g.) was gradually added to the paste of 4-methylphthalic anhydride which had been produced by cooling a solution of 4 g. of the anhydride in 21 g. of warm *o*-xylene. The anhydride redissolved, the dark red solution evolved hydrogen chloride, and, after being heated at 90—100° until no more hydrogen chloride was disengaged, the mixture was cooled, diluted with water, and the excess of *o*-xylene removed in steam. The dark brown, gummy product was extracted with sodium carbonate solution, the extract acidified, and the resinous precipitate left with a little benzene until it solidified. Repeated crystallisations of the solid from benzene and acetic acid yielded 3 g. of pure compound. In the condensation of 4-methylphthalic anhydride with toluene (see below) the carbonyl group meta to the methyl group probably becomes attached to the nucleus of the hydrocarbon and it is reasonable to suppose that condensation takes place in the same sense in the case of *o*-xylene, to yield 3 : 4 : 3′-*trimethylbenzophenone*-6′-*carboxylic acid*, which forms colourless needles, m. p. 162° (corr.) (Found: C, 76·2; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

3 : 4 : 3′-Trimethylbenzophenone-6′-carboxylic acid (1 g.) was dissolved in 10 g. of concentrated sulphuric acid and the yellowish-brown solution was kept at 120—130° during 1 hour before being poured into water. The precipitated crude 2 : 3 : 6-trimethylanthraquinone (0·8 g.), after two crystallisations from acetic acid, furnished the quinone melting at 240° and identical both with the quinone from the foregoing synthesis and with the specimen obtained from the anthracene fraction of low-temperature tar distillate.

(2) 2 : 6-*Dimethylanthraquinone*. Condensation was carried out with 9·0 g. of methylphthalic anhydride, 40·0 g. of toluene, and 15·0 g. of aluminium chloride, and the acid product (5·0 g.) purified as before. The formation of 2 : 6-dimethylanthraquinone solely, on ring closure, shows that this intermediate acid is almost certainly 3 : 4′-*dimethylbenzophenone*-6-*carboxylic acid*. It crystallises in colourless needles or long prisms, m. p. 164° (corr.), from benzene or acetic acid (Found: C, 75·6; H, 5·6. $C_{16}H_{14}O_3$ requires C, 75·6; H, 5·5%).

The condensation product (1 g.) gave 0·9 g. of 2 : 6-dimethylanthraquinone which, after repeated crystallisation from acetic acid, melted at 242° (corr.), and this melting point was not depressed by admixture with an authentic specimen of the quinone prepared as described in Part I (*loc. cit.*).

Summary.

1. 2 : 3 : 6-Trimethylanthracene (m. p. 255° corr.) and 2 : 3 : 6-trimethyl-9-anthrone (m. p. 196° corr.) have been synthesised by methods which establish definitely the orientation of the three methyl groups, and these compounds have been oxidised to 2 : 3 : 6-trimethylanthraquinone (m. p. 240° corr.).

2. Supplementary syntheses of 2 : 3 : 6-trimethylanthraquinone and 2 : 6-dimethylanthraquinone have been effected with 4-methylphthalic anhydride.

3. The heavy neutral oils of low-temperature tar from the carbonis-

ation of bituminous coal contain a mixture of anthracene derivatives, including 2 : 3 : 6-trimethylanthracene, from which 2 : 3 : 6-trimethylanthraquinone has been obtained by oxidation.

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