LXXXVII.—*The Condensation of Aromatic Aldehydes with Phenylacetonitrile.*

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FROST (*Annalen*, 1889, **250**, 157) showed that benzaldehyde condenses with phenylacetonitrile in presence of sodium ethoxide, giving an excellent yield of α-phenylcinnamonitrile. The reaction has now been extended to a series of phenolic aldehydes and their methylethers, and it has been found that (i) 2 : 4-dimethoxybenzaldehyde, veratraldehyde, and anisaldehyde give almost quantitative yields of 2 : 4-*dimethoxy*-, 3 : 4-*dimethoxy*-, and 4-methoxy-α-phenylcinnamonitrile (for the last-mentioned, compare Frost, *loc. cit.*) respectively; (ii) hydroxybenzaldehydes give poor yields of the condensation products, which, however, are much improved in presence of potassium hydroxide in alcohol. The nature of the condensation product depends essentially on the position of the hydroxyl group in the aldehyde, the presence of *o*-hydroxyl favouring the formation of coumarins (compare Borsche and Streitberger, *Ber.*, 1904, **37**, 3165); for instance, 2-hydroxy-4-methoxybenzaldehyde and *o*-vanillin yield respectively 7-methoxy-3-phenylcoumarin and 8-*methoxy*-3-*phenylcoumarin*. The latter are formed almost quantitatively in presence of 6*N*-alcoholic potash.

4-Hydroxy-2-methoxybenzaldehyde and vanillin condense with phenylacetonitrile in presence of sodium ethoxide to give 4-*hydroxy*-2-*methoxy*- and 4-*hydroxy*-3-*methoxy*-α-*phenylcinnamonitrile* respectively. The yield of the latter nitrile was 40% (Bistrzycki and Stelling, *Ber.*, 1901, **34**, 3081, state that vanillin does not condense with phenylacetonitrile in presence of sodium ethoxide), and the yields of both nitriles were increased to 90% when 6*N*-alcoholic potash was used. The poor yields of condensation products obtained when sodium ethoxide was employed were due to the fact that the sodium salts of the hydroxybenzaldehydes mentioned above are all sparingly soluble in alcohol.

As all attempts to hydrolyse the nitriles formed in the condensations were unsuccessful, it would appear that they are *cis*-forms, in view of the observations of Pfeiffer (*Annalen*, 1928, **467**, 162) that *cis*-forms of certain olefinic nitriles resist hydrolysis whereas the *trans*-modifications are hydrolysed with comparative ease.

EXPERIMENTAL.

The general procedure for the condensations in which sodium ethoxide was employed consisted in dissolving the aldehyde (1 mol.) and phenylacetonitrile (1 mol.) in the minimum amount of alcohol and adding sodium ethoxide (1 mol.) in alcohol. Methoxybenzaldehydes condensed readily under these conditions, heat being evolved, and the product crystallised within a few minutes. Hydroxybenzaldehydes required to be left for 2 days before condensation was complete; the product was then precipitated by addition of dilute hydrochloric acid. Condensations in which alcoholic potassium hydroxide was employed required heating on the water-bath for 8 hours. An excess of phenylacetonitrile (3 mols.) and potassium hydroxide (4 mols.) was employed, the excess of the former being afterwards removed in steam. The product separated, on acidification of the cold alkaline solution, as an oil which slowly solidified.

2 : 4-*Dimethoxy-α-phenylcinnamonitrile* crystallises from alcohol in long, pale yellow needles, m. p. 95°, readily soluble in the usual solvents (Found: C, 77·1; H, 5·7. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7%). Unlike 2 : 4-dimethoxy-α-phenylcinnamic acid, the nitrile could not be demethylated.

3 : 4-*Dimethoxy-α-phenylcinnamonitrile* forms long, pale cream needles, m. p. 88°, from alcohol. Kaufmann (*Ber.*, 1919, **52**, 1434) predicted the colour of this compound as white. It is insoluble in water, but readily soluble in the usual organic solvents (Found: C, 77·0; H, 5·6; OMe, 24·25. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7; OMe, 24·15%).

8-*Methoxy-3-phenylcoumarin* forms straw-coloured needles, m. p. 155·5°, insoluble in water, but readily soluble in hot methyl or ethyl alcohol (Found: C, 76·2; H, 4·8; OMe, 12·2. $C_{16}H_{12}O_3$ requires C, 76·2; H, 4·8; OMe, 12·3%).

4-*Hydroxy-2-methoxy-α-phenylcinnamonitrile* crystallises from acetic acid in pale yellow needles, m. p. 195° (Found: C, 76·5; H, 5·2; OMe, 12·1. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·15; OMe, 12·2%).

2-*Methoxy-4-acetoxy-α-phenylcinnamonitrile*, obtained by boiling the above nitrile with acetic anhydride for 4 hours, formed white rhombic plates, m. p. 158°, from acetic acid (Found: C, 73·4; H, 4·9. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1%). It was also isolated in an attempted demethylation of the above nitrile with hydriodic acid dissolved in acetic anhydride, but on demethylation by Zeisel's method 7-hydroxy-3-phenylcoumarin, m. p. 208°, was obtained.

4-*Hydroxy-3-methoxy-α-phenylcinnamonitrile* forms pale cream-coloured needles, m. p. 99°, from dilute alcohol. It gives a bright yellow solution in hot water. The solutions in methyl and ethyl alcohols have a pale yellow colour, and the solutions in benzene and chloroform are almost colourless (Found: C, 76·4; H, 4·9; OMe, 12·0%).

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