The Structure of Hydrocyansalide, a New Reagent for Magnesium

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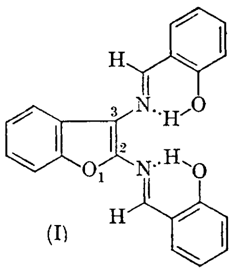
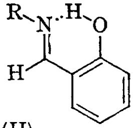
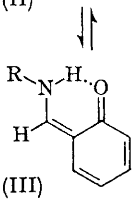
RECENTLY a very useful reagent for the determination of magnesium by the fluorescence technique has been described,[1,2] namely Hydrocyansalide originally prepared by Reinecke and Beilstein[3] from ammonia, hydrogen cyanide, and salicylaldehyde. Because of its newly discovered importance and in connection with other work† we have investigated the, as yet unknown, structure of this compound and present here the expression (I) for the yellow form. Another modification, called "brown Hydrocyansalide", was obtained[3] by heating the yellow form under reflux in ethanol and is probably the result of the thermochromism, (II) to (III), as has already been observed in salicylidene anils.[4]

The molecular formula[3] was confirmed by mass spectrometry, and the spectral properties, $\nu_{\max}$ (Nujol) 3050, 1620 cm.$^{-1}$, and $\lambda_{\max}$ (ethanol) 286, 344, 431 mμ (ϵ 24,500, 23,600 and 26,900) were comparable in part to those of salicylidene-*p*-toluidine [(II), R = *p*-tolyl] $\lambda_{\max}$ (ethanol) 342 mμ (ϵ 14,200) and in part to other salicylidene-2-aminobenzofurans (VI) prepared from secondary amines (see later). The n.m.r. spectrum defined the two unsplit methine protons at τ 1.40 and 1·15 and also two exchangeable, intramolecularly hydrogen-bonded protons at τ −2·35 and −3·05, in deuterochloroform. The presence of two potential salicylidene residues was further demonstrated by acid hydrolysis, which provided an almost quantitative yield of salicylaldehyde along with the amino-acid (IV; R = CO_2H) and a trace of the corresponding diketopiperazine. Identification of (IV; R = CO_2H) was completed by comparison with an authentic specimen, obtained by hydrolysis and demethylation of the hydantoin from *o*-methoxybenzaldehyde.

Although the spectral and chemical evidence cited here is in accord with the structure (I) we


(I)


(II)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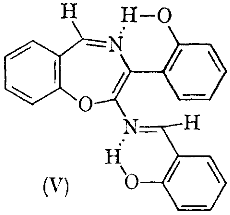
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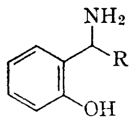
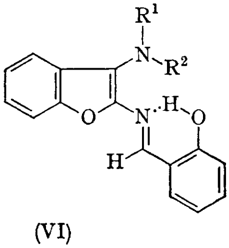
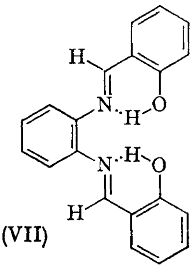

(IV)


(VI)


(VII)

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† We thank Professor D. H. R. Barton for access to some of his unpublished work in this field.

sought to eliminate other possible isomers, *e.g.*, the 1,4-benzoxazepine (V), which because of the unknown nature of its chromophore could not be readily excluded by the spectral data. Such an exclusion was achieved through bromination (pyridine perbromide) of (I) to a bromo-derivative having the same spectral properties as the starting material. Hydrolysis produced a mixture of bromosalicylaldehydes and the amino-acid (IV; R = CO_2H). No salicylaldehyde was detected by an isolation procedure carefully standardized with authentic material. The structure of Hydrocyansalide follows as the diaminobenzofuran (I).

The mechanism of formation of this product presumably involves the salicylidene-anil of the amino-nitrile (IV; R = CN) in which the cyano-function undergoes an intramolecular attack by the neighbouring hydroxyl group, thereby releasing this second amino-function for reaction with the aldehyde. In accord with this suggestion a secondary base, *e.g.*, diethylamine or *N*-methylaniline, with salicylaldehyde and potassium cyanide gives the corresponding benzofuran (VI) in good yield.

The ultraviolet spectrum of the diethylamine derivative (VI; $R^1 = R^2 =$ Et) has λ_{max} (ethanol) 413 mμ (ϵ 22,800) and the *N*-methylaniline derivative (VI; R^1 = Ph, R^2 = Me) has λ_{max} (ethanol) 425 mμ (ϵ 17,400). This suggests that the chromophore in (VI) as well as in (I) is the salicylidene-2-aminobenzofuran with an auxochromic substituent at position 3. The strong bathochromic shift ($\Delta\lambda$ = 98 mμ) compared to bis-salicylidene-*o*-phenylenediamine (VII) is paralleled in other benzofurans. *e,g.*, 2-acetylbenzofuran[5a] and acetophenone[5b] ($\Delta\lambda$ = 50—55 mμ).

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[1] R. M. Dagnall, R. Smith, and T. S. West, *J. Chem. Soc.* (*A*), 1966, 1595.

[2] R. M. Dagnall, R. Smith, and T. S. West, *Analyst*, 1967, **92**, 20.

[3] A. Reinecke and F. Beilstein, *Annalen*, 1865, **136**, 169.

[4] A. Hantzsch, *Ber.*, 1906, **39**, 3080; M. D. Cohen and G. M. J. Schmidt, *J. Phys. Chem.*, 1962, **66**, 2442.

[5] (a) "Organic Electronic Spectral Data", Vol. II, ed. H. E. Ungnade, Interscience, New York and London, 1960, p. 203; (b) *ibid.*, p. 134.