345. *The Action of Benzaldehyde on* o-, m-, *and* p-*Xylene in the Presence of Aluminium Chloride.*

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Previous work (J., 1935, 72) has shown that the action of benzaldehyde on toluene in presence of aluminium chloride gives, among other products, a mixture of 2 : 6- and 2 : 7-dimethylanthracene, which is substantially identical with the product obtainable from the action of methylene dichloride on toluene in presence of aluminium chloride. Similar parallel experiments have now been carried out with the three xylenes. From *m*-xylene a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene is obtained, *p*-xylene yields 1 : 4 : 5 : 8-*tetramethylanthracene*, and *o*-xylene gives 2 : 3 : 6 : 7-tetramethylanthracene. By using a solution of diphenyl in carbon disulphide, a mixture of 2 : 6- and 2 : 7-*diphenylanthracene* is obtained both with benzaldehyde and with methylene dichloride in presence of aluminium chloride. The view that the benzaldehyde serves only to supply the *meso*-carbon atoms in the anthracenoid structures is further substantiated.

SCHAARSCHMIDT, HERMANN, and SZEMZÖ (*Ber.*, 1925, **58**, 1914) have shown that anthracene and triphenylmethane are formed by the interaction of benzaldehyde with benzene in the presence of aluminium chloride. In an attempt to elucidate the mechanism of the formation of anthracene in this reaction experiments were carried out with toluene in place of benzene, and also with methyl- and chloro-benzaldehydes in place of benzaldehyde (Hey, J., 1935, 72). The rather unexpected conclusions drawn from the results of these experiments were (a) that it is the hydrocarbon nuclei alone which go to form the two end rings in the anthracene molecule and the three rings in triphenylmethane, and (b) that the aromatic aldehyde supplies only the *meso*-carbon atoms in the anthracene molecule and the methane carbon atom in triphenylmethane. Further confirmation for these views was provided by the fact that both furfuraldehyde and a mixture of carbon monoxide and hydrogen chloride could be used in the reaction in place of the aromatic aldehyde. Similar results had been obtained previously by Dewar and Jones (J., 1904, **85**, 212), using nickel carbonyl, and also by Frankforter and Kokatnur (*J. Amer. Chem. Soc.*, 1914, **36**, 1529), using trioxymethylene.

It is now found that the action of dry carbon monoxide alone on boiling benzene in presence of aluminium chloride gives only a trace of triphenylmethane, whereas, if a mixture of carbon monoxide and hydrogen chloride is used, some anthracene is formed. When carbon monoxide alone is used together with the more reactive aluminium bromide in place of the chloride, a small quantity of anthracene is obtained. In none of these experiments, however, is the formation of benzaldehyde perceptible, although it is known (Longman, *J. Soc. Chem. Ind.*, 1916, **35**, 384; Holloway and Krase, *Ind. Eng. Chem.*, 1933, **25**, 497) that benzaldehyde is formed, especially in the presence of hydrogen chloride, if the pressure is increased. These results substantiate the conclusion previously drawn (Hey, *loc. cit.*) that the production of the free aldehyde is not an essential intermediate stage in the formation of the anthracene molecule. This is contrary to the conclusions arrived at by Dewar and Jones (*loc. cit.*) for their reactions between nickel carbonyl and aromatic hydrocarbons, but the arguments used by these workers have since been proved invalid by Morgan and Coulson (J., 1929, 2203) on other grounds. In a recent review of the reactions of pure hydrocarbons in the presence of aluminium chloride (Egloff, Wilson, Hulla, and van Arsdell, *Chem. Reviews*, 1937, **20**, 388) it is reported that anthracene is frequently found as a product of the action of aluminium chloride on benzene and that, since the odour of benzaldehyde is also noted, it is believed that the formation of anthracene results from the condensation of two molecules of benzaldehyde. This is essentially the viewpoint of Dewar and Jones, which, as indicated above, is not in agreement with experimental facts.

With regard to the detailed mechanism of the manner in which anthracenes are formed in these reactions little decisive information is forthcoming. Free carbon monoxide or even a mixture of carbon monoxide and hydrogen chloride does not give results comparable, either quantitatively or qualitatively, with those obtained when benzaldehyde is used. The fact that the aromatic aldehyde supplies the *meso*-carbon atoms indicates a severance of the bond uniting the aldehyde group to the nucleus, as has indeed been proved in the experiments with substituted benzaldehydes (Hey, *loc. cit.*). In this manner carbon monoxide in an active or nascent form or possibly formyl chloride might be the effective agent.

When benzaldehyde reacts with the xylenes in presence of aluminium chloride the anticipated tetramethylanthracenes are formed. In the reaction with *m*-xylene two products are possible, namely, 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene, with *p*-xylene only 1 : 4 : 5 : 8-tetramethylanthracene can result, whereas with *o*-xylene there are four possibilities, namely, 1 : 2 : 5 : 6-, 1 : 2 : 6 : 7-, 1 : 2 : 7 : 8-, and 2 : 3 : 6 : 7-tetramethylanthracene. In arriving at these constitutions no cognisance is taken of the well-known fact that the methyl groups attached to an aromatic nucleus can undergo migration, possibly both intra- and inter-molecular, in the presence of aluminium chloride. In addition to the tetramethylanthracenes listed above, the presence, in small quantity, of other isomerides as well as of compounds containing both more and less than four methyl groups must also be anticipated (see Baddeley and Kenner, J., 1935, 303; Egloff, Wilson, Hulla, and van Arsdell, *loc. cit.*, pp. 387—389). In each of the reactions with the xylenes studied, the melting point of the product was raised only very slowly by repeated crystallisation and this may be regarded as an indication of the presence of isomerides and of the contamination of the product with other hydrocarbons of similar constitution. Further, in the same way that triphenylmethane is formed in the reaction between benzaldehyde and benzene, the formation of trixylylmethanes would be anticipated in the corresponding reactions with the xylenes. The viscous by-products encountered in the latter reactions presumably contain trixylylmethanes, but since the number of isomerides which might be formed is large the isolation of chemical individuals of this type is not possible.

Several of the isomeric tetramethylanthracenes have been prepared by previous workers, but there has been considerable controversy with regard to the constitutions assigned to individual members. Anschütz (*Annalen*, 1886, **235**, 173), from the action of acetylene tetrabromide on *m*-xylene in the presence of aluminium chloride, obtained a tetramethylanthracene, m. p. 280°, which on oxidation gave a quinone, m. p. 300°. A similar reaction with *p*-xylene gave a hydrocarbon, m. p. about 280°, and with *o*-xylene a hydrocarbon, m. p. above 280°, was obtained : oxidation of these two hydrocarbons gave inconsistent results. Anschütz made no statement with regard to the orientation of the methyl groups in these products, which probably consisted largely of mixtures of isomerides. Friedel and Crafts (*Ann. Chim. Phys.*, 1887, **11**, 267), from the interaction of methylene dichloride with *m*-xylene in the presence of aluminium chloride, obtained a hydrocarbon, m. p. 162—163°, regarded from its method of formation as either 1 : 3 : 5 : 7- or 1 : 3 : 6 : 8-tetramethylanthracene, which on oxidation gave a quinone, m. p. 206°. Dewar and Jones (*loc. cit.*), from the reaction between nickel carbonyl and *m*-xylene in the presence of aluminium chloride, obtained, in addition to 2 : 4-dimethylbenzaldehyde, a tetramethylanthracene, m. p. 280°, which on oxidation gave a quinone, m. p. 228—230°. Dewar and Jones regarded this hydrocarbon as identical with that previously prepared by Anschütz (*loc. cit.*), and since they believed that the 2 : 4-dimethylbenzaldehyde was an essential intermediate product, they regarded it as 1 : 3 : 5 : 7-tetramethylanthracene, the sole isomeride which could arise directly from the condensation of two molecules of the aldehyde by elimination of two atoms of hydrogen and two of oxygen. They further concluded that the tetramethylanthracene, m. p. 162—163°, of Friedel and Crafts must therefore be 1 : 3 : 6 : 8-tetramethylanthracene, which is the other possible isomeride obtainable from *m*-xylene. As has been mentioned above, however, the argument of Dewar and Jones is invalid and the above conclusions are therefore unsound. Seer (*Monatsh.*, 1912, **33**, 33) synthesised 1 : 3 : 5 : 7-tetramethylanthracene and the corresponding anthraquinone by unambiguous methods and found them to melt at 163—164° and 235° respectively, and the quinone has been synthesised more recently by Scholl, Meyer, and Keller (*Annalen*, 1934, **513**, 298), who record m. p. 237°. These compounds are obviously different from those of the same name previously prepared by Dewar and Jones, which were therefore now regarded as the 1 : 3 : 6 : 8-isomerides, while it appeared that the hydrocarbon, m. p. 162—163°, of Friedel and Crafts was 1 : 3 : 5 : 7-tetramethylanthracene. It will be noted, however, that the quinone obtained by Friedel and Crafts melted at 206°, although Dewar and Jones give the melting point as 235°, which is that recorded some years later by Seer for his authentic 1 : 3 : 5 : 7-tetramethylanthraquinone. Seer concluded that the products obtained by Friedel and Crafts were not quite pure and he further showed that, if the experimental conditions of Friedel and Crafts were slightly modified, a small quantity of a second tetramethylanthracene, m. p. 281—283°, presumably 1 : 3 : 6 : 8-tetramethylanthracene, was formed which appeared to be the same as that prepared by Dewar and Jones. Frankforter and Kokatnur (*loc. cit.*) obtained a tetramethylanthracene, m. p. 233—235°, from the action of trioxymethylene on *o*-xylene in the presence of aluminium chloride (see also Huston and Ewing, *J. Amer. Chem. Soc.*, 1915, **37**, 2394), and another tetramethylanthracene, m. p. 286—287°, was formed as a by-product in a similar reaction on mesitylene. No definite statements were made, however, with regard to the positions occupied by the methyl groups in these compounds. 2 : 3 : 6 : 7-Tetramethylanthracene (m. p. 308° corr.; quinone, m. p. 338° corr.) has been shown to be present in coal tar from low-temperature distillation (Morgan and Coulson, *J. Soc. Chem. Ind.*, 1934, **53**, 71T) and has also been synthesised by unambiguous methods (Morgan and Coulson, J., 1931, 2323) : the same hydrocarbon (m. p. 299°; quinone, m. p. 326°) has also been obtained by Barnett, Goodway, and Watson (*Ber.*, 1933, **66**, 1876) by the action of methylene dichloride on *o*-xylene in the presence of aluminium chloride, although the formation of other isomerides is also theoretically possible in this reaction (compare also I.G., D.R.P. 544,522). In addition, both 1 : 4 : 6 : 7- and 1 : 3 : 6 : 7-tetramethylanthraquinone have been prepared by Fieser and Fieser (*J. Amer. Chem. Soc.*, 1935, **57**, 1679) by synthetic methods.

The present position of our knowledge of the tetramethyl-anthracenes and -anthraquinones of known constitution may be summarised as follows :

1 : 3 : 5 : 7-Tetramethylanthracene, m. p. 163—164°; quinone, m. p. 235°, 237°.*
1 : 3 : 6 : 8-Tetramethylanthracene, m. p. 281—283°, 280°; quinone, m. p. 228—230°.*
2 : 3 : 6 : 7-Tetramethylanthracene, m. p. 308° corr., 299°; quinone, m. p. 338° corr., 326°.
1 : 3 : 6 : 7-Tetramethylanthracene, m. p. —; quinone, m. p. 196°.
1 : 4 : 6 : 7-Tetramethylanthracene, m. p. —; quinone, m. p. 178°.

* The melting points of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthraquinone quoted by Morgan and Coulson (J., 1931, 2324) as 206° and 300° are those due to Friedel and Crafts and to Anschütz respectively.

The action of benzaldehyde on *m*-xylene in the presence of aluminium chloride is now shown to give a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene, which after several crystallisations melts at 163—164°. This agrees both with the melting point of the product obtained by Friedel and Crafts (*loc. cit.*) and also with that recorded by Seer (*loc. cit.*) for pure 1 : 3 : 5 : 7-tetramethylanthracene. That the product now obtained from the benzaldehyde reaction is not pure 1 : 3 : 5 : 7-tetramethylanthracene is shown by the fact that on oxidation a mixture of quinones, m. p. 160—162°, is obtained, which can be partially separated by fractional crystallisation. On the other hand, pure 1 : 3 : 5 : 7-tetramethylanthraquinone melts at 235°. The closely related reaction of methylene dichloride and *m*-xylene in the presence of aluminium chloride has been carried out by Friedel and Crafts (*loc. cit.*), who obtained a product, m. p. 162—163°. A repetition of this reaction gave a product indistinguishable from that obtained above from *m*-xylene and benzaldehyde and further, the quinones obtained on oxidation of the two products were also identical. It seems therefore that, as indicated by Seer (*loc. cit.*), the product obtained by Friedel and Crafts was also a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene. The claims made by Friedel and Crafts and by Dewar and Jones (*loc. cit.*) to have obtained a quinone, m. p. 206° and m. p. 235° respectively, from the oxidation of the product obtained by them in the methylene dichloride reaction must be interpreted as the result of continued recrystallisation of the oxidation product, which would effect some separation leading to the preferential isolation of one or other of the constituent isomeric tetramethylanthraquinones in varying degrees of purity. The concomitant formation of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene in these reactions is an exact parallel to the production together of 2 : 6- and 2 : 7-dimethylanthracene in the corresponding reactions with toluene (Hey, *loc. cit.*), a mixture which was shown by Lavaux (*Ann. Chim. Phys.*, 1910, **20**, 433; **21**, 131) to behave as a chemical entity with a sharp melting point.

The action of benzaldehyde on *p*-xylene in the presence of aluminium chloride gave a compound, m. p. 270° (corr.), which must be 1 : 4 : 5 : 8-*tetramethylanthracene*, the sole isomeride which can arise directly from *p*-xylene, provided always that the migration of one or more of the four α-methyl groups has not taken place. Oxidation with chromic anhydride gave 1 : 4 : 5 : 8-*tetramethylanthraquinone*, m. p. 258—260°. In the corresponding reaction between methylene dichloride and *p*-xylene a hydrocarbon resulted identical with the above 1 : 4 : 5 : 8-tetramethylanthracene and the identity was confirmed by the preparation of the quinone. A second *tetramethylanthraquinone*, obtained on oxidation of the residues from a mother-liquor, melted at 223—226°. This probably resulted from the migration of one or more methyl groups under the influence of aluminium chloride in the original condensation.

The action of benzaldehyde on *o*-xylene in the presence of aluminium chloride gave rise to a tetramethylanthracene which, after several crystallisations, melted at 304° (corr.) and may be regarded as 2 : 3 : 6 : 7-tetramethylanthracene, identical with that previously prepared by Barnett, Goodway, and Watson (*loc. cit.*) from methylene dichloride and *o*-xylene, and also with that synthesised by Morgan and Coulson (J., 1931, 2323). As indicated previously, it is possible for other isomerides to be formed in the reaction with *o*-xylene, although, on theoretical grounds and by analogy with the corresponding reactions with toluene, which give rise to anthracenes in which the methyl groups occupy only the β-positions, it seems very likely that the formation of 2 : 3 : 6 : 7-tetramethylanthracene will predominate. In this connection it may be recalled that Morgan and Coulson (*J. Soc. Chem. Ind.*, 1934, **53**, 71T) found that the anthracenoid hydrocarbons so far identified in low-temperature tar contain their alkyl groups exclusively in the β-positions.

An attempt was made to see if the reaction with benzaldehyde could be applied to a solid hydrocarbon dissolved in a suitable inert solvent. For this purpose the action of benzaldehyde on diphenyl in carbon disulphide solution in the presence of aluminium chloride was studied. Although reaction was incomplete, a *product* was obtained, probably consisting of a mixture of 2 : 6- and 2 : 7-diphenylanthracene, m. p. 312° (corr.), which on oxidation with chromic anhydride gave the corresponding anthraquinones, m. p. 194—196°. The same product resulted from the action of methylene dichloride on a solution of diphenyl in carbon disulphide in the presence of aluminium chloride.

EXPERIMENTAL.

Action of Carbon Monoxide on Benzene in Presence of Aluminium Chloride.—(a) *In absence of hydrogen chloride.* Dry carbon monoxide was passed for 6 hours into boiling dry benzene (150 c.c.) in presence of powdered aluminium chloride (75 g.) contained in a flask fitted with a mechanical stirrer and a reflux condenser to which was attached a calcium chloride guard-tube. After standing overnight, the mixture was poured on ice and distilled with steam. The benzene layer in the steam distillate yielded only a small quantity of a brown oil (2 g.), which smelled strongly of triphenylmethane but from which no crystalline material could be obtained. The brown non-steam-volatile residue was extracted with hot alcohol. Concentration of this extract deposited a small quantity of crude triphenylmethane, m. p. 90—91° after recrystallisation.

(b) *In presence of hydrogen chloride.* The procedure was as described under (a), but in place of carbon monoxide a mixture of carbon monoxide and hydrogen chloride was used in the approximate proportion of 1 : 2. After removal of benzene by steam-distillation the viscous oily residue was extracted with hot alcohol. Distillation of this extract gave a brown viscous oil (6 g.), b. p. 330—370°, which was oxidised in boiling acetic acid solution with chromic anhydride (9 g.) in 90% acetic acid; the anthraquinone obtained (4 g.) had, after two recrystallisations from alcohol, m. p. 273°, alone and when mixed with an authentic specimen.

Action of Carbon Monoxide on Benzene in Presence of Aluminium Bromide.—This experiment was carried out as described above, but aluminium bromide was used in place of the chloride. Distillation of the dried benzene layer in the steam-distillate gave a high-boiling residue (3 g.; b. p. 200—260°), which, on cooling, deposited anthracene (0·2 g.), m. p. 215° after purification by sublimation. The alcoholic extract of the non-steam-volatile residue deposited a brown solid (3 g.) when cold, which yielded anthraquinone, m. p. 273—274°, on oxidation with chromic anhydride as described above.

Action of Benzaldehyde on m-*Xylene in Presence of Aluminium Chloride.*—Benzaldehyde (50 c.c.), freshly distilled in an atmosphere of nitrogen, was dropped slowly into a stirred mixture of *m*-xylene (200 c.c.) and powdered aluminium chloride (150 g.). The flask (reflux condenser and calcium chloride guard-tube) was immersed in a water-bath, which served for cooling purposes during the initial stages of the reaction and subsequently to maintain the reaction mixture at 60° for 6 hours. This form of apparatus was used in all the subsequent experiments. The reaction mixture became dark in colour and hydrogen chloride was evolved. The product was poured on ice and distilled with steam. The *m*-xylene layer in the steam-distillate contained very little benzaldehyde. The non-volatile residue, which solidified on cooling, was extracted first with hot alcohol and then with benzene. The alcoholic extract was boiled with charcoal and filtered, and, on cooling, a crop of brown crystals (35 g.; m. p. 125—155°) separated. After several crystallisations from alcohol the m. p. of the product, which consisted of a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene, was raised slowly to a constant value at 163—164° (pale yellow plates) (Found: C, 92·4; H, 7·5. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). In a subsequent experiment it was found that the number of crystallisations could be reduced considerably if the product was sublimed at 10^{-3} mm. prior to crystallisation. Further quantities of this mixture of hydrocarbons were obtained from the mother-liquors and finally a small quantity of another hydrocarbon, m. p. 233—235°, was isolated, which was probably a trimethylanthracene (Found: C, 92·8, 93·1; H, 7·2, 6·9. $C_{17}H_{16}$ requires C, 92·7; H, 7·3%). The benzene extract was decanted from some tarry matter and, after removal of solvent by distillation, the residue was collected at 250—300°/20 mm. Several crystallisations from alcohol of the solid distillate gave a mixture of tetramethylanthracenes, m. p. 159—164°, substantially identical with that obtained from the alcoholic extract. Complete removal of solvent from the final mother-liquors left a viscous oil probably consisting of a mixture of trixylylmethanes.

Oxidation (cf. Morgan and Coulson, *J. Soc. Chem. Ind.*, 1934, **53**, 71T). The mixture of the two hydrocarbons (0·5 g.) in boiling glacial acetic acid (15 c.c.) was oxidised by the gradual addition of a concentrated solution of chromic anhydride (0·8 g.) in dilute acetic acid. After

½ hour the product was poured into water, and the precipitated tetramethylanthraquinones extracted with ether. The extract was washed successively with water, dilute sulphuric acid, aqueous sodium carbonate, and again with water. Removal of the ether from the dried extract by distillation left a yellow solid residue of a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthraquinone, which, after two crystallisations from ethyl alcohol, was obtained in yellow needles, m. p. 160—162° (Found : C, 82·0; H, 6·2. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%). By further repeated crystallisation a small quantity of impure 1 : 3 : 5 : 7- or 1 : 3 : 6 : 8-tetramethylanthraquinone was isolated in yellow prisms, m. p. *ca.* 200° (Found : C, 81·7; H, 6·3%).

Action of Methylene Dichloride on m-*Xylene in Presence of Aluminium Chloride* (cf. Friedel and Crafts, *loc. cit.*).—Methylene dichloride (50 g.) was added during 50 minutes to a stirred mixture of *m*-xylene (173 g.) and aluminium chloride (60 g.) maintained at room temperature. The temperature was then slowly raised to 60°, and after 3 hours to 80° until evolution of hydrogen chloride had ceased. When cold, the product was poured on ice and distilled with steam to remove the excess of *m*-xylene. The non-volatile residue (55 g.) was extracted with hot alcohol, and the extract boiled with charcoal and filtered; a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthracene separated, m. p. 162—163° after further crystallisations (Found : C, 92·2; H, 7·8. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%), which was indistinguishable from the corresponding product obtained from the reaction between benzaldehyde and *m*-xylene. Oxidation with chromic anhydride, as described above, again gave a mixture of 1 : 3 : 5 : 7- and 1 : 3 : 6 : 8-tetramethylanthraquinone, m. p. 160—163° after crystallisation from ethyl alcohol (Found : C, 81·7; H, 6·0. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%). As before, on further crystallisation a partial separation could be effected, giving a tetramethylanthraquinone, m. p. *ca.* 200°.

Action of Benzaldehyde on p-*Xylene in Presence of Aluminium Chloride.*—The method and quantities used were the same as in the corresponding reaction with *m*-xylene described above, but the reaction was rather less vigorous. No unchanged benzaldehyde was detected in the steam-distillate. The hot alcoholic extract of the non-steam-volatile residue yielded 1 : 4 : 5 : 8-*tetramethylanthracene*, which, after several crystallisations from ethyl alcohol and finally from benzene–light petroleum (b. p. 80—100°), was obtained in fine needles, m. p. 270° (corr.) (Found : C, 92·4; H, 7·6. $C_{18}H_{18}$ requires C, 92·3; H, 7·7%). Concentration of the alcoholic mother-liquors ultimately yielded a viscous non-crystallisable oil, probably consisting of trixylylmethanes. Oxidation of the tetramethylanthracene with chromic anhydride in the manner previously described gave 1 : 4 : 5 : 8-*tetramethylanthraquinone*, which, after repeated crystallisation from ethyl alcohol, was obtained in yellow needles, m. p. 258—260° (Found : C, 81·4; H, 5·6. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Action of Methylene Dichloride on p-*Xylene in Presence of Aluminium Chloride.*—This reaction was carried out as described above for the corresponding reaction with *m*-xylene. The non-steam-volatile residue was extracted, first with hot alcohol and then with benzene, and the extracts boiled with charcoal and filtered. The sticky solid deposited from the alcoholic extract on cooling was purified, either by distillation, or by repeated crystallisation from ethyl alcohol, and yielded 1 : 4 : 5 : 8-tetramethylanthracene, m. p. 260—265°. The benzene extract, worked up in similar manner, also yielded 1 : 4 : 5 : 8-tetramethylanthracene, which separated from benzene–light petroleum (b. p. 80—100°) in pale yellow needles, m. p. 260—265° (Found : C, 92·6; H, 7·2. Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). Oxidation of the hydrocarbon, in the manner previously described, gave 1 : 4 : 5 : 8-tetramethylanthraquinone in fine yellow needles, m. p. 256—258° after several crystallisations from ethyl alcohol (Found : C, 81·4; H, 6·1. Calc. for $C_{18}H_{16}O_2$: C, 81·8; H, 6·1%). Both the hydrocarbon and the quinone were indistinguishable, apart from showing a slightly lower m. p., from the corresponding products resulting from the reaction between benzaldehyde and *p*-xylene. In both reactions the m. p. of the hydrocarbon was raised only slowly by repeated crystallisation. This is probably due to contamination of the product with isomeric hydrocarbons in which one or more of the methyl groups have migrated, under the influence of aluminium chloride, to a β-position. Further support for this view was revealed by the fact that from the oxidation of a crude hydrocarbon obtained from the mother-liquors a second *tetramethylanthraquinone*, m. p. 223—226°, was isolated (Found : C, 81·9; H, 6·1. $C_{18}H_{16}O_2$ requires C, 81·8; H, 6·1%).

Action of Benzaldehyde on o-*Xylene in Presence of Aluminium Chloride.*—This reaction was carried out exactly as described for the corresponding reaction with *m*-xylene. The non-steam-volatile residue (50 g.) was dissolved in benzene, dried, and distilled at 5 mm. The yellow solid distillate was crystallised several times from benzene and yielded 2 : 3 : 6 : 7-tetramethylanthracene in faintly yellow needles, m. p. 304° (corr.) (Found : C, 92·3; H, 8·0.

Calc. for $C_{18}H_{18}$: C, 92·3; H, 7·7%). The hydrocarbon was almost insoluble in alcohol and is probably identical with that obtained by Barnett, Goodway, and Watson (*loc. cit.*) by the action of methylene dichloride on *o*-xylene in presence of aluminium chloride (see also Morgan and Coulson, J., 1931, 2323). Concentration of the mother-liquors again gave a viscous non-crystallisable residue of trixylylmethanes.

Action of Benzaldehyde on Diphenyl in Carbon Disulphide Solution in Presence of Aluminium Chloride.—Benzaldehyde (33 c.c.) was added gradually to a stirred solution of diphenyl (45 g.) in dry carbon disulphide (200 c.c.) at 30° to which finely powdered aluminium chloride (100 g.) had been added. Stirring was continued at 35° for 5 hours and finally at 40° for 1 hour. Hydrogen chloride was evolved slowly throughout. After standing overnight, the product was poured on ice and distilled with steam, which removed the carbon disulphide together with some benzaldehyde and diphenyl. The residual brown oil (25 g.) solidified and on sublimation in a vacuum a yellow solid *product*, regarded as a mixture of 2 : 6- and 2 : 7-diphenylanthracene, was obtained which, after crystallisation from benzene–light petroleum (b. p. 80—100°), melted at 312° (corr.) (Found : C, 94·3; H, 5·7. $C_{26}H_{18}$ requires C, 94·55; H, 5·45%). On oxidation with chromic anhydride, in the manner previously described, a mixture of 2 : 6- and 2 : 7-diphenylanthraquinones was obtained, m. p. 194—196° after crystallisation from alcohol (Found : C, 86·8; H, 4·4. $C_{26}H_{16}O_2$ requires C, 86·7; H, 4·4%).

Action of Methylene Dichloride on Diphenyl in Carbon Disulphide Solution in Presence of Aluminium Chloride.—Methylene dichloride (30 g.) was added slowly to a stirred solution of diphenyl (45 g.) in dry carbon disulphide (200 c.c.) at 25° to which aluminium chloride (100 g.) had been added. The reaction was more vigorous than the corresponding reaction with benzaldehyde and the temperature was maintained at 25° for 4 hours and then raised to 45° for 2 hours. The product was isolated as described above for the benzaldehyde reaction. To a hot solution of the non-steam-volatile residue (50 g.) in benzene, light petroleum (b. p. 80—100°) was added in small portions. After the first addition some tarry matter was precipitated, which was removed by decantation. Subsequent additions of light petroleum precipitated successive crops of a yellow solid, which was further purified by sublimation at 160—180°/10^{-3} mm. After recrystallisation from benzene the product had m. p. 310° (corr.), not depressed by the product obtained from the corresponding reaction with benzaldehyde. The identity of the products was confirmed by a mixed m. p. of the quinones obtained on oxidation with chromic anhydride.

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[*Received, June 9th*, 1938.]