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; $n^{24}\mathrm{D}$ 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; $n^{24}\mathrm{D}$ 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; $n^{24}\mathrm{D}$ 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; $n^{24}\mathrm{D}$ 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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DANIEL SIEFF RESEARCH INSTITUTE
WEIZMANN INSTITUTE OF SCIENCE
REHOVOTH, ISRAEL

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 above-named 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%)

of formaldehyde bis-(β-ethoxyethyl)-acetal, b. p. 108° (13 mm.)[1]; d^{24}_{24} 0.9688; n^{24}_D 1.4200; mol. refraction, 50.21 (calcd., 50.33). The colorless substance, which is only sparingly soluble in water, liberates formaldehyde upon treatment with dilute sulfuric acid.

Anal. Calcd. for $C_9H_{20}O_4$: C, 56.3; H, 10.4. Found: C, 56.5; H, 10.4.

(b) The same reaction, carried out with 134 g. (1 mole) of diethyleneglycol monoethyl ether, gave 65 g. of potassium chloride and 30 g. (21%) of formaldehyde bis-[β-(β-ethoxyethoxy)-ethyl]-acetal, b. p. 170–174° (19 mm.); d^{24}_{24} 1.033; n^{24}_D 1.4445; mol. refraction, 72.00 (calcd., 72.09). The substance is easily soluble in water.

Anal. Calcd. for $C_{13}H_{28}O_6$: C, 55.7; H, 10.0. Found: C, 55.4; H, 9.8.

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(1) Palomaa and Aalto (*Ber.*, **66**, 468 (1933)) mention this substance, without describing its preparation or physical constants.

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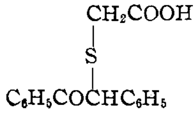
LONDON, ENGLAND

RECEIVED JULY 22, 1949

Reaction of Benzoins with Thioglycolic Acid

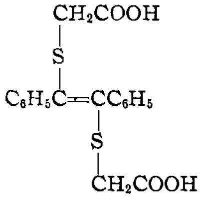
BY SYLVIA TEICH[1] AND DAVID Y. CURTIN

The reaction of benzoin with thioglycolic acid at 100° in the presence of hydrogen chloride has been shown to lead to S-desylthioglycolic acid (I) and a lesser amount of the substituted stilbene (II).[2]



$$\begin{array}{c} CH_2COOH \\ | \\ S \\ | \\ C_6H_5CO\underset{}{C}HC_6H_5 \end{array}$$

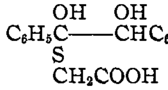
I



$$\begin{array}{c} CH_2COOH \\ | \\ S \\ | \\ C_6H_5C{=}CC_6H_5 \\ | \\ S \\ | \\ CH_2COOH \end{array}$$

II

While the over-all result of the reaction is an acid-catalyzed replacement of hydroxyl by the mercaptan,[3] it seemed possible that its course might be a more complicated one involving the hemimercaptol (III) as an intermediate. A pinacol-type rearrangement of III with migration of hydrogen would lead to I.



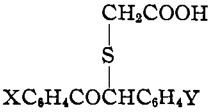
$$\begin{array}{l} \quad\ OH\quad OH \\ C_6H_5C\text{——}CHC_6H_5 \\ \qquad S \\ \quad CH_2COOH \end{array}$$

III

We had hoped to decide between these two alternatives by subjecting unsymmetrically substituted benzoins to the reaction. When a molecule with structure IV undergoes the reaction, a direct replacement should lead to V but a mechanism involving attack at the carbonyl group followed by rearrangement should give VI.

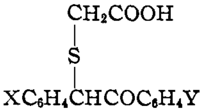
$XC_6H_4COCHOHC_6H_4Y$

IV



$$\begin{array}{c} CH_2COOH \\ | \\ S \\ | \\ XC_6H_4COCHC_6H_4Y \end{array}$$

V



$$\begin{array}{c} CH_2COOH \\ | \\ S \\ | \\ XC_6H_4CHCOC_6H_4Y \end{array}$$

VI

Five unsymmetrical benzoins (Table I) were prepared and treated with thioglycolic acid and hydrogen chloride. The desyl thioglycolic acids were not isolated but were cleaved with dilute sodium hydroxide to the corresponding desoxybenzoins. This cleavage reaction has been found to give desoxybenzoins in good yields without rearrangement.[1,4] The results are summarized in Table I. The mixtures of desoxybenzoins were analyzed either by isolation of the constituents or, in the case of the *p*-chlorodesoxybenzoins, by the use of a melting point diagram.

It will be seen that a nearly identical mixture of products was obtained from either the 4- or 4'-substituted benzoin. This suggests either that equilibrium is established between the two benzoins prior to reaction (or between two intermediates during the reaction) or that the two isomers react by way of a common intermediate. A small amount of 4'-chlorobenzoin could be recovered from the reaction of 4-chlorobenzoin with thioglycolic acid.

The acid-catalyzed isomerization of 4'-methoxybenzoin has been reported by Blum-Bergmann[5]

TABLE I

REACTION OF BENZOINS $X–C_6H_4COCHOHC_6H_4–Y$ WITH THIOGLYCOLIC ACID

Benzoin $X—C_6H_4COHOHC_6H_4—Y$	Ref. to synthesis	Conditions °C.	Minutes	Yield of ketones, % $X—C_6H_4COCH_2C_6H_4—Y$	$X—C_6H_4CH_2COC_6H_4—Y$	% yield of stilbene deriv. $X—C_6H_4C(SCH_2COOH){=}C(SCH_2COOH)C_6H_4—Y$
X = *p*CH_3O–	[a]	100	30	70	0	10[b]
Y = H		45	30	60	0	10
X = H	[c]	45	35	60	0	10
Y = *p*-CH_3O–		0	30	35	0	10
X = H	[d]	100	30	35	20	20[e]
Y = *p*-Cl						
X = *p*-Cl	[f]	100	30	35	20	20
Y = H						
X = *p*-$(CH_3)_2N$–	[g]	80	45	50	40	
Y = H						

[a] Jenkins, THIS JOURNAL, 54, 1155 (1932). [b] Recrystallized from ethyl acetate–petroleum ether (b. p. 65–110°), m. p. 189–190° (dec.). *Anal.* Calcd. for $C_{19}H_{18}O_5S_2$: C, 58.5; H, 4.8; neut. equiv., 390. Found: C, 5.86; H, 4.8; neut. equiv., 391. [c] Ref. 4. [d] Arnold and Fuson, THIS JOURNAL, 58, 1295 (1936). [e] Recrystallized from aqueous formic acid or ethyl acetate–petroleum ether (b. p. 30–60°), m. p. 183–184 (dec.). *Anal.* Calcd. for $C_{18}H_{15}O_4S_2Cl$: C, 54.8; H, 3.8; neut. equiv., 395. Found: C, 54.7; H, 4.0; neut. equiv., 395. [f] Ref. 11. [g] Staudinger, *Ber.*, 46, 3535 (1913).

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(1) American Cyanamid Fellow, 1947–1948. Present address: Department of Chemistry, Amherst College, Amherst, Massachusetts.

(2) Behagel and Schneider, *Ber.*, **68**, 1588 (1935).

(3) Compare Holmberg, *J. prakt. Chem.*, [2] **141**, 93 (1934).

(4) Teich and Curtin, in press.

(5) Blum-Bergmann, *J. Chem. Soc.*, 723 (1938).