157. *Hydrogen Cyanide Synthesis of Aromatic Aldehydes. Part I. Dibenzfuran-3-aldehyde.*

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NOT only phenols and phenolic ethers (compare Gattermann, *Annalen*, 1907, **357**, 313) but also many aromatic hydrocarbons lend themselves to the hydrogen cyanide aldehyde synthesis (J., 1936, 339). It has now been found that, in general, the introduction of substituents other than chlorine (J., 1936, 342), hydroxyl or alkoxyl tends partly or completely to inhibit aldehyde formation. For instance, the following compounds, when subjected to the reaction, are either recovered unchanged, or in several cases, converted into resin-like solids: nitrobenzene, *o*-nitrophenol, benzoic and cinnamic acids, aniline, diphenylamine and dimethylaniline, azobenzene, benzophenone, anthraquinone and 1 : 5-dihydroxyanthraquinone. Although phenol and diphenyl readily yield aldehydes, yet, contrary to expectation, 2-hydroxydiphenyl, 2-methoxydiphenyl and 2 : 2′-dihydroxydiphenyl do not. In the last case, the aluminium chloride causes the removal of a molecule of water, resulting in an almost quantitative conversion into dibenzfuran (diphenylene-oxide). The isolation of this compound, however, suggested that the introduction of the ethereal oxygen bridge into diphenyl should, at any rate, not inhibit the introduction of the aldehyde group. This expectation has been realised and the reactions of the resulting aldehyde have been investigated.

The aldehyde group in dibenzfuranaldehyde occupies position 3 (para to the oxygen link), since oxidation yields dibenzfuran-3-carboxylic acid, m. p. 247° (Mayer and Krieger, *Ber.*, 1922, **55**, 1659). *Dibenzfuran*-3-*aldehyde* displays the characteristic properties of aromatic aldehydes and readily undergoes the benzoin condensation, the corresponding benzil and benzilic acid thence being obtained in the usual manner.

When the aldehyde is subjected to the Perkin reaction, the corresponding *acrylic acid* is obtained, which yields very sparingly soluble salts with alkalis, the ammonium salt being the most and the sodium salt the least soluble in water. The aldehyde also condenses with malonic acid, yielding a dibasic acid which on heating is converted into the same acrylic acid.

With dimethylaniline, condensation proceeds normally to yield a leuco-base, which is readily oxidised to an intense green dye of the malachite-green series.

EXPERIMENTAL.

Preparation of Dibenzfuran-3-aldehyde.—The procedure was that described by Hinkel, Ayling, and Beynon for the general preparation of aldehydes (J., 1936, 341). Dibenzfuran (21 g., 1 mol.), tetrachloroethane (80 c.c.), hydrogen cyanide (15 c.c., 3 mols.), and aluminium chloride (42 g., 2·5 mols.) were allowed to react in presence of a stream of hydrogen chloride for 5 hours at 80°. The dark viscous mixture was poured on ice and concentrated hydrochloric acid and boiled for a few minutes, and the solvent distilled in steam; the residual oil solidified on cooling. The solid was extracted with ether, the ethereal solution shaken for 8 hours with excess of saturated aqueous sodium bisulphite, and the light brown bisulphite compound removed, washed with ether, and boiled for 5 minutes with dilute sulphuric acid. The oil obtained solidified on cooling and crystallisation from light petroleum (b. p. 80—100°) yielded *dibenzfuran-3-aldehyde* (21 g.; 81%) in colourless laminæ, m. p. 68° (Found: C, 79·0; H, 4·2. $C_{13}H_8O_2$ requires C, 79·6; H, 4·1%). The aldehyde readily yielded the following derivatives by the usual methods: the *phenylhydrazone*, pale yellow plates, m. p. 162°, from alcohol (Found: N, 9·8. $C_{19}H_{14}ON_2$ requires N, 9·8%); the *aniline* derivative, pale yellow needles, m. p. 131°, from light petroleum (b. p. 80—100°) (Found: N, 5·1. $C_{19}H_{13}ON$ requires N, 5·2%); the *semicarbazone*, colourless plates, m. p. 240°, from alcohol (Found: N, 16·5. $C_{14}H_{11}O_2N_3$ requires N, 16·6%); and the *oxime*, colourless laminæ, m. p. 129°, from light petroleum (b. p. 80—100°) (Found: N, 6·6. $C_{13}H_9O_2N$ requires N, 6·6%).

Oxidation of Dibenzfuran-3-aldehyde.—The aldehyde (1·0 g.), suspended in 4*N*-sodium hydroxide (1 c.c.), was boiled with a solution of potassium permanganate (1·2 g.) in water (100 c.c.) until the colour had disappeared. The filtered liquid, on acidification with concentrated hydrochloric acid, yielded a white precipitate, which was washed with water and crystallised from aqueous alcohol, dibenzfuran-3-carboxylic acid (0·7 g.) separating in colourless needles, m. p. 247° after slight softening at 237° (Found: equiv., 212. Calc., 212) (Mayer and Kreiger, *loc. cit.*, record m. p. 246—247°, and name it diphenyleneoxide-5-carboxylic acid on their system of ring numbering).

Benzoin Condensation of Dibenzfuran-3-aldehyde.—The aldehyde (4 g.) was boiled under reflux for 3 hours with a solution of potassium cyanide (0·45 g.) in alcohol (15 c.c.) and water (5 c.c.), and the resulting mixture poured into water (20 c.c.); an oily layer then separated. This, on crystallisation from benzene–light petroleum (b. p. 80—100°), yielded *3-dibenzfuroyl-3-dibenzfurylcarbinol*, $C_{12}H_7O{\cdot}CO{\cdot}CH(OH){\cdot}C_{12}H_7O$, in very pale yellow, stellate clusters (3 g.), m. p. 130° (Found: C, 79·5; H, 4·1. $C_{26}H_{16}O_4$ requires C, 79·6; H, 4·1%).

Oxidation of the Carbinol.—The carbinol (2 g.) and nitric acid (*d* 1·42, 1·7 c.c.) were heated at 100° for 2 hours, and the resulting brown solid washed with water. *Bis-3-dibenzfuryl diketone* (1·8 g.) crystallised from alcohol in microscopic yellow needles, m. p. 236—237° (Found: C, 79·9; H, 3·65. $C_{26}H_{14}O_4$ requires C, 80·0; H, 3·6%).

"*Benzilic Acid*" *Transformation.*—The diketone (2 g.) and potassium hydroxide (1·2 g.) were heated with water (3 c.c.) and alcohol (14 c.c.) for 10 minutes at 100°, the mixture poured into water (100 c.c.), and the filtered liquid acidified with concentrated hydrochloric acid. The precipitate, crystallised from aqueous alcohol, gave *bis-3-dibenzfurylglycollic acid* (2 g.) in pale yellow, microscopic needles, m. p. 248° (Found: C, 76·6; H, 3·9. $C_{26}H_{16}O_5$ requires C, 76·5; H, 3·9%).

β-Dibenzfuran-3-acrylic Acid.—Dibenzfuran-3-aldehyde (5 g.) was boiled under reflux with fused sodium acetate (4 g.) and acetic anhydride (25 c.c.) for 8 hours and the mixture was poured into water (200 c.c.) and warmed with an excess of sodium carbonate. The brown product, crystallised from toluene, yielded *β-dibenzfuran-3-acrylic acid* (6 g.) in colourless needles, m. p. 239—240° (Found: C, 75·6; H, 4·2. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%), almost insoluble in sodium carbonate and sodium hydroxide but more soluble in potassium hydroxide and ammonia solutions. The *methyl* ester, prepared by heating the acid (1·2 g.) with hydrogen chloride in methyl alcohol (60 c.c.), crystallised from aqueous alcohol in colourless plates, m. p. 130° (Found: C, 76·1; H, 4·7. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8%).

Dibenzfuryl-3-methylenemalonic Acid.—Dibenzfuran-3-aldehyde (4 g.), malonic acid (2·1 g.), and glacial acetic acid (2·0 c.c.) were heated at 100° for 3 hours. The solid obtained on cooling was washed with chloroform (20 c.c.) and crystallised from aqueous alcohol, *dibenzfuryl-3-methylenemalonic acid* (3 g.) separating in very pale yellow needles, m. p. 213° (decomp.) (Found : C, 67·9; H, 3·5. $C_{16}H_{10}O_5$ requires C, 68·1; H, 3·5%), readily soluble in alkalis, alcohol and acetic acid. The acid lost carbon dioxide rapidly at 213—215° and the residue, crystallised from toluene, yielded β-dibenzfuran-3-acrylic acid, m. p. and mixed m. p. 239—240°.

Condensation of Dibenzfuran-3-aldehyde with Dimethylaniline.—The aldehyde (4 g.), dimethylaniline (25 c.c.), and freshly fused zinc chloride (33 g.) were heated at 100° for 5 hours with frequent stirring. Water (200 c.c.) was added to the dark green, viscous liquid and the removal of the excess of dimethylaniline by distillation in steam left an oil which solidified on cooling. The solid was crystallised from alcohol, in which it was sparingly soluble, and then from alcohol–benzene, yielding the leuco-base, *3-dibenzfuryl-*pp′*-bis(dimethylamino)diphenylmethane* (7 g.), in colourless needles, m. p. 172° (Found : C, 82·7; H, 6·5; N, 6·5. $C_{29}H_{28}ON_2$ requires C, 82·8; H, 6·6; N, 6·6%).

Oxidation of the Leuco-base.—The leuco-base (4 g.) was dissolved in 4*N*-hydrochloric acid (10 c.c.) and water (400 c.c.), dilute acetic acid (1·6 g. in 5 c.c. of water) added, and the solution stirred while a paste of lead peroxide (3 g.) in water was added. After 10 minutes a solution of sodium sulphate crystals (6 g.) in water (20 c.c.) was added, and the well-stirred mixture filtered to remove lead sulphate. The addition of anhydrous zinc chloride (6 g.) in water (50 c.c.) to the green filtrate, followed by saturated aqueous sodium chloride (500 c.c.), resulted in the deposition of the zinc chloride double salt of 3-dibenzfuryl-*pp′*-bis(dimethylamino)-diphenylmethyl chloride in greenish-purple needles (5·1 g.). It was not, however, found possible to obtain the compound sufficiently pure for analysis.

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