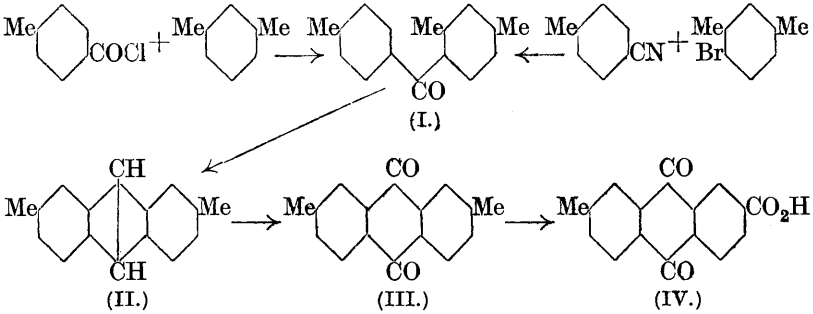
CCLXXXII.—*Synthesis of Anthracene Homologues. Part I. 2:6- and 2:7-Dimethylanthracenes.*

By Gilbert T. Morgan and Edward Auty Coulson.

During a study of the higher aromatic hydrocarbons from low-temperature tar certain products were obtained which on oxidation yielded two dimethylanthraquinones, and it became desirable to prepare for reference purposes 2 : 6- and 2 : 7-dimethylanthracenes and the corresponding quinones.

The methods employed in the preparation of the 2 : 7-compounds are symbolised in the following diagram :

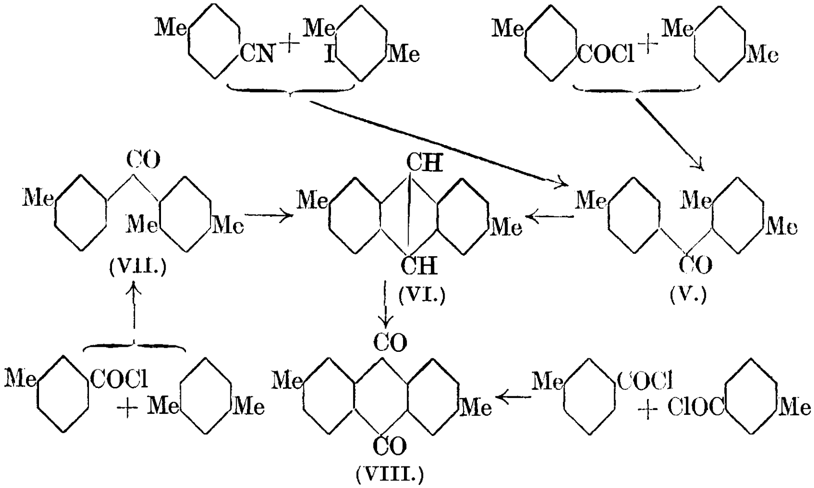


The essential compound in this synthesis, 2 : 4 : 4′-*trimethylbenzophenone* (I), is prepared most conveniently by condensing *m*-xylene with *p*-toluoyl chloride in presence of aluminium chloride, but, as the condensation might occur in one or other of three directions, the structure of the ketone is proved by treating *p*-toluonitrile with the Grignard compounds of 4-bromo-*m*-xylene and 4-iodo-*m*-xylene respectively. A ketimine is thus synthesised which is readily hydrolysed to 2 : 4 : 4′-trimethylbenzophenone, an oily ketone characterised by its crystalline *oxime*.

When maintained at its boiling point, 2 : 4 : 4′-trimethylbenzophenone is transformed slowly by loss of water into 2 : 7-*dimethylanthracene* (II), which is thus obtained by a synthetic method free from the ambiguity attaching to Friedel–Crafts condensations.

A comparison of the properties of this synthesised hydrocarbon with those of other dimethylanthracenes cited in the literature shows that it is identical with a hydrocarbon considered by Lavaux to be 1 : 6- or 1 : 7-dimethylanthracene (*Ann. Chim.*, 1910, **20**, 433; **21**, 131).

This discordance, which will be elucidated in the sequel, becomes intensified by the circumstance that Lavaux described another hydrocarbon as 2 : 7-dimethylanthracene which is identical with the hydrocarbon produced by the following syntheses :



2 : 5 : 4′-*Trimethylbenzophenone* (V) is prepared in quantity by condensing *p*-xylene and *p*-toluoyl chloride with aluminium chloride, and its constitution is confirmed by synthesis from *p*-toluonitrile and the Grignard compound of 2-iodo-*p*-xylene. When maintained at its boiling point, this ketone loses water to form a hydrocarbon which can only be 2 : 6-*dimethylanthracene* (VI).

In addition to this rigid proof of chemical constitution a supplementary synthesis was effected by repeating a condensation due to Seer (*Monatsh.*, 1911, **32**, 143) in which *m*-xylene and *m*-toluoyl chloride interact in presence of aluminium chloride to yield 2 : 4 : 3′-trimethylbenzophenone (VII). This ketone is also dehydrated on boiling and transformed into 2 : 6-dimethylanthracene (VI). Since Seer's condensation could take place in three different ways to yield isomeric ketones from which, by dehydration, 1 : 5-, 1 : 7- or 2 : 6-dimethylanthracene or mixtures of these hydrocarbons might result, it follows that these condensations cannot furnish any definite proof of the orientation of the two methyl groups. Nevertheless it is significant that, apart from actual migrations of methyl groups, Seer's condensation could not give rise to 2 : 7-dimethylanthracene.

On oxidation 2 : 6-dimethylanthracene yields 2 : 6-dimethylanthraquinone (m. p. 242°) (VIII), which was also prepared by Seer (*loc. cit.*), who obtained it as the main product of the action of aluminium chloride on *m*-toluoyl chloride alone at 130—140°.

Seer's synthesis of 2 : 6-dimethylanthraquinone is of significance in regard to the discrepancy between our results and those of Lavaux, because it is clear that, apart from possible migrations of methyl groups, *m*-toluoyl chloride alone could not condense to yield 2 : 7-dimethylanthraquinone. Our attempt to obtain this quinone by the action of aluminium chloride on a mixture of *m*-toluoyl chloride and *p*-toluoyl chloride led only to a small yield of 2 : 6-dimethylanthraquinone which was evidently obtained exclusively from *m*-toluoyl chloride, for when the experiment was repeated on *p*-toluoyl chloride alone no dimethylanthraquinone was obtained, although theoretically this acid chloride could only furnish the 2 : 6-isomeride. These experiments indicate that in the Friedel–Crafts condensations under review only those hydrogen atoms which are in the para-position with respect to methyl groups are displaceable in the form of hydrogen chloride.

The foregoing syntheses of 2 : 6- and 2 : 7-dimethylanthracenes and of their quinones have enabled us to identify two quinones present in the oxidation products of the homologues of anthracene in low-temperature tar, namely, 2 : 7-dimethylanthraquinone, m. p. 170°, and 2 : 6-dimethylanthraquinone, m. p. 242°. Moreover our syntheses of the two dimethylanthracenes offer a simpler explanation than has hitherto been possible of the conflicting statements in the literature regarding the dimethylanthracenes.

In a series of papers (*Compt. rend.*, 1904, **139**, 976; 1905, **140**, 44; 1905, **141**, 204, 354; 1906, **143**, 687; 1908, **146**, 135, 345; 1911, **152**, 1400; *Ann. Chim.*, 1910, **20**, 433; **21**, 131), Lavaux examined critically many previous researches in which dimethylanthracenes had been obtained. The reactions in question are cited below in chronological order :—

(*a*) Crude xylyl chloride, $CH_3{\cdot}C_6H_4{\cdot}CH_2Cl$, with water under pressure (van Dorp, *Annalen*, 1873, **169**, 207) or with aluminium chloride (Friedel and Crafts, *Bull. Soc. chim.*, 1882, **37**, 530).

(*b*) Benzyl chloride and toluene with aluminium chloride (Friedel and Crafts, *loc. cit.*).

(*c*) Toluene and chloroform with aluminium chloride (Schwarz, *Ber.*, 1881, **14**, 1528; Elbs and Wittich, *Ber.*, 1885, **18**, 347).

(*d*) Toluene and methylene chloride with aluminium chloride (Friedel and Crafts, *Bull. Soc. chim.*, 1884, **41**, 323; *Ann. Chim. Phys.*, 1887, **11**, 265).

(*e*) Toluene with aluminium chloride (Anschütz and Immendorf, *Ber.*, 1884, **17**, 2817).

(*f*) Toluene and acetylene tetrabromide with aluminium chloride (Anschütz, *Annalen*, 1886, **235**, 172).

Lavaux showed that the crude dimethylanthracenes from these reactions behaved as a chemical entity with a melting point of 225—

226°. When, however, this product was washed repeatedly with toluene a separation into two isomerides was effected. The residue on crystallisation from toluene yielded a single compound, Lavaux's so-called " A " dimethylanthracene (m. p. 240°), which on oxidation furnished a dimethylanthraquinone melting at 169°. This hydrocarbon and its quinone are identical respectively with our 2 : 7-dimethylanthracene and 2 : 7-dimethylanthraquinone.

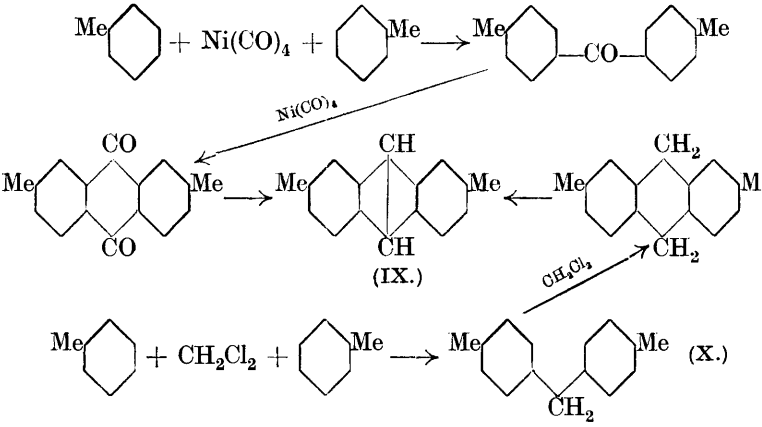
From the toluene extracts Lavaux recovered a more soluble hydrocarbon which on oxidation yielded a dimethylanthraquinone melting at 236·5°. This quinone on reduction gave a single hydrocarbon, Lavaux's " B " dimethylanthracene melting at 244·5°. This hydrocarbon and its quinone are identical respectively with our 2 : 6-dimethylanthracene and 2 : 6-dimethylanthraquinone.

Lavaux identified his B dimethylanthracene with the hydrocarbon obtained by the interaction of toluene, ethylidene chloride, and aluminium chloride (Anschütz, *Annalen*, 1886, **235**, 313) and he also conjectured that a dimethylanthracene of m. p. 224—225° (quinone, m. p. 155°) obtained from a tar oil by Zincke and Wachendorff (*Ber.*, 1877, **10**, 1481) contained both A and B isomerides.

Lavaux was led to believe that his B hydrocarbon was 2 : 7-dimethylanthracene because its quinone was oxidisable to an anthraquinonedicarboxylic acid which on prolonged alkali fusion was hydrolysed to yield *iso*phthalic and terephthalic acids. From this result he deduced that the quinonedicarboxylic acid was either the 2 : 6- or the 2 : 7-derivative. But since the parent hydrocarbon differed from that prepared by Dewar and Jones (m. p. 215—216°; quinone, m. p. 159—160°), who regarded their product as 2 : 6-dimethylanthracene (J., 1904, **85**, 212), Lavaux assumed by exclusion that his B hydrocarbon was 2 : 7-dimethylanthracene.

Seer (*loc. cit.*), however, suggested that Dewar and Jones's hydrocarbon was the then unknown 2 : 7-isomeride and it now appears probable that although impure it consisted mainly of this hydrocarbon. The suggestion of Dewar and Jones that its formation from toluene and nickel carbonyl took place through *p*-tolualdehyde by loss of hydrogen peroxide must be rejected, because only the 2 : 6-isomeride could be formed in this way. A more probable explanation is formulated on p. 2207.

Lavaux attempted to confirm his view of the 2 : 7-configuration of his B hydrocarbon by synthesising it from *pp'*-ditolylmethane (X) and methylene chloride by a condensation with aluminium chloride, but he always obtained a mixture of A and B isomerides, either in this condensation or by starting with toluene and methylene chloride. Migration of methyl groups must have occurred in the first case, for otherwise only his A compound (IX) would be obtained. On repeating Lavaux's preparation with toluene and methylene chloride we find in fact that the 2 : 7-isomeride predominates, whereas the 2 : 6-hydrocarbon (Lavaux's B compound) is present only to a small extent.



Lavaux regarded his A hydrocarbon as either 1 : 6- or 1 : 7-dimethylanthracene, since on oxidation it gave an anthraquinonedicarboxylic acid which, on prolonged alkali fusion, yielded as degradation products phthalic, *iso*phthalic, and terephthalic acids. He considered the 1 : 6-configuration to be the more probable, but our synthesis of this A hydrocarbon (III) proves that it is really 2 : 7-dimethylanthracene. With this configuration determined, it is easy to understand why it is the predominant product (IX) in the condensation with *pp*′-ditolylmethane and methylene chloride (above).

Since the completion of Lavaux's researches a product (m. p. 225—226°) containing dimethylanthracene has been prepared by Frankforter and Kokatnur (*J. Amer. Chem. Soc.*, 1914, **36**, 1534), who condensed trioxymethylene and toluene with aluminium chloride, but these observers, who made no reference to Lavaux's correction, did not separate the two isomerides. Cook and Chambers (*J. Amer. Chem. Soc.*, 1921, **43**, 338), who obtained the two isomerides, together with β-methylanthracene, by the interaction of acetylene and toluene, accepted Lavaux's view of the constitution of the two dimethylanthracenes. The A isomeride was prepared by Börnstein, Schliewiensky, and Szczesny-Heyl (*Ber.*, 1926, **59**, 2814), who also adopted Lavaux's 1 : 6- or 1 : 7-orientation now shown to be incorrect.

Seer had assumed (*loc. cit.*) that his dimethylanthracene from 2 : 4 : 3′-trimethylbenzophenone was identical with Lavaux's B hydrocarbon and he concluded that the methyl groups were in the

2 : 6-positions. An elegant proof of this 2 : 6-orientation has since been supplied by Flumiani (*Monatsh.*, 1924, **45**, 43), who condensed 2 : 5-dihydroxy-*m*-toluic acid with concentrated sulphuric acid and obtained 1 : 4 : 5 : 8-tetrahydroxy- 2 : 6-dimethylanthraquinone which on distillation with zinc dust furnished 2 : 6-dimethylanthracene identical with Seer's product.

EXPERIMENTAL.

4-Iodo-*m*-xylene (36 g.), prepared from *m*-xylidine by a modification of the method of Willgerodt and Howells (*Ber.*, 1900, **33**, 842), was dissolved in sulphuric acid (60 g. of concentrated acid in 450 c.c. of water) and diazotised below 5° with sodium nitrite solution (21 g. in 60 c.c. of water). The filtered diazo-solution was added to aqueous potassium iodide (50 g. in 60 c.c. of water), and after an hour at the ordinary temperature the mixture was warmed until effervescence ceased, sufficient solid sodium bisulphite being added to remove free iodine. The 4-iodo-*m*-xylene, which had separated as a viscid oil, was extracted with ether, washed with 10% caustic soda solution, and dried over calcium chloride. After removal of ether the residual oil was distilled from solid caustic potash and collected at 225—240°, 33 g. of pure iodo-compound, b. p. 231—235°, being obtained.

4-Bromo-*m*-xylene was prepared by two methods : (*a*) Direct bromination by the method of Cohen and Dakin (J., 1899, **75**, 895) : it was found advantageous to add the bromine more slowly than these authors recommended (3 hours instead of ½ hour) and 28 g. of pure bromo-compound of b. p. 203—205° were obtained from 50 g. of *m*-xylene. (*b*) From *m*-xylidine : 60 g. of *m*-xylidine diazotised as previously described were poured into a cold solution of cuprous bromide (made with 100 g. of crystallised copper sulphate) in fuming hydrobromic acid (170 c.c.). A pasty yellow mass separated but began to decompose and to liquefy on warming until presently the decomposition became moderately violent with generation of heat; the reaction was completed on the steam-bath. The oily bromo-compound was taken up in chloroform, washed with 10% caustic soda solution, dried over calcium chloride, and distilled, after removal of the solvent, from solid caustic soda. The fraction, b. p. 200—210°, was redistilled and yielded 20 g., b. p. 203—208°.

2 : 4 : 4′-*Trimethylbenzophenone* (I).—(*a*) From *m*-xylene and *p*-toluoyl chloride : *p*-Toluoyl chloride was prepared by boiling *p*-toluic acid under reflux with three times its weight of thionyl chloride for 6 hours. The excess of thionyl chloride was distilled off and the residue, fractionated in a vacuum, yielded the acid chloride, b. p. 125°/36 mm., in almost theoretical yield.

Equivalent weights of *p*-toluoyl chloride (89 g.) and *m*-xylene (61 g.) were mixed and dissolved in an equal volume of carbon disulphide. The solution was gradually added to powdered aluminium chloride (89 g.) covered with carbon disulphide contained in a reflux apparatus. Heat was generated, the aluminium chloride dissolved to a dark brown solution, and hydrogen chloride was evolved. When the reaction had subsided, the solution was boiled on the steam-bath for 2 hours; the product was mixed with water and the *m*-xylene and carbon disulphide were distilled in steam. The residue was extracted with ether, and the ethereal solution after repeated washing with 10% caustic soda solution was dried over calcium chloride. After removal of the ether the oily ketone was fractionated in a vacuum, 105 g., b. p. 169°/4 mm., being obtained (yield, 82%).

(*b*) From 4-iodo-*m*-xylene and *p*-toluonitrile: 33·0 G. of 4-iodo-*m*-xylene were gradually added to 2·4 g. of magnesium turnings covered with dry ether. On warming, the magnesium dissolved. *p*-Toluonitrile (8 g.), dissolved in ether, was added and the solution was boiled for an hour and poured into dilute sulphuric acid, more ether being added to take up the crude ketone, which was purified as already described (yield, 2—3 g.).

(*c*) From 4-bromo-*m*-xylene and *p*-toluonitrile: The synthesis of 2 : 4 : 4′-*trimethylbenzophenone* was carried out with each preparation of 4-bromo-*m*-xylene by exactly the same methods as those employed with the iodoxylene. The bromo-compound does not form a magnesium derivative so readily as the iodo-compound, but the yield of ketone finally obtained was a trifle higher (3 g. from 20 g.).

At the ordinary temperature the ketone remained as a viscid pale yellow oil, b. p. 169°/4 mm., 340° (corr.)/760 mm. (Found: C, 85·4; H, 7·1. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). It yielded no phenylhydrazone on prolonged boiling with phenylhydrazine in alcohol or acetic acid, and it did not react with semicarbazide. Its interaction with hydroxylamine took place very slowly. These properties may be due to steric hindrance by the ortho-methyl group.

The elimination of the elements of water took place slowly when the ketone was boiled. The reaction, which appears to be general for compounds of this type (compare Elbs and Larsen, *Ber.*, 1884, **17**, 2847; Elbs and Olberg, *Ber.*, 1886, **19**, 408; Elbs, *J. pr. Chem.*, 1886, **33**, 185; 1887, **35**, 465; 1890, **41**, 1, 121; I. G. Farb. A. G., Meister, Lucius and Brüning, E. P. 251, 270), is not appreciably facilitated by the action of water-removing catalysts such as piperidine, acetic anhydride, fused zinc chloride or concentrated sulphuric acid. On heating with the last-mentioned reagent the ketone was hydrolysed into *p*-toluic acid and *m*-xylene.

The ketone was not oximated by the action of hydroxylamine hydrochloride and anhydrous sodium acetate in boiling aqueous alcohol after 2 days. Neither did heating in sealed tubes at 100—150° bring about any marked reaction, but shaking for a fortnight at the ordinary temperature with a great excess of hydroxylamine hydrochloride and anhydrous sodium acetate in aqueous alcohol gave an oily product which became partly crystalline after a month. On recrystallisation from alcohol it furnished 2 : 4 : 4′-*trimethylbenzophenoneoxime*, $CH_3{\cdot}C_6H_4{\cdot}C(NOH){\cdot}C_6H_3(CH_3)_2$, in large colourless rhombs, m. p. 132° (Found : N, 6·2. $C_{16}H_{17}ON$ requires N, 5·9%).

2 : 7-*Dimethylanthracene* (II) *from* 2 : 4 : 4′-*Trimethylbenzophenone*.—The ketone (36·0 g.) made from *m*-xylene and *p*-toluoyl chloride was boiled beneath an air reflux for 6 hours and cooled; a thick crystalline precipitate of crude dimethylanthracene then separated which was washed with ether. The ethereal washings were added to the filtrate of unchanged ketone, the ether was removed, and the boiling continued. It was of considerable advantage to remove the dimethylanthracene at intervals, as it underwent decomposition at the temperature (350—360°) of its formation. After 19·5 g. of crude dimethylanthracene (m. p. 185—195°) had been obtained there remained 12 g. of unchanged ketone, which was distilled in a vacuum to separate it from charred by-products.

Pure 2 : 7-dimethylanthracene was obtained by subliming the crude product and by repeated crystallisation from carbon disulphide and from acetic acid.

This preparation, when repeated with the smaller quantities of 2 : 4 : 4′-trimethylbenzophenone from 4-iodo- or 4-bromo-*m*-xylene and *p*-toluonitrile, furnished dimethylanthracene having the same m. p. and showing no depression on admixture.

2 : 7-*Dimethylanthracene* (II) crystallised from carbon disulphide, acetic acid, petroleum (b. p. 60—80° and 80—100°), and other organic solvents in very pale yellow, curled, rhombic flakes, m. p. 241° (corr.), with a purple fluorescence (Found : C, 92·5; H, 6·8. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%).

Lavaux's observation that this dimethylanthracene formed no picrate was confirmed.

2 : 7-*Dimethylanthraquinone* (III).—Three g. of 2 : 7-dimethylanthracene were dissolved in boiling acetic acid and 4·0 g. of chromic anhydride dissolved in a little water were slowly added. The solution was boiled till the chromic acid was reduced ($\frac{1}{2}$—$\frac{3}{4}$ hour), and the green solution poured into water, which precipitated the crude quinone. This product was boiled with dilute caustic soda solution, to remove the small amount of 2-methylanthraquinone-7-

carboxylic acid formed as by-product, and filtered hot, because the sodium salt of the latter was sparingly soluble in the cold. The crude 2 : 7-*dimethylanthraquinone* (3·5 g.), when purified by recrystallisation from alcohol, formed colourless needles, m. p. 170° (corr.) (Found : C, 80·9; H, 5·3. $C_{16}H_{12}O_2$ requires C, 81·3; H, 5·1%). The quinone dissolved in concentrated sulphuric acid to a golden-yellow solution; with zinc dust and ammonia it formed a blood-red vat.

2-*Methylanthraquinone*-7-*carboxylic acid* (IV) was obtained by boiling 2 : 7-dimethylanthraquinone (2·4 g.) with chromic anhydride (2·7 g.) in acetic acid for 3 hours. The product was worked up as before, the acid being separated from unoxidised quinone by extraction with boiling dilute caustic soda solution and by precipitation on acidification of the alkaline solution. When crystallised from acetic acid, in which it was fairly readily soluble, the acid separated in small clusters of pale yellow needles, m. p. 283° (corr.). The sodium salt was sparingly soluble in cold water; with zinc dust and ammonia it formed a blood-red vat. These properties showed it to be the compound regarded as 6-methylanthraquinone-1-carboxylic acid by Lavaux.

Anthraquinone-2 : 7-*dicarboxylic acid*, produced when 2-methylanthraquinone-7-carboxylic acid was boiled with excess of chromic anhydride in acetic acid, slowly separated and was washed with more acetic acid. It formed very pale yellow, rhombic plates, not molten at 360° (Found : C, 64·8; H, 2·8. $C_{16}H_8O_8$ requires C, 64·9; H, 2·7%). It gave a deep crimson vat when treated with zinc dust and ammonia.

2-Bromo-*p*-xylene and 2-iodo-*p*-xylene were prepared from *p*-xylidine by methods similar to those described for the preparation of 4-bromo- and 4-iodo-*m*-xylene, but as *p*-xylenediazonium sulphate was much less soluble than *m*-xylenediazonium sulphate it was necessary to dissolve the *p*-xylidine in more diluted sulphuric acid (100 g. of concentrated sulphuric acid in 800 c.c. of water for 60 g. of the base). From 60 g. of the base there were obtained 12 g. of pure 2-bromo-*p*-xylene, b. p. 205—210°/770 mm., and 24 g. of 2-iodo-*p*-xylene, b. p. 230—235°/770 mm.

2 : 5 : 4′-*Trimethylbenzophenone* (V).—(*a*) From *p*-xylene and *p*-toluoyl chloride : This condensation resembled the preparation of the 2 : 4 : 4′-isomeride, 53 g. of *p*-toluoyl chloride, 40 g. of *p*-xylene, and 58 g. of aluminium chloride being used. The crude product, a low-melting solid, yielded after fractional distillation in a vacuum 68 g. of pure ketone, b. p. 202°/23 mm. (89% of the theoretical).

(*b*) From 4-iodo-*p*-xylene and *p*-toluonitrile : The synthesis was carried out with 22 g. of iodo-compound, 2 g. of magnesium, and 8 g.

of *p*-toluonitrile and a small yield (2 g.) of ketone, b. p. 330—340°/750 mm., was obtained. The corresponding bromo-compound dissolved magnesium very slowly, if at all, and no ketone was obtained when it was used in place of the iodo-compound.

The *ketone* formed large, colourless, rhombic plates, m. p. 54° (corr.), b. p. 202°/23 mm., 337°/760 mm. (Found : C, 85·5; H, 7·35. $C_{16}H_{16}O$ requires C, 85·7; H, 7·1%). It showed the same reluctance to form the usual ketonic derivatives as the 2 : 4 : 4′-isomeride and probably for the same reason.

2 : 6-*Dimethylanthracene* (VI) *from* 2 : 5 : 4′-*Trimethylbenzophenone* (V).—By working in exactly the same way as with 2 : 4 : 4′-trimethylbenzophenone (above) there were obtained from 30 g. of 2 : 5 : 4′-trimethylbenzophenone (prepared from *p*-xylene and *p*-toluoyl chloride) 19 g. of crude 2 : 6-dimethylanthracene and 8 g. of unchanged ketone. Pure 2 : 6-dimethylanthracene, m. p. 250° (corr.), was obtained after one sublimation and two crystallisations from carbon disulphide. The smaller preparation of ketone from the Grignard synthesis yielded the same dimethylanthracene, thus confirming the structure of the ketone prepared from *p*-xylene and *p*-toluoyl chloride as 2 : 5 : 4′-trimethylbenzophenone.

2 : 6-*Dimethylanthracene* is remarkably similar in physical and chemical properties to the 2 : 7-isomeride (Found : C, 93·1; H, 6·9. $C_{16}H_{14}$ requires C, 93·2; H, 6·8%). The m. p. (250°) of our preparation was somewhat higher than that given by Lavaux (244·5°) and Seer (243°).

2 : 6-Dimethylanthraquinone (X), prepared from 16·5 g. of crude dimethylanthracene by boiling with 22·0 g. of chromic anhydride in acetic acid for ½ hour, was worked up precisely as 2 : 7-dimethylanthraquinone (above), 13·5 g., m. p. 230°, being obtained. On crystallisation from acetic acid the m. p. rose to 242° (corr.), the compound forming colourless or pale yellow needles (Found : C, 80·9; H, 5·1. Calc. for $C_{16}H_{12}O_2$: C, 81·3; H, 5·1%).

Preparation of Lavaux's A Dimethylanthracene.—The preparation of the mixed isomeric A and B dimethylanthracenes from toluene, methylene chloride and aluminium chloride was carried out as described by Lavaux (*Compt. rend.*, 1905, **140**, 44), but the crude product, m. p. 226°, was recrystallised seven times from carbon disulphide, as this was found to be a more advantageous method of obtaining the A isomeride than by washing with cold toluene. After the seventh crystallisation, pure A isomeride, m. p. 241° (corr.), was obtained, which was identical with the 2 : 7-dimethylanthracene prepared from 2 : 4 : 4′-trimethylbenzophenone.

Separation of Lavaux's Isomeric Dimethylanthraquinones.—A simple method of separating the isomerides consists in fractional extraction of the mixed A and B dimethylanthraquinones with boiling alcohol.

Fifteen g. of the crude mixture of A and B dimethylanthracene prepared as described by Lavaux were oxidised to the mixed quinones by chromic anhydride, 11 g., m. p. 167°, being obtained. The A (or 2 : 7-) isomeride rapidly dissolved in boiling alcohol, whereas the B (or 2 : 6-) isomeride remained for the most part undissolved. The alcoholic extract on cooling furnished crystals almost free from the B isomeride. After two recrystallisations from alcohol, pure A isomeride (8 g.) was obtained, m. p. 168° (corr.).

The residues after two crystallisations from acetic acid had m. p. 239° (corr.) and amounted only to 0·6 g., thus indicating that 2 : 7-dimethylanthracene greatly predominates in Lavaux's mixture of hydrocarbons.

Mixed melting point determinations showed that the A and B quinones were identical respectively with our 2 : 7- and 2 : 6-dimethylanthraquinones.

It is now possible to assign a probable structure to the dinitro-derivative (m. p. 323°) prepared by Lavaux from A dimethylanthraquinone (the 2 : 7-isomeride) (*Ann. Chim.*, 1910, **21**, 133). Substitution being controlled by the methyl groups as in β-methylanthraquinone, the product should be 1 : 8-dinitro-2 : 7-dimethylanthraquinone, and the corresponding diamine should have the same orientation of methyl groups which also obtains in Lavaux's dimethylanthracene 9 : 10-dibromide.

Preparation of 2 : 6-*Dimethylanthracene and* 2 : 6-*Dimethylanthraquinone by Seer's Methods.*—Condensation of *m*-xylene and *m*-toluoyl chloride yielded 2 : 4 : 3′-trimethylbenzophenone (VII), an uncrystallisable oil, b. p. 195°/17 mm., 335°/760 mm. It is, however, advisable not to boil this ketone for the long period recommended by Seer in the transformation into dimethylanthracene but to separate the reaction product at short intervals and thus avoid charring. The ketone can be transformed into 2 : 6-dimethylanthracene as smoothly and completely as its 2 : 5 : 4′-isomeride. The product, purified as before, was identical with the specimen made from the 2 : 5 : 4′-trimethylbenzophenone, and the dimethylanthraquinone obtained by oxidation was identical with that obtained by our synthesis.

Summary.

(1) 2 : 7-Dimethylanthracene (m. p. 241° corr.) has been synthesised by a method which establishes definitely the orientation of the two methyl groups, and the hydrocarbon has been oxidised to 2 : 7-dimethylanthraquinone (m. p. 170° corr.).

(2) These 2 : 7-dimethyl derivatives are identical respectively

with the "A" dimethylanthracene (m. p. 240°) and its quinone (m. p. 169°) isolated by Lavaux and considered to have the 1 : 6-configuration. This orientation is now shown to be incorrect.

(3) 2 : 6-Dimethylanthracene (m. p. 250° corr.) has been synthesised definitely and oxidised to 2 : 6-dimethylanthraquinone (m. p. 242° corr.).

(4) These 2 : 6-dimethyl derivatives are identical respectively with "B" dimethylanthracene and its quinone isolated by Lavaux and regarded by him as 2 : 7-derivatives, although the correct 2 : 6-orientation was suggested subsequently by Seer.

(5) The heavy neutral oils of low-temperature tar from the carbonisation of bituminous coal contain a mixture of anthracene derivatives from which 2 : 6- and 2 : 7-dimethylanthraquinones have been obtained by oxidation.

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