78. *Studies on Hydrogen Cyanide. Part VII. Aldehydes from Aromatic Hydrocarbons.*

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It was shown by Hinkel, Ayling, and Morgan (J., 1932, 2793) that Gattermann's hydrogen cyanide aldehyde synthesis, thitherto regarded as inapplicable to aromatic hydrocarbons (Houben and Fischer, *J. pr. Chem.*, 1929, **123**, 319; Wieland and Dorrer, *Ber.*, 1930, **63**, **404**), could, by variation of the reaction temperature, be applied to benzene for the synthesis of benzaldehyde (Brit. Pat., 397,124, 1933), contrary to the observations of Gattermann, who used benzene as a solvent in the synthesis. The reaction was extended to other liquid hydrocarbons, such as toluene and the xylenes, and in each case an excess of the hydrocarbon was used as a solvent in the reaction. This method, however, has its limitations and can only be used in those cases where the hydrocarbon is liquid, easily procurable and, furthermore, unaffected by the presence of the free aluminium chloride which has been shown to be necessary in the reaction.

The applicability of the process for the complete conversion of hydrocarbons into the corresponding aldehydes by means of an excess of hydrogen cyanide and aluminium chloride in the presence of suitable solvents has now been studied.

Tetrachloroethane, *o*-dichlorobenzene, and chlorobenzene can be used as reaction media in the preparation of resorcylaldehyde (this vol., p. 184). These liquids are also particularly suitable for the aluminium chloride reactions, since they serve as solvents not only for the hydrocarbons but also for the hydrogen cyanide and the final products, and their relatively high boiling points render possible a study of the reaction over a wide range of temperature. In addition, none of them is affected by aluminium chloride or gives rise to the Friedel–Crafts reaction under the conditions used, although chlorobenzene can be made to yield *p*-chlorobenzaldehyde in small amount under special conditions.

The choice of solvent is a matter of importance, since the solvent appears to exert a marked influence on the reaction, depending on its chlorine content. Tetrachloroethane, with its high chlorine content, appears to enhance the aldehyde synthesis with most hydrocarbons, but on the other hand it also considerably increases the tendency for the polymerisation or condensation of those hydrocarbons which are prone to these reactions in the presence of aluminium chloride (compare Scholl and Seer, *Ber.*, 1922, **55**, 109, 330; Scholl and Neumann, *ibid.*, p. 118; Scholl and Schwarzer, *ibid.*, p. 324; Schaarschmidt, Mayer-Bugström, and Sevon, *Ber.*, 1925, **58**, 156; Homer, J., 1907, **91**, 1103; Wieland and Dorrer, *Ber.*, 1930, **63**, 404). The latter tendency is usually preferential to, and in some cases completely inhibits, the aldehyde synthesis, as, for example, with indene. In these cases, the polymerisation may be prevented to a large extent by using a solvent with a lower chlorine content, such as chlorobenzene, and also by using a smaller excess of aluminium chloride with a longer duration of the reaction period.

The union of hydrogen chloride with the compound $AlCl_3,2HCN$, although inappreciable at the ordinary temperature, is fairly rapid at 80° and the resulting compound $AlCl_3(HCN)_2HCl$ readily dissociates at 100° (J., 1935, 674). The choice of the reaction temperature in the aldehyde synthesis is thus governed by two opposing factors, since, though the rate of formation of arylmethyleneformamidine hydrochloride, $R{\cdot}CH{:}N{\cdot}CH{:}NH,HCl$, increases with rise in temperature, the tendency for the aluminium chloride to cause polymerisation and nuclear condensation is also increased. For most cases the results obtained indicate 70° as the approximate optimum reaction temperature. It may be stated as a broad generalisation that, when the hydrocarbon is not readily acted upon by aluminium chloride, one molecule of free aluminium chloride is necessary for optimum conversion of the hydrocarbon into aldehyde. When the reactivity of the hydrocarbon is great, the necessary concentration of free aluminium chloride must be reduced and the reaction period increased accordingly.

Chloromethyleneformamidine reacts with benzene in the presence of aluminium chloride to yield benzaldehyde (Hinkel and Dunn, J., 1930, 1836), and this reaction has now been extended to the following hydrocarbons : acenaphthene, anthracene, diphenyl, hydrindene, and naphthalene. It was hoped that in some cases it might be possible to prepare dialdehydes, since some hydrocarbons readily yield diketones in the Friedel–Crafts reaction (compare Dziewonski and Schnayder, *Bull. intern. acad. polonaise*, 1930, *A*, 529; Dziewonski and Spirer, *ibid.*, 1931, *A*, 232). In all cases, however, with the exception of diphenyl, only the monoaldehydes are obtained, identical with those prepared by the hydrogen cyanide method.

Diphenyl, besides being the only hydrocarbon examined with which a dialdehyde could be formed, presents a case with some novel features. The formation of this dialdehyde proceeds in an unusual manner, both the aldehyde groups being introduced simultaneously, since under no conditions can the monoaldehyde be converted into the dialdehyde. In each reaction with diphenyl, the product is always either diphenyl-4-aldehyde and unchanged diphenyl or, on the other hand, when disubstitution occurs, diphenyl-4 : 4′-dialdehyde and unchanged diphenyl, a mixture of the two aldehydes never being obtained. In this reaction the solvent exerts a marked influence. With chlorobenzene or *o*-dichlorobenzene, the product consists of the monoaldehyde, but with tetrachloroethane, only the dialdehyde results.

The following new aldehydes have been isolated : *acenaphthene*-3-*aldehyde, anthracene*-9-*aldehyde*, 1 : 6-*dimethyl*-4-*naphthaldehyde*, 2 : 6-*dimethyl*-1-*naphthaldehyde*, and *fluorene*-2-*aldehyde*. An anthracene-9-aldehyde has been previously prepared, but no proof of its constitution has been given (I. G. Farbenind. A.-G. and Carpmael, Brit. Pat., 311,208, 1928; *Brit. Chem. Abs.*, 1929, *B*, 747). The aldehyde now synthesised is quantitatively oxidised to 9 : 10-anthraquinone and the aldehyde group must therefore be in the 9-position. Oxidation of acenaphthenealdehyde yielded naphthalene-1 : 4 : 5-tricarboxylic acid, and the two dimethylnaphthaldehydes similarly yielded 1 : 6-dimethyl-4- and 2 : 6-dimethyl-1-naphthoic acids respectively, thereby establishing the constitutions of these compounds.

Braun and Engel (*Ber.*, 1924, **57**, 191) describe a fluorene-2-aldehyde, m. p. 174—175°; semicarbazone, m. p. 245—247°, which they prepared from 2-cyanofluorene through 2-fluorenylmethyl bromide by the method of Sommelet (*Compt. rend.*, 1913, **157**, 852). The fluorenealdehyde obtained by the hydrogen cyanide method differs considerably, however, from that of Braun and Engel, since it melts at 90° and yields a semicarbazone, m. p. 278°. On oxidation it yields fluorene-2-carboxylic acid and fluorenone-2-carboxylic acid, both of which are identical with the acids obtained from 2-cyanofluorene by the method of Fortner (*Monatsh.*, 1904, **25**, 451). Similarly the fluorenone-2-carboxylic acid, obtained either by oxidation of the fluorenealdehyde or from 2-cyanofluorene, yields the authentic diphenyl-2 : 4′-dicarboxylic acid when fused with potash (compare Kruber, *Ber.*, 1932, **65**, 1382). The constitution of the aldehyde is further established by its conversion into 2-methylfluorene (Kruber, *Ber.*, 1932, **65**, 1382).

Since 2-nitrofluorene (Diels, *Ber.*, 1901, **34**, 1758) was used both by Braun and Engel and by Fortner for the production of 2-cyanofluorene, there can be no doubt that the fluorenealdehyde now obtained by the hydrogen cyanide method is fluorene-2-aldehyde. It therefore seems that Braun and Engel could not have obtained a pure aldehyde by their method. An attempt to convert 2-cyanofluorene directly into fluorene-2-aldehyde by the method of Stephen (J., 1925, **127**, 1874) was unsuccessful, 2-cyanofluorene being quantitatively recovered.

EXPERIMENTAL.

Apparatus and Materials.—The apparatus was similar to that described by Hinkel, Ayling, and Morgan (*loc. cit.*). The hydrogen chloride was dried by means of phosphoric oxide, and anhydrous hydrogen cyanide was obtained by fractionation of the commercial material, followed by drying with phosphoric oxide and refractionation. Commercial tetrachloroethane, chlorobenzene, and *o*-dichlorobenzene, supplied by Imperial Chemical Industries, Ltd., were dried over calcium chloride, and fractionally distilled. Benzene was purified by sulphuric acid, dried over calcium chloride, followed by sodium, and distilled. Aluminium chloride was obtained from Imperial Chemical Industries, Ltd., and other chemicals were purchased as pure materials.

General Procedure for the Preparation of Aldehydes.—Powdered aluminium chloride was suspended in the solvent and hydrogen cyanide was added slowly during 15 minutes through the dropping-funnel, the reaction vessel being shaken and cooled in ice-water. The mixture, in which the solid increased in bulk owing to the formation of the double compound $AlCl_3,2HCN$ as a white crystalline powder, was kept at room temperature for 15 minutes with frequent shaking in order to complete the union of the aluminium chloride with the hydrogen cyanide. The requisite hydrocarbon was then added, and a slow current of hydrogen chloride passed through the mixture for 15 minutes at room temperature. The mixture was then heated in a water-bath for the period and temperature specified (reaction period and temperature), the passage of dry hydrogen chloride through the mixture, which was well shaken at 10-minute intervals, being maintained throughout. The dark viscous product was poured on ice and concentrated hydrochloric acid, and the mixture boiled for 15 minutes. The aldehydic product was then isolated as described in each particular instance.

As the above procedure was used in each case, only the quantities of materials, the temperature, and the reaction period are given in the individual cases; furthermore, the experimental details refer only to those experiments in which the optimum yield of aldehyde was obtained. The yields of aldehydes are calculated on the chloromethyleneformamidine basis and expressed in terms of the hydrocarbon.

Chlorobenzene.—This was subjected to the reaction in order to test its suitability as a solvent. Chlorobenzene (112 g., 10 mols.), hydrogen cyanide (16 c.c., 4 mols.), and aluminium chloride (53 g., 4 mols.) were subjected to the general procedure for 6 hours at 100°. Yield: 2·2 g., 8% (calc. on the HCN). The decomposed reaction mixture was distilled in steam, and the aldehydic distillate extracted with ether. The extract was shaken for 8 hours with saturated aqueous sodium bisulphite, and the bisulphite compound and solution decomposed by boiling for 5 minutes with *N*-sulphuric acid. The liberated *p*-chlorobenzaldehyde was isolated by distillation in steam, extraction in ether, and fractionation in colourless needles, m. p. 45°, b. p. 212—214°.

Mesitylene.—Mesitylene (14 c.c., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (24 c.c., 6 mols.), aluminium chloride (53·4 g., 4 mols.); time, 4 hours at 80°. Yield: 12·3 g., 83%. From the resulting reaction mixture, 2 : 4 : 6-trimethylbenzaldehyde, b. p. 236—237°, was isolated according to the procedure described by Hinkel, Ayling, and Morgan (*loc. cit.*).

When the proportion of aluminium chloride was increased from 4 to 5 mols., with the other quantities and conditions as given above, the yield of aldehyde was diminished to 67%.

Ethylbenzene.—Ethylbenzene (21·2 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (32 c.c., 4 mols.), aluminium chloride (66·8 g., 2·5 mols.); time, 4 hours at 100°. Yield: (liquid, b. p. 224—228°), 6 g., 22·4%. The decomposed reaction mixture was distilled in steam, the aldehydic distillate extracted with ether, the extract shaken for 8 hours with excess of saturated aqueous sodium bisulphite, and the bisulphite solution removed, acidified with excess of 4*N*-sulphuric acid, and distilled in steam. The dried ethereal extract of this aldehydic distillate, on fractionation, yielded a mixture, b. p. 215—260°. Further distillation yielded no definitely pure fraction, although *p*-ethylbenzaldehyde (b. p. 221°) was proved to be present in the fraction, b. p. 224—228°, by means of its semicarbazone (compare Fournier, *Compt. rend.*, 1903, **136**, 558; Hinkel, Ayling, and Morgan, *loc. cit.*).

With tetrachloroethane (100 c.c.) as solvent, the yield of liquid (b. p. 224—228°) was only 15%.

Diphenyl.—Diphenyl (15·4 g., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (12 c.c., 3 mols.), aluminium chloride (33·4 g., 2·5 mols.); time, 7 hours at 75°. Yield: 13·6 g., 75%. The resulting diphenyl-4-aldehyde was isolated from the decomposed reaction mixture according to the procedure described by Hey (J., 1931, 2476). It crystallised from light petroleum (b. p. 80—100°) in very pale yellow laminae, m. p. 60°, and was further identified by means of its phenylhydrazone, m. p. 188—189° (compare Gattermann, *Annalen*, 1906, **347**, 381), and its 2 : 4-dinitrophenylhydrazone, m. p. 239° (compare Hey, *loc. cit.*).

Naphthalene.—Naphthalene (25·6 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 3 mols.), aluminium chloride (66·8 g., 2·5 mols.); time, 5 hours at 70°. Yield: 18·7 g., 60%. The decomposed reaction product was steam-distilled, and the aldehydic distillate extracted with ether. The α-naphthaldehyde was isolated by means of its sodium bisulphite compound in the usual way and obtained as a pale yellow oil, b. p. 291—292°, identified by means of its oxime, m. p. 98° (compare Brandis, *Ber.*, 1889, **22**, 2151).

The optimum temperature of 70° is shown by the results of three experiments, identical save for reaction temperature, which yielded aldehyde as follows: 50°, 31%; 70°, 52%; 80°, 32·5%.

1-*Methylnaphthalene.*—1-Methylnaphthalene (21·5 c.c., 1 mol.), *o*-dichlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 75°. Yield: 12·9 g., 51%. The resulting 1-methyl-4-naphthaldehyde was isolated according to the procedure described for ethylbenzene as a pale yellow oil, b. p. 171°/11 mm., and identified by means of its semicarbazone, which crystallised from alcohol in colourless plates, m. p. 229° (compare Ziegler and Tiemann, *Ber.*, 1922, **55**, 3416, and Robinson and Thomson, J., 1932, 2015, who record m. p. 228° and 237° respectively).

1 : 6-*Dimethylnaphthalene.*—1 : 6-Dimethylnaphthalene (31·2 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 3 mols.), aluminium chloride (66·8 g., 2·5 mols.); time, 5 hours at 70°. Yield: 21·3 g., 58%. After removal of the solvent from the decomposed

reaction mixture by distillation in steam, the residual non-volatile oil was extracted with ether. The ethereal extract was shaken for 8 hours with excess of saturated aqueous sodium bisulphite, the light brown bisulphite compound removed and washed with ether, and the aldehyde liberated as an oil by boiling with a slight excess of *N*-sulphuric acid for 5 minutes. Fractionation of the dried ethereal extract of the oil yielded 1 : 6-*dimethyl*-4-*naphthaldehyde* as a pale yellow oil, b. p. 191·5°/16 mm. (Found : C, 84·7; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The *oxime* crystallised from light petroleum (b. p. 80—100°) in colourless laminae, m. p. 123° (Found : N, 7·0. $C_{13}H_{13}ON$ requires N, 7·0%), the *semicarbazone* from aqueous alcohol in colourless laminae, m. p. 202° (Found : N, 17·4. $C_{14}H_{15}ON_3$ requires N, 17·5%), and the *phenylhydrazone* from light petroleum (b. p. 60—100°) in yellow warts, m. p. 110° (Found : N, 10·1. $C_{19}H_{18}N_2$ requires N, 10·2%).

Oxidation of 1 : 6-*Dimethyl*-4-*naphthaldehyde*.—(a) *With aqueous potassium permanganate.* The aldehyde (3·6 g.), suspended in water (100 c.c.), was heated at 100° with a solution of potassium permanganate (3 g.) in water (100 c.c.) until the colour disappeared. The filtered liquid, on acidification with concentrated hydrochloric acid, yielded a white precipitate, which was washed with water, dried, and crystallised from benzene, 1 : 6-dimethyl-4-naphthoic acid (1·0 g.) separating in colourless needles, m. p. 188—189° (Found : equiv., 200·6. Calc., 200) (compare Barnett and Cook, J., 1933, 22).

(b) *Aerial oxidation.* A current of air was drawn through the aldehyde (2·0 g.), maintained at 150°, for 2 hours. The resulting brown solid was extracted with dilute sodium hydroxide solution, and the alkaline solution washed with ether and acidified. Crystallisation of the resulting precipitate from benzene yielded the above 1 : 6-dimethyl-4-naphthoic acid (1·5 g.).

2 : 6-*Dimethylnaphthalene*.—2 : 6-Dimethylnaphthalene (19·5 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (15 c.c., 3 mols.), aluminium chloride (33·4 g., 2 mols.); time, 5 hours at 70°. Yield : 14·1 g., 60%. The aldehyde was isolated through its sodium bisulphite compound by a procedure similar to that described under 1 : 6-dimethylnaphthalene. Crystallisation from light petroleum (b. p. 40—60°) yielded 2 : 6-*dimethyl*-1-*naphthaldehyde* in colourless laminae, m. p. 57° (Found : C, 84·8; H, 6·6. $C_{13}H_{12}O$ requires C, 84·8; H, 6·5%). The *oxime* crystallised from light petroleum (b. p. 80—100°) in colourless laminae, m. p. 122—123° (Found : N, 7·0. $C_{13}H_{13}ON$ requires N, 7·0%), the *semicarbazone* from alcohol in colourless laminae, m. p. 214° (Found : N, 17·3. $C_{14}H_{15}ON_3$ requires N, 17·5%), the *phenylhydrazone* from aqueous alcohol in pale yellow laminae, m. p. 122° (Found : N, 10·1. $C_{19}H_{18}N_2$ requires N, 10·2%), and the *aniline* derivative from light petroleum (b. p. 40—60°) in yellow plates, m. p. 78° (Found : N, 5·4. $C_{19}H_{17}N$ requires N, 5·4%).

Oxidation of 2 : 6-*Dimethyl*-1-*naphthaldehyde*.—The aldehyde (1·2 g.), oxidised with potassium permanganate (1 g.) according to the procedure described for 1 : 6-dimethyl-4-naphthaldehyde, yielded 2 : 6-dimethyl-1-naphthoic acid (0·6 g.), which crystallised from benzene in colourless prisms, m. p. 170—171° (Found : equiv., 200. Calc., 200) (Baeyer and Villiger, *Ber.*, 1899, **32**, 2429, record m. p. 168—171°).

1 : 2 : 3 : 4-*Tetrahydronaphthalene* (*Tetralin*).—Tetralin (20 c.c., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 75°. Yield : 0·96 g., 4%. The resulting aldehyde was isolated according to the procedure described for ethylbenzene. Fractionation of the dried ethereal extract of the aldehydic distillate yielded 1 : 2 : 3 : 4-tetrahydro-6-naphthaldehyde as a colourless oil, b. p. 138°/14 mm., further identified by its semicarbazone, which separated from alcohol in colourless needles, m. p. 219° (compare Braun, Moldänke, Dirlam, and Gruber, *Ber.*, 1922, **55**, 1700, who also obtained a 4% yield of the aldehyde by the action of carbon monoxide and hydrogen chloride in the presence of aluminium chloride). The tetralin is mainly converted into a non-aldehydic resinous product, owing to its great reactivity towards aluminium chloride (compare Schroeter, *Ber.*, 1924, **57**, 1990).

Hydrindene.—Hydrindene (20 c.c., 1 mol., prepared according to the method of Krämer and Spilker, *Ber.*, 1890, **23**, 3276), tetrachloroethane (100 c.c.), hydrogen cyanide (20 c.c., 3 mols.), aluminium chloride (56 g., 2·5 mols.); time, 6 hours at 80°. Yield : 11 g., 45%. The decomposed reaction mixture was distilled in steam, and the aldehydic distillate extracted with ether. Fractionation of the dried ethereal extract yielded hydrindene-5-aldehyde, b. p. 255—257°, further identified by means of its aniline derivative, m. p. 85° (compare Gattermann, *Annalen*, 1906, **347**, 347). The remainder of the hydrindene was converted by the aluminium chloride into a brown, non-volatile, non-aldehydic, ether-insoluble solid (12 g.).

Indene was completely polymerised to a brown, non-aldehydic, nitrogen-free solid, insoluble in acids and alkalis, under the conditions of the aldehyde synthesis, even when all the aluminium chloride was combined as the compound $AlCl_3,2HCN$. This agrees with the ready activity of unsaturated compounds with aluminium chloride (compare Wieland and Dorrer, *loc. cit.*).

Anthracene.—Anthracene (27·7 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 70°. Yield: 18·5 g., 60%. After removal of the solvent from the decomposed reaction mixture by distillation in steam, the dark brown solid was crushed, washed with water, and extracted with ether. Evaporation of the extract deposited *anthracene-9-aldehyde*, which crystallised from dilute acetic acid in long orange needles, m. p. 104—105° (Found: C, 87·2; H, 4·8. $C_{15}H_{10}O$ requires C, 87·4; H, 4·9%).

When solutions of the aldehyde in alcohol or ether were allowed to crystallise slowly in sunlight, the resulting solid melted over a wide range, mainly at 104°, but not completely until 115° (compare Brit. Pat. 311,208, 1928, where anthracene-9-aldehyde is described as orange needles, m. p. about 104°). On prolonged keeping in sunlight, the aldehyde, m. p. 104—105°, assumed an indistinct melting range and appeared to be partly transformed into a solid of much higher m. p., complete fusion not occurring until 135°. No separation into fractions having melting ranges other than 104—105° could, however, be obtained by fractional crystallisation from any of the common solvents.

Anthracene-9-aldehyde displays similarity with anthraquinone in the non-formation of a sodium bisulphite compound at the ordinary temperature. It readily yields, however, the following derivatives by the usual methods: the *aniline* derivative crystallised from alcohol in orange needles, m. p. 175° (Found: N, 4·9. $C_{21}H_{15}N$ requires N, 5·0%), the *phenylhydrazone* from alcohol in orange needles, m. p. 207° (Found: N, 9·4. $C_{21}H_{16}N_2$ requires N, 9·5%), the *oxime* from alcohol in pale yellow laminae, m. p. 186—187° (Found: N, 6·25. $C_{15}H_{11}ON$ requires N, 6·3%), and the *semicarbazone* from alcohol in bright yellow, microscopic laminae, m. p. 291° (Found: N, 16·1. $C_{16}H_{13}ON_3$ requires N, 16·0%).

Oxidation of Anthracene-9-aldehyde.—Chromic acid (30 g.) in glacial acetic acid (20 c.c.) and water (20 c.c.) was added during 2 hours to the aldehyde (2 g.) in glacial acetic acid (30 c.c.) boiling under reflux, and the heating continued for a further 2 hours. Addition to water (1 l.) and crystallisation of the resulting white precipitate from aqueous acetic acid yielded anthraquinone (2 g.) in colourless needles, m. p. and mixed m. p. 281°.

Phenanthrene.—Phenanthrene (17·8 g., 1 mol.), chlorobenzene (100 c.c.), hydrogen cyanide (12 c.c., 3 mols.), aluminium chloride (26·7 g., 2 mols.); time, 5 hours at 50°. Yield: 9 g., 44%. The solvent was removed from the decomposed reaction mixture by distillation with steam, and the residual tarry aldehydic material extracted with ether. The filtered extract, shaken for 12 hours with excess of saturated aqueous sodium bisulphite, yielded a light brown solid, which was washed with ether and then decomposed by boiling for 5 minutes with excess of dilute sodium carbonate solution. The viscous oil formed was extracted with ether and fractionation of the extract yielded phenanthrene-9-aldehyde, b. p. 231—233°/12 mm., which solidified on cooling and crystallised from methyl alcohol in colourless needles, m. p. 100—101°; its oxime crystallised from aqueous alcohol in colourless plates, m. p. 157° (compare Mossetig and van de Kamp, *J. Amer. Chem. Soc.*, 1933, **55**, 2995).

Phenanthrene is readily polymerised by aluminium chloride (compare Scholl and Schwarzer; Schaarschmidt, Mayer-Bugström, and Sevon, *locc. cit.*) and the necessity for the use of chlorobenzene and a temperature of only 50° is shown by yields of 23% and 25% obtained with tetrachloroethane as solvent and with a temperature of 75° respectively.

Acenaphthene.—Acenaphthene (15·4 g., 1 mol.), tetrachloroethane (100 c.c.), hydrogen cyanide (16 c.c., 4 mols.), aluminium chloride (30 g., 2·25 mols.); time, 5 hours at 80°. Yield: 12·7 g., 70%. The procedure described above (phenanthrene) was then followed, and the light brown bisulphite compound obtained was boiled for 5 minutes with a slight excess of *N*-sulphuric acid. The oil obtained solidified on cooling and crystallisation from aqueous alcohol or light petroleum (b. p. 80—100°) yielded *acenaphthene-3-aldehyde* in colourless laminae, m. p. 87° (Found: C, 86·3; H, 5·7. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%). The aldehyde yielded a bright red solution with concentrated sulphuric acid and the following derivatives were obtained by the usual procedures: the *phenylhydrazone* crystallised from aqueous alcohol in orange needles, m. p. 140° (Found: N, 10·2. $C_{19}H_{16}N_2$ requires N, 10·3%), the 2 : 4-*dinitrophenylhydrazone* from alcohol in scarlet needles, m. p. 273° (Found: N, 15·1. $C_{19}H_{14}O_4N_4$ requires N, 14·7%), the *oxime* from light petroleum (b. p. 60—80°) in clusters of colourless needles, m. p. 126·5° (Found: N, 7·0. $C_{13}H_{11}ON$ requires N, 7·1%), the *semicarbazone* from methyl alcohol in small needles, m. p. 234° (Found: N, 17·3. $C_{14}H_{13}ON_3$ requires N, 17·6%), and the *aniline* derivative from ether–light petroleum (b. p. 60—80°) in orange needles, m. p. 97° (Found : N, 5·4. $C_{19}H_{15}N$ requires N, 5·4%).

Oxidation of Acenaphthene-3-aldehyde.—The aldehyde (1 g.), oxidised with potassium permanganate (3·6 g.) according to the procedure described above for 1 : 6-dimethyl-4-naphthaldehyde, yielded a white powdery precipitate (0·7 g.). Washing with water and drying in a vacuum gave naphthalene-1 : 4 : 5-tricarboxylic acid (Found : equiv., 87·1. Calc., 86·7), which on heating yielded the anhydride, m. p. 243° (compare Graebe and Haas, *Annalen*, 1903, **327**, 95).

Fluorene.—Fluorene (25 g., 1 mol.); chlorobenzene (100 c.c.), hydrogen cyanide (24 c.c., 4 mols.), aluminium chloride (60 g., 3 mols.); time, 5 hours at 70°. Yield : 22 g., 75·7%. The aldehyde was isolated through its bisulphite compound by the procedure adopted for diphenyl-4-aldehyde. Crystallisation from aqueous alcohol or light petroleum (b. p. 80—100°) yielded *fluorene-2-aldehyde* in colourless needles, m. p. 90° (Found : C, 86·3; H, 5·1. $C_{14}H_{10}O$ requires C, 86·6; H, 5·15%).

The influence of the solvent is very well illustrated with fluorene, since by replacement of the chlorobenzene by *o*-dichlorobenzene or tetrachloroethane, the above quantities and conditions being used, the yield is diminished to 62% and 52% respectively.

Fluorene-2-aldehyde readily yields the following derivatives : the *aniline* derivative crystallised from aqueous alcohol in pale yellow plates, m. p. 158° (Found : N, 5·2. $C_{20}H_{15}N$ requires N, 5·2%), the *phenylhydrazone* from alcohol in pale yellow leaflets, m. p. 202—203° (Found : N, 9·95. $C_{20}H_{16}N_2$ requires N, 10·0%), the *oxime* from light petroleum (b. p. 60—80°) in colourless plates, m. p. 156—157° (Found : N, 6·65. $C_{14}H_{11}ON$ requires N, 6·7%), and the *semicarbazone* from alcohol in colourless plates, m. p. 278° (Found : N, 16·6. $C_{16}H_{13}ON_3$ requires N, 16·7%).

Oxidation of Fluorene-2-aldehyde.—(a) *With alkaline potassium permanganate.* The aldehyde (1·9 g.) was oxidised with potassium permanganate as described above for dimethylnaphthaldehyde and yielded fluorenone-2-carboxylic acid (1·5 g.), which crystallised from alcohol in bright yellow needles, m. p. 338° with sublimation, unchanged by admixture with an authentic specimen, m. p. 338°, prepared as described below (Found : equiv., 223. Calc., 224) (Kruber, *Ber.*, 1932, **65**, 1382, and Dziewonski and Schnayder, *Bull. intern. acad. polonaise*, 1930, *A*, 529, record m. p. 332° and sublimation at about 340° respectively).

(b) *With sodium dichromate.* The aldehyde (3 g.) in glacial acetic acid (100 c.c.) was heated at 100° for 3 hours with sodium dichromate (10 g.), and the mixture poured into water (300 c.c.). The resulting precipitate was washed with water and dried; crystallisation from alcohol yielded fluorenone-2-carboxylic acid (1·5 g.), m. p. and mixed m. p. 338°. The alcoholic liquor, on concentration and dilution with water, yielded fluorene-2-carboxylic acid (0·9 g.) in white prisms, m. p. 275° (decomp. and partial sublimation), unchanged by admixture with a specimen prepared as described below (Found : equiv., 209. Calc., 210). On oxidation with potassium permanganate the fluorene-2-carboxylic acid was converted into fluorenone-2-carboxylic acid.

Fluorene- and Fluorenone-2-carboxylic Acids.—2-Aminofluorene, prepared from fluorene by Diels's method (*Ber.*, 1901, **34**, 1758), was converted into 2-cyanofluorene as described by Fortner (*Monatsh.*, 1904, **25**, 447). Hydrolysis of 2-cyanofluorene (3·5 g.) with hydrochloric acid yielded fluorene-2-carboxylic acid (2 g.) in colourless prismatic needles, decomposing at 275° with partial sublimation (Fortner records m. p. > 265°). Oxidation of this acid (1·5 g.) yielded fluorenone-2-carboxylic acid (1·1 g.) in bright yellow needles, m. p. 338° with sublimation (Fortner records m. p. > 275°; Kruber; and Dziewonski and Schnayder, *locc. cit.*).

Fluorenone-2-carboxylic acid (1 g.), obtained by oxidation of fluorenealdehyde, was added to fused potassium hydroxide (10 g.). The cooled melt, treated according to the procedure described by Kruber (*loc. cit.*), yielded diphenyl-2 : 4′-dicarboxylic acid (0·9 g.) in colourless prisms, m. p. 271—272° (Found : equiv., 121·5. Calc., 121) (Kruber records m. p. 272°).

Conversion of Fluorene-2-aldehyde into 2-Methylfluorene.—To zinc (20 g.), amalgamated by standing with 5% aqueous mercuric chloride solution (40 c.c.) for 1 hour, fluorene-2-aldehyde (5 g.) and hydrochloric acid (1 part conc. acid : 2 parts of water by vol.) (40 c.c.) were added. The mixture was heated under reflux for about 8 hours with addition of small amounts of concentrated hydrochloric acid until the zinc had dissolved. Dilution with water (100 c.c.) and distillation in steam yielded 2-methylfluorene (1 g.), which crystallised from aqueous alcohol in colourless plates, m. p. 102—103° (Kruber, *loc. cit.*, records m. p. 104°).

Experiments with Chloromethyleneformamidine.—A mixture of chloromethyleneformamidine (Hinkel, Ayling, and Beynon, J., 1935, 676), powdered aluminium chloride, and the hydrocarbon in the requisite solvent was protected from moisture and heated, with frequent shaking, in a water-bath. A series of experiments, in which the proportions of the reactants, the reaction temperature, and the period of heating were varied, was carried out with each hydrocarbon. Dark viscous liquids were obtained and the resulting aldehydes were isolated according to the procedure previously described for each aldehyde. The effect of varying the conditions was generally similar to that observed in the hydrogen cyanide synthesis with the same hydrocarbon. The following table gives the optimum conditions with the hydrocarbons studied; tetrachloroethane (50 c.c.) was used as solvent with the hydrocarbon (0·1 g.-mol.), the other proportions being referred to the hydrocarbon as unity. In no case here was the formation of a dialdehyde observed.

Hydrocarbon.	$(HCN)_2HCl$, mols.	$AlCl_3$, mols.	Reaction. Temp.	Reaction. Hours.	% Yield of aldehyde.
Benzene	2·5	4·0	65°	5	75
Naphthalene	2·0	0·5	70	4	66
Anthracene	2·0	2·0	50	3	50
Hydrindene	2·0	0·5	50	4	60
Acenaphthene	1·0	2·0	50	1·5	90
Fluorene	1·25	1·25	50	4	70

Diphenyl-4-aldehyde and -4 : 4′-dialdehyde.—Diphenyl (15·4 g., 1 mol.), heated with chloromethyleneformamidine (20 g., 2·2 mols.) and aluminium chloride (40 g., 3 mols.) in chlorobenzene (50 c.c.) for 5 hours at 80°, yielded diphenyl-4-aldehyde, m. p. 60°. A similar result was obtained with *o*-dichlorobenzene (50 c.c.) as the solvent. When tetrachloroethane (50 c.c.) was used as the solvent, the only aldehydic product was diphenyl-4 : 4′-dialdehyde, m. p. 145° (2·1 g.; 10%); phenylhydrazone, m. p. 278° (compare Ullmann, *Annalen*, 1904, **332**, 38). With less aluminium chloride (33·3 g., 2·5 mols.) and reaction at 60° for 6 hours in tetrachloroethane (50 c.c.), only dialdehyde (2·7 g.; 13%) was again obtained. In each tetrachloroethane experiment, the remainder of the diphenyl was partly unchanged and partly converted into a brown non-steam-volatile solid.

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