TABLE I

	Methyl	Ethyl	*n*-Propyl	*n*-Butyl
Sp. gr. at 25°	1.48	1.35	1.28	1.23
Ref. index 20°	1.414	1.416	1.422	1.427
B. p., °C.	48.1 at 29 mm.	42.3 at 10 mm.	53.2 at 10 mm.	69 at 10 mm.
% S, calcd.	24.53	22.18	20.18	18.65
% S, found	24.8 ± 0.2	22.0 ± 0.2	20.4 ± 0.2	18.3 ± 0.2
% Cl, calcd.	27.13	24.54	22.38	20.56
% Cl, found	27.0 ± 0.1	24.5 ± 0.1	22.2 ± 0.1	20.5 ± 0.1

They are colorless liquids, insoluble in water, but quite soluble in the common organic solvents.

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Nitrogen-Terminated Conjugated Systems and Maleic Anhydride

BY FELIX BERGMANN

The ability of 9-vinylphenanthrenes to condense with maleic anhydride[1] induced us to investigate whether conjugated systems consisting of a cyclic C–N double bond and an exocyclic ethylenic linkage would add maleic anhydride. 2-Styrylquinoline gave a well-defined reaction product, which, however, besides the components, contained one molecule of water, and therefore was styrylquinolinium maleate. This became obvious in its reaction with diazomethane, yielding dimethylpyrazoline-4,5-dicarboxylate.[2] Analogous observations have been made recently by La Parola[3] in the case of antipyrine and pyramidone. For comparison purposes, we studied the interaction between maleic anhydride and cinnamylidene-aniline, which contains the nitrogen-terminated conjugated system entirely in an open chain. Here, too, the reaction involves one molecule of water (from the air), but the maleate, presumably formed as above, is unstable and decomposes spontaneously into cinnamic aldehyde and maleanilic acid, HOOCCH=CHCONNH-C_6H_5.

Experimental

2-Styrylquinoline[4] (1.2 g.) and **maleic anhydride** (0.5 g.) were heated on the water-bath or in xylene solution for some minutes. The mixture turned yellow at once and deposited on cooling yellow crystals, which were recrystallized from xylene or butyl acetate. 2-Styrylquinolinium maleate formed long, silky needles, m. p. 165–167°. *Anal.* Calcd. for $C_{21}H_{17}O_4N$: C, 72.6; H, 4.9. Found: C, 72.8; H, 5.3. The salt was kept in contact with an excess of ethereal diazomethane solution; on evaporation a crystalline mass was obtained which was triturated with light petroleum (b. p. 80–100°) and recrystallized from the same solvent. Dimethyl pyrazoline-4,5-dicarboxylate was obtained in the form of leaflets, m. p. 103–105°. *Anal.* Calcd. for $C_7H_{10}O_4N_2$: C, 45.2; H, 5.4; N, 15.1. Found: C, 44.8; H, 5.5; N, 15.6.

Cinnamylidene-aniline[5] (1 g.) and **maleic anhydride** (0.5 g.) were heated together on the water-bath; the mixture turned brown, then red and an intense odor of cinnamic aldehyde developed. After fifteen minutes, benzene was added, whereupon maleanilic acid crystallized, yield 300 mg.; from butyl acetate as rhombohedra, m. p. 210°.[6] *Anal.* Calcd. for $C_{10}H_9O_3N$: C, 62.8; H, 4.7; N, 7.3. Found: C, 62.5; H, 4.5; N, 7.7. Diazomethane gave as above the expected methyl ester-anilide of pyrazoline-4,5-dicarboxylic acid, from xylene or butyl acetate; crystals, m. p. 175° (dec.). *Anal.* Calcd. for $C_{12}H_{13}O_3N_3$: N, 17.0. Found: N, 17.4.

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(1) E. Bergmann and F. Bergmann, THIS JOURNAL, **59**, 1443 (1937).

(2) Von Pechmann, *Ber.*, **27**, 1888 (1894); v. Pechmann and Burkard, *ibid.*, **33**, 3590 (1900).

(3) La Parola, *Gazz. chim. ital.*, **67**, 645 (1937).

(4) Skraup and Boehm, *Ber.*, **59**, 1013 (1927).

(5) Doebner and v. Miller, *ibid.*, **16**, 1665 (1883).

(6) The highest m. p. recorded before is 198° [Auwers and Schleicher, *Ann.*, **309**, 347 (1899)]. A preparation made according to Anschütz [*Ber.*, **20**, 3214 (1897)] showed m. p. 210°, after recrystallization from butyl acetate or butyl alcohol.

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The Calculation of the Dissociation Constant of Weak Acids in H_2O–D_2O Mixtures

BY FRANK BRESCIA

From the exchange equilibria

$$\begin{array}{lll} 2\mathrm{DCl} + \mathrm{QH_2} = 2\mathrm{HCl} + \mathrm{QD_2} & K_1 = 14.64 & (1) \\ \mathrm{QH_2} + \mathrm{D_2O} = \mathrm{QD_2} + \mathrm{H_2O} & K_2 = 0.96 & (2) \\ \mathrm{H_2O} + \mathrm{D_2O} = 2\mathrm{HDO} & K_3 = 3.27 & (3) \end{array}$$

Korman and La Mer[1] have calculated the equilibrium constant for the process, $D^+ + H_2O = H^+ + HDO$, to be $K_4 = 7.1$. Their derived equation for the calculation of dissociation constants of weak acids in H_2O–D_2O mixtures

$$K_{\mathrm{M}} = K_{\mathrm{D}} \left[1 + 7.1 \frac{C_{\mathrm{H_2O}}}{C_{\mathrm{HDO}}} \Big/ 1 + 7.1 \left(\frac{K_{\mathrm{D}}}{K_{\mathrm{H}}}\right) \frac{C_{\mathrm{H_2O}}}{C_{\mathrm{HDO}}}\right] \quad (5)$$

contains, therefore, the factor 7.1. K_{M} is the dissociation constant of the acid in the mixtures of H_2O–D_2O, K_{D} is the dissociation constant of

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(1) Korman and La Mer, THIS JOURNAL, **58**, 1396 (1936).