complexes of tertiary amines with acids and relatively non-polar, whereas true salts like sodium or lithium salts are not sufficiently soluble in benzene to test; and (2) ions in benzene solution are not "free" (*i. e.*, solvated by only solvent), but are predominantly associated into pairs and higher aggregates, which should have much less effect on the polarity of the medium than free ions.

Before it was known from the experiments described above that there is no second order capture of any intermediate by tertiary ammonium chlorides, experiments were made in the hope of demonstrating such a competition by using tertiary ammonium chlorides with trityl bromide.[6] If competition were successful, trityl chloride should be produced. With 0.105 *M* trityl bromide, 0.146 *M* diethylaniline, 0.142 *M* methanol and 0.161 *M* diethylanilinium chloride (solubility 0.085 *M*), most of the trityl bromide was converted to trityl chloride (0.068 *M* at forty-three min., the first point analyzed), which then exhibited the expected half life for subsequent methanolysis of three hours. A control experiment omitting the diethylanilinium chloride confirmed that the half life for methanolysis of the trityl bromide was less than ten minutes. With 0.105 *M* trityl bromide and 0.138 *M* diethylanilinium chloride (solubility in this medium 0.026 *M*) *in the absence of both methanol and diethylaniline,* nearly quantitative conversion to trityl chloride (established by kinetic analysis with methanol) occurred with a half life of less than five minutes.

We plan to investigate this surprising halide exchange further, using trityl fluoride, which may react sufficiently slowly to permit a kinetic study. Based on the results obtained thus far, however, it seems likely that the rate determining step is again a concerted, push-pull process, this time involving chloride ion acting as the nucleophilic reagent (N) to attack carbon, and diethylanilinium ion or hydrogen chloride as the electrophilic reagent (E) to attack bromine.

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[6] These experiments were suggested by Dr. Hine.

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Dialkyl Ethers of Ethyleneglycol and Diethyleneglycol

BY M. SULZBACHER AND E. BERGMANN

The observation that potassium hydroxide dissolves readily in monoalkyl ethers of ethyleneglycol and diethyleneglycol,[1] facilitates the preparation of corresponding dialkyl ethers.[2]

Glycol Ethyl (2-Ethylhexyl) Ether.—At a temperature of 35° and with good agitation, 97.5 g. (0.505 mole) of 2-ethylhexyl bromide[3] was added to a solution of 33 g. of technical potassium hydroxide (0.5 mole) in 135 g. (1.5 mole) of ethyleneglycol monoethyl ether. The slightly exothermic reaction was complete when the mixture was heated at 70° for two hours. The filtered solution was fractionated: (a) b. p. 108–109°, 2-ethylhexene,[4] 25 g. (45% of theory); (b) b. p. 130–140°, excess ethyleneglycol monoethyl ether; (c) b. p. 118–119° (15 mm.) glycol ethyl (2-ethylhexyl) ether, 48.6 g. (48%); d^{24}_{24} 0.8460; $n^{24}\text{D}$ 1.4198; mol. refraction, 60.40 (calcd., 60.91).

Anal. Calcd. for $C_{12}H_{26}O_2$: C, 71.3; H, 12.9. Found: C, 71.0; H, 12.9.

Glycol ethyl benzyl ether was obtained in a yield of 140 g. (62.5%) by adding to 66 g. of technical potassium hydroxide (1 mole) in 180 g. (2 moles) of glycol monoethyl ether, 126 g. (1 mole) of benzyl chloride at 45° and heating at 65° for one hour; b. p. 124° (16 mm.); d^{24}_{24} 1.005; $n^{24}\text{D}$ 1.4905; mol. refraction, 52.04 (calcd., 52.70).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.3; H, 9.0. Found: C, 73.0; H, 9.3.

Glycol ethyl allyl ether was obtained in a yield of 45.5 g. (92.4%) when 60.5 (0.5 mole) of allyl bromide was added to a solution of 33 g. of technical potassium hydroxide (0.5 mole) in 90 g. (1 mole) of glycol monoethyl ether. The reaction was considerably exothermic (67°); b. p. 135°; d^{24}_{24} 0.884; $n^{24}\text{D}$ 1.4093; mol. refraction, 36.90 (calcd., 37.35).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.6; H, 10.8. Found: C, 64.5; H, 11.1.

Cyclohexyl bromide gave only cyclohexene under the above conditions.

Diethyleneglycol Ethyl Butyl Ether.—Technical potassium hydroxide (66 g., 1 mole) dissolved in 134 g. (1 mole) of diethyleneglycol monoethyl ether (b. p. 85–87° (12 mm.)) with liberation of heat. Addition of 50 cc. of toluene produced a clear solution, to which 140 g. (1.02 moles) of butyl bromide was added gradually. The slightly exothermic reaction was completed at 80° (one hour). Under these conditions, 35% of the butyl bromide remained unchanged, and 100 g. (52.6% of theory) of the desired ether was isolated. When only 0.25 mole of butyl bromide was employed, the yield of the ethyl butyl ether was quantitative; b. p. 104–105° (13 mm.); d^{24}_{24} 0.977; $n^{24}\text{D}$ 1.4599; mol. refraction, 53.00 (calcd., 53.31).

Anal. Calcd. for $C_{10}H_{22}O_3$: C, 63.2; H, 11.6. Found: C, 63.0; H, 11.9.

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[1] Ch. Weizmann and co-workers, *J. Soc. Chem. Ind.*, **67**, 203 (1948).

[2] Berggardh, *Chem. Zentr.*, **105**, I, 2267 (1934); Liston and Dehn, THIS JOURNAL, **60**, 1264 (1938); Van Duzee and Adkins, *ibid.*, **57**, 147 (1935).

[3] J. v. Braun and Manz, *Ber.*, **67**, 1696 (1934); Ch. Weizmann, E. Bergmann and L. Haskelberg, *Chem. and Ind.*, **56**, 587 (1937).

[4] J. v. Braun and Manz, *loc. cit.*, Church, Whitmore and McGrew, THIS JOURNAL, **56**, 176 (1934).

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Formaldehyde Bis-(β-ethoxyethyl) and Bis-[β-(β-ethoxyethoxy)-ethyl]-acetal

BY M. SULZBACHER

Methylene chloride reacted with the monoethyl ethers of glycol and diethyleneglycol in presence of potassium hydroxide to give the abovenamed compounds.

(a) To a solution of 66 g. of technical potassium hydroxide (1 mole potassium hydroxide) in 90 g. (1 mole) of glycol monoethyl ether, a solution of 43 g. (0.5 mole) of methylene chloride in 25 cc. of toluene was added and the mixture heated at 60–70° for three hours. Fractional distillation of the solution, which had been filtered from the potassium chloride formed (42 g.), gave 35 g. (36%)