14. *The Action of Aromatic Aldehydes on Benzene and Toluene in Presence of Aluminium Chloride.*

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GATTERMANN and KOCH'S method (*Ber.*, 1897, **30**, 1622) for the synthesis of aromatic aldehydes, namely, the action of a mixture of hydrogen chloride and carbon monoxide on a homologue of benzene in presence of aluminium and cuprous chlorides, is stated to be inapplicable to benzene itself (Gattermann and Koch, *loc. cit.*; Gattermann, *Annalen*, 1906, **347**, 347). Benzene is therefore recommended as a solvent or diluent for the reaction in place of carbon disulphide, which, since it does not dissolve the cuprous chloride, tends to inhibit the reaction. The product obtained by this method from diphenyl in benzene solution (J., 1931, 2477) contained, however, benzaldehyde in addition to diphenyl-4-aldehyde; and in a reaction carried out on benzene alone, at 45°, benzaldehyde was formed together with a small quantity of anthracene.

Benzene does not react with hydrogen cyanide and hydrogen chloride in the presence of aluminium chloride at 40° (Gattermann and co-workers, *Ber.*, 1898, **31**, 1149, 1765), but at a higher temperature a considerable quantity of benzaldehyde is formed (Hinkel, Ayling, and Morgan, J., 1932, 2793). The formation of benzaldehyde from benzene in the carbon monoxide reaction is therefore not unexpected, especially since it is known that benzaldehyde is readily formed when aluminium bromide is used in place of the chloride. Further, in presence of aluminium chloride, aldehydes are formed from aromatic hydrocarbons, including benzene, and carbon monoxide under pressure (Boehringer, D.R.-P. 1914, 281,212; Longman, *J. Soc. Chem. Ind.*, 1916, **35**, 384; B.P. 1915, 3152; see also Holloway and Krase, *Ind. Eng. Chem.*, 1933, **25**, 497) and from benzene and toluene reacting with nickel carbonyl (Dewar and Jones, J., 1904, **85**, 212). The interaction of benzaldehyde with benzene in presence of aluminium chloride with formation of anthracene (Schaarschmidt, Hermann, and Szemzö, *Ber.*, 1925, **58**, 1914) may partly account for the inability of Gattermann and his co-workers to observe the formation of the aldehyde from benzene.

To elucidate the formation of anthracene in this reaction, experiments were carried out with toluene in place of benzene, and with methyl- and chloro-benzaldehydes replacing benzaldehyde. The action of benzaldehyde on benzene in presence of aluminium chloride at 60° gave, as recorded by Schaarschmidt, Hermann, and Szemzö (*loc. cit.*), anthracene and triphenylmethane, but with toluene in place of benzene a mixture of 2 : 6- and 2 : 7-dimethylanthracene was obtained—a further example of the production together of these two isomerides (see Lavaux, *Compt. rend.*, 1904, **139**, 976; 1905, **140**, 44; **141**, 204, 354; 1906, **143**, 687; 1908, **146**, 135, 345; 1911, **152**, 1400; *Ann. Chim.*, 1910, **20**, 433; **21**, 131). Lavaux showed that the mixture behaved as a chemical entity with a sharp melting point, but, although a separation into the two isomerides was effected, the constitutions originally assigned to them have been since shown by Morgan and Coulson (J., 1929, 2203) to be at fault.

On the other hand, when *m*-tolualdehyde, *p*-tolualdehyde, or *o*-chlorobenzaldehyde reacted with benzene in presence of aluminium chloride, the product consisted of anthracene and triphenylmethane, together with toluene and *m*-xylene (from the tolualdehydes) and chlorobenzene (from *o*-chlorobenzaldehyde).

From these results it must be inferred (*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 aldehyde supplies the *meso*-carbon atoms in the anthracene molecule and the methane carbon atom in triphenylmethane. The formation of a triarylmethane by elimination of water from one molecule of aldehyde and two molecules of hydrocarbon, as has been shown to take place between benzaldehyde and benzene or toluene in presence of zinc chloride at a high temperature (Griepentrog, *Ber.*, 1886, **19**, 1876; cf. Kliegl, *Ber.*, 1905, **38**, 85), does not occur.

The formation of toluene, *m*-xylene, and chlorobenzene (above) would indicate that the carbonyl group is severed from the aldehyde, and this would imply the reversibility of the reaction between benzene and carbon monoxide, thus $C_6H_5{\cdot}CHO \rightleftharpoons C_6H_6 + CO$.

In order to test this possibility the action of aluminium chloride on benzaldehyde alone was studied and it was found that much heat was evolved, together with a water-insoluble gas which burned with the characteristic blue flame of carbon monoxide and was capable of oxidation to carbon dioxide. Further, when carbon monoxide was passed into hot toluene containing aluminium chloride, a mixture of 2 : 6- and 2 : 7-dimethylanthracene was formed, together with a liquid product probably consisting of a mixture of tritolylmethanes.* The action of furfuraldehyde on toluene in presence of aluminium chloride also gave the mixture of dimethylanthracenes, thus further confirming the fact that the nucleus to which the aldehyde group is attached plays no part in the building up of the anthracene molecule. The experiments of Frankforter and Kokatnur (*J. Amer. Chem. Soc.*, 1914, **36**, 1529), who condensed trioxymethylene with benzene and with toluene in presence of aluminium chloride, also support this view : in the former case anthracene was obtained, and in the latter dimethylanthracene, which, however, was not separated into the two possible isomerides. The formation of anthracene from benzene and of dimethylanthracene from toluene, in presence of nickel carbonyl and aluminium chloride at 100°, as demonstrated by Dewar and Jones (*loc. cit.*), is also in agreement with the view now proffered, but the mechanism suggested by these authors, involving the aromatic aldehyde as an essential intermediate, is no longer tenable. This mechanism has been previously rejected by Morgan and Coulson (*loc. cit.*) on other grounds.

The main inferences drawn with regard to the mechanism of the building of the anthracene and triphenylmethane molecules, in the reaction between the aldehyde and the aromatic hydrocarbon in presence of aluminium chloride, are thus clearly substantiated. It is obvious, however, that several minor reactions may also occur in presence of the aluminium chloride, *e.g.*, the conversion of triphenylmethane into diphenylmethane, benzene, and anthracene (Friedel and Crafts, *Ann. Chim.*, 1884, **1**, 492; Scholl and Seer, *Ber.*, 1922, **55**, 335), the transference of methyl groups, and also the pyrogenic-like fission of the aromatic nuclei.

EXPERIMENTAL.

Action of Carbon Monoxide and Hydrogen Chloride on Benzene in Presence of Aluminium and Cuprous Chlorides.—A stream of dry carbon monoxide and hydrogen chloride was passed for 7 hours into a well-stirred mixture of benzene (200 g.), aluminium chloride (100 g.), and cuprous chloride (15 g.) at 45°. The product was poured on ice and distilled with steam. The benzene layer in the distillate was separated, the aqueous layer extracted with more benzene, and the combined benzene extracts dried and distilled, giving, after removal of the benzene, a fraction, b. p. 175—182°, consisting almost wholly of benzaldehyde (8·5 g.), and a small residue of benzoic acid. The solid non-steam-volatile residue was digested with hot absolute alcohol, from which a yellow crystalline solid (0·75 g.) separated on cooling. Recrystallisation from absolute alcohol gave anthracene in white flakes (m. p. and mixed m. p. 212—213°). The picrate separated from alcohol in red needles (m. p. and mixed m. p. 141—142°).

Action of Benzaldehyde on Toluene in Presence of Aluminium Chloride.—Benzaldehyde (53 g.) was added slowly to a mixture of toluene (160 g.) and aluminium chloride (150 g.). The mixture, which darkened and became warm, was stirred for 6 hours at 60°. The product was poured on ice and distilled with steam. Toluene and benzaldehyde (12 g.) were collected in the distillate, together with a small quantity of a mixture of 2 : 6- and 2 : 7-dimethylanthracene (m. p. 219—220°). The non-steam-volatile residue yielded a yellow solid (34 g.) on distillation, which after crystallisation from toluene gave a mixture of 2 : 6- and 2 : 7-dimethylanthracene, m. p. 221—222° (Found : C, 92·9; H, 6·5. Calc. for $C_{16}H_{14}$: C, 93·2; H, 6·8%). On treatment with concentrated sulphuric acid and a trace of nitric acid, a deep purple coloration was obtained (cf. Dewar and Jones, J., 1904, **85**, 216). No monomethylanthracene could be detected in the product. A portion of the mixture of dimethylanthracenes (11 g.) was oxidised in boiling glacial acetic acid with a concentrated solution of chromic anhydride (15 g.) in water. After ½ hour the green solution was poured into water, which precipitated the mixture of dimethylanthraquinones (12 g., m. p. 155—170°). This mixture, after several crystallisations from absolute alcohol, gave mainly 2 : 6-dimethylanthraquinone (m. p. 234—236° after recrystallisation from glacial acetic acid), and a smaller quantity of 2 : 7-dimethylanthraquinone (m. p. 159—160°) was obtained

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* Anschütz and Immendorff (*Ber.*, 1884, **17**, 2816; 1885, **18**, 657) have shown that the action of aluminium chloride on boiling toluene alone produces some dimethylanthracene, but the yield in this case is only minute (cf. Lavaux, *Ann. Chim.*, 1910, **20**, 468).

from the mother-liquors. The identity of the two dimethylanthraquinones was proved by means of mixed melting points with the corresponding compounds prepared by oxidation of the mixture of hydrocarbons obtained by the method of Lavaux from toluene, methylene dichloride, and aluminium chloride (*Compt. rend.*, 1905, **140**, 44), a reaction which has been shown by Morgan and Coulson (J., 1929, 2212) to give rise to a mixture of 2 : 6- and 2 : 7-dimethylanthracene. The mixture of the two hydrocarbons thus obtained melted at 224°, and did not depress the melting point of the product prepared from benzaldehyde, toluene, and aluminium chloride. Oxidation with chromic anhydride and subsequent fractionation by crystallisation from absolute alcohol gave mainly 2 : 7-dimethylanthraquinone (m. p. 160—162°), together with a smaller quantity of 2 : 6-dimethylanthraquinone (m. p. 232—234°).

Action of p-*Tolualdehyde on Benzene in Presence of Aluminium Chloride.*—*p*-Tolualdehyde (25 g.) was added gradually to a well-stirred mixture of benzene (150 c.c.) and aluminium chloride (75 g.), which was kept at 60° for 6 hours; hydrogen chloride was freely evolved. After standing for 12 hours, the mixture was poured on ice, and distilled with steam until white fluorescent crystals of anthracene began to collect in the condenser. The dark brown solid residue was digested with hot absolute alcohol : anthracene (4 g.) separated from the filtrate, and sublimation of the insoluble residue (7 g.) also gave anthracene in white flakes (m. p. and mixed m. p. 212—213°). Oxidation with chromic anhydride and acetic acid gave anthraquinone (m. p. and mixed m. p. 276—277°, after crystallisation from acetic acid). Four successive fractions of crude anthracene separated from the alcoholic filtrate, but no evidence could be obtained of the presence of any mono- or di-methylanthracene. A portion of the residue from the alcoholic mother-liquor was distilled and collected mainly between 340° and 360°. This fraction solidified on cooling, and crystallisation from alcohol gave triphenylmethane (m. p. and mixed m. p. 90—92°). A second portion of the residue was oxidised in glacial acetic acid with chromic anhydride ($\frac{1}{2}$ hour's boiling) : the product precipitated by water was removed, and ether extracted *p*-toluic and terephthalic acids from the filtrate. The precipitated product was dissolved in glacial acetic acid, from which a little anthraquinone separated. The mother-liquor, evaporated almost to dryness and triturated with cold absolute alcohol, deposited a crystalline solid, which was recrystallised from hot absolute alcohol. After the separation of a further small quantity of anthraquinone, colourless crystals were deposited, which after a further crystallisation from aqueous alcohol melted at 159—160°, both alone and on admixture with triphenylcarbinol (Found : C, 86·8; H, 6·0. Calc. for $C_{19}H_{16}O$: C, 87·6; H, 6·15%).

The benzene layer in the steam distillate was heated on the steam-bath to remove benzene, and further distillation gave a small colourless fraction (b. p. 110—130°) and finally unchanged *p*-tolualdehyde (6 g.). The former was nitrated by warming on the water-bath with an equivolume mixture of concentrated sulphuric and fuming nitric acids. The nitration product was precipitated by the addition of water, and crystallisation from benzene gave fine, pale yellow needles, m. p. 180° alone or mixed with trinitro-*m*-xylene (Found : C, 40·3; H, 2·95; N, 17·4. Calc. for $C_8H_7O_6N_3$: C, 39·8; H, 2·9; N, 17·4%). A small quantity of *m*-dinitrobenzene separated from the mother-liquor.

Action of m-*Tolualdehyde on Benzene in Presence of Aluminium Chloride.*—The product from the reaction between *m*-tolualdehyde (23 g.), benzene (150 c.c.), and aluminium chloride (75 g.), carried out as described for *p*-tolualdehyde, was poured on ice and distilled with steam. The dark brown non-volatile residue was digested with hot absolute alcohol and filtered. Several crops of crude anthracene (7 g.) separated from the filtrate, and sublimation of the insoluble residue (9 g.) also gave anthracene. No methylanthracenes could be detected in the product. The alcoholic mother-liquor was finally distilled and a main fraction, b. p. 340—360°, was collected which solidified when cold. Crystallisation from absolute alcohol gave triphenylmethane (m. p. and mixed m. p. 89—91°).

The benzene layer in the steam distillate was dried and distilled with a Dufton column. Three fractions were collected, (i) b. p. 80—95°, (ii) b. p. 110—115°, and (iii) b. p. 135—145°, leaving a small residue boiling above 145° and consisting mainly of unchanged *m*-tolualdehyde. Fractions (ii) and (iii) were each nitrated by warming on the water-bath with concentrated sulphuric and fuming nitric acids, and the products were precipitated by water. From fraction (ii), 2 : 4-dinitrotoluene was obtained in pale yellow needles, m. p. 70—71° (after two crystallisations from alcohol), both alone and on admixture with an authentic specimen. The product from fraction (iii) was washed with hot alcohol, and crystallisation from benzene gave trinitro-*m*-xylene in yellow needles, m. p. and mixed m. p. 179—181°.

Action of o-*Chlorobenzaldehyde on Benzene in Presence of Aluminium Chloride.*—The reaction between *o*-chlorobenzaldehyde (25 g.), benzene (150 c.c.), and aluminium chloride (75 g.) was carried out in the manner previously described, and the product was poured on ice and distilled with steam. The non-volatile residue was digested with hot absolute alcohol and filtered. The residue (6 g.) was heated with a mixture of toluene and glacial acetic acid and, after filtration, anthracene separated from the solution (m. p. and mixed m. p. 212—213°, after recrystallisation). The alcoholic filtrate also deposited anthracene (7 g.), and finally the mother-liquor was distilled and gave a dark oil (b. p. 340—355°, 11 g.), which solidified. Recrystallisation of the latter from alcohol gave triphenylmethane, m. p. and mixed m. p. 90—91° (Found : C, 93·4; H, 6·5. Calc. for $C_{19}H_{16}$: C, 93·4; H, 6·6%). The benzene layer in the steam distillate was separated, and the benzene removed on the steam-bath. The residual liquid, on distillation with a Dufton column, gave one main fraction (8·1 g.), b. p. 130—133°, which was identified as chlorobenzene (*a*) by nitration with fuming nitric acid to give *p*-chloronitrobenzene (m. p. and mixed m. p. 83—84°; piperidino-derivative, m. p. 76—77°), and (*b*) by nitration with fuming nitric and concentrated sulphuric acids to give 2 : 4-dinitrochlorobenzene (m. p. 46°), which on warming with aniline gave 2 : 4-dinitrodiphenylamine (m. p. 156°).

Action of Furfuraldehyde on Toluene in Presence of Aluminium Chloride.—Furfuraldehyde (32 g.) was added gradually to a well-stirred mixture of toluene (110 c.c.) and aluminium chloride (100 g.), and the mixture was kept at 60° for 6 hours; evolution of hydrogen chloride occurred. After standing for 12 hours, the mixture set to a stiff black paste, which was transferred to ice and distilled with steam. The non-steam-volatile residue set to a solid black brittle mass (96 g.), which was distilled in portions and yielded a dark viscous oil (48 g., b. p. 300—420°). This was subsequently redistilled and collected in four fractions, (i) 5 g., b. p. 280—320°, (ii) 9 g., b. p. 320—360°, (iii) 10·5 g., b. p. 360—400°, and (iv) 12 g., b. p. 400—430°. Fractions (i), (ii), and (iii) deposited crystalline precipitates of dimethylanthracenes on standing, which were filtered off and recrystallised from toluene (m. p. and mixed m. p. 221—222°; 4 g.). Difficulty was experienced in isolating further quantities of dimethylanthracenes owing to their contamination with an excessive quantity of a viscous oily by-product.

Action of Carbon Monoxide and Hydrogen Chloride on Boiling Toluene in Presence of Aluminium Chloride.—A steady stream of dry carbon monoxide and hydrogen chloride was passed for 6 hours into boiling toluene (150 c.c.) in presence of aluminium chloride (75 g.). After standing for 12 hours, the dark viscous fluid was poured on ice and distilled with steam. The toluene layer in the steam distillate was separated and distillation gave three fractions, (i) b. p. 90—165° (62 c.c., recovered hydrocarbons), (ii) b. p. 170—200° (3 c.c.), and (iii) b. p. 200—230° (3 c.c.). Fractions (ii) and (iii), consisting of colourless clear oils, were treated together with an excess of warm aqueous potassium permanganate, but only a small portion was oxidisable. After saturation with sulphur dioxide, ether was added, and the aqueous layer drawn off. The ethereal layer was washed with aqueous sodium hydroxide, and acidification of the alkaline washings gave a minute precipitate only. Evaporation of the dried ethereal extract left an oil, which would not decolorise potassium permanganate but reacted readily with 2 : 4-dinitrophenylhydrazine, giving a 2 : 4-dinitrophenylhydrazone, which separated from absolute alcohol in crimson needles, m. p. 245° (decomp.). The non-steam-volatile viscous residue was extracted with hot toluene and distilled. After removal of the solvent, two fractions were collected, (i) b. p. 200—290° (3·5 g.), and (ii) b. p. 290—380° (36 g.). The latter consisted of a dark red oil, which on trituration with benzene slowly deposited a mixture of 2 : 6- and 2 : 7-dimethylanthracene (5 g., m. p. 220—221°). The residual oil, which would not solidify, probably consisted mainly of a mixture of tritolylmethanes from which the further separation of dimethylanthracene was difficult.

Action of Aluminium Chloride on Benzaldehyde.—(*a*) On adding benzaldehyde to powdered aluminium chloride, considerable heat was developed and some hydrogen chloride was evolved. The evolved gases were passed through a wash-bottle containing water and then collected over water. The gas thus collected burned with a blue flame.

(*b*) A slow stream of nitrogen was passed over a mixture of benzaldehyde (200 g.) and aluminium chloride (100 g.) at 60—70° and then successively through a trap cooled in ice, a bulb containing water, a soda–lime tube, a potash bulb, a bulb containing baryta water (B_1), a tube containing heated copper oxide, a second bulb containing baryta water (B_2), and finally a soda–lime tube. The baryta water in the bulb B_1 remained clear, whereas that in B_2 soon became cloudy and deposited a precipitate of barium carbonate. No products were evolved which could be condensed at 0°. The mixture of benzaldehyde and aluminium chloride became viscous and finally set to a solid black mass when cold. Steam distillation of this product gave benzaldehyde (150 g.) and a non-volatile buff amorphous solid (27 g.), insoluble in alcohol, containing aluminium but no chlorine, and from which benzaldehyde and benzoic acid were liberated on treatment with aqueous alkali or acid.

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[*Received, October 8th*, 1934.]