limed *in vacuo;* melting points were: ortho 102.5–103°, meta 110.5–111°, para 177–178°.

The discharge chamber is shown in Fig. 1. It was connected through stopcocks to a manifold and to a product gas storage bulb. During a run, the acids were distilled through the discharge which occurred in the region A. The surface B acted as an air condenser for the distillate. The acids were kept at the melting point by the mercury bath C which also served as one of the electrodes. The discharge was produced by a Tesla-type transformer which gave a peak potential of 7000 volts at a frequency of 0.5 megacycle. A Toepler pump was used to transfer the product gases from the storage bulb to a micro gas analyzer.[8] The entire system could be evacuated to 10^{-5} mm. by a mercury diffusion pump which was connected to the system through a trap immersed in liquid air.

In a typical run approximately 3 g. of purified acid was placed in the discharge chamber which was then sealed into the vacuum system. The acid was degassed by alternate freezing and thawing under vacuum. After adjusting the temperature of the mercury bath to the melting point of the acid, the discharge was started and continued until the pressure in the product bulb reached 3 mm. This pressure was equivalent to 70 ml. of gas at standard conditions.

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[8] C. N. Stover, W. S. Partridge and W. M. Garrison, *Anal. Chem.*, **21**, 1013 (1949).

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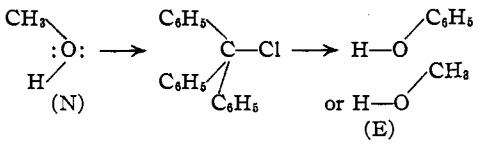
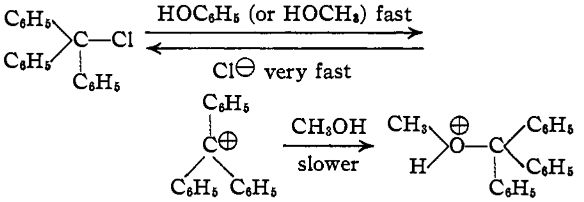
Concerted Displacement Reactions. IV. Halide Exchange of Triphenylmethyl Halides in Benzene Solution[1]

BY C. GARDNER SWAIN

The first paper of this series showed that the methanolysis of triphenylmethyl (trityl) chloride in benzene solution was third order, practically unaffected by the concentration of tertiary amines or tertiary ammonium chlorides, but accelerated seven-fold by the presence of 0.05 *M* phenol, a substance which reacted with trityl chloride only very slowly by itself. The *rate-determining step* appeared to be a concerted, push-pull process, requiring two hydroxylic molecules, one acting as a nucleophilic reagent (N) to attack carbon and the other acting as an electrophilic reagent (E) to attack halogen.[2]



Recently it was suggested that there may be a competition between chloride ion and methanol for an intermediate formed by reaction of trityl chloride with *only one hydroxylic molecule,* which solvates only the halide ion.[3]



This scheme would also explain the third-order kinetics. It was suggested that if this mechanism holds, increasing the concentration of tertiary ammonium chlorides in the solution should increase the rate of the very fast reverse reaction. The fact that no such "mass effect," or decrease in the net forward rate was observed experimentally required that there be a fortuitous compensation by an equally large "salt effect" by these tertiary ammonium chlorides on the fast, forward ionization step.

The existence of such a competition has now been disproved experimentally by replacing the tertiary ammonium chlorides by tertiary ammonium sulfonates, which cannot give a "mass effect," but should still show the large "salt effect," if one exists with tertiary ammonium salts of this type. The effect on the rate was found to be negligibly small.

Quinolinium benzenesulfonate, *p*-toluenesulfonate, naphthalene-*β*-sulfonate and quinolinium *dl*-camphorsulfonate are all very sparingly soluble in benzene (*ca.* 0.01 *M*). However, quinolinium *d*-camphorsulfonate, proved to be thirty times as soluble as the *dl* form. This salt could be highly purified, had a decomposition point of 118–120° and was extremely soluble in water. *Anal.* Calcd. for $C_{19}H_{23}NSO_4$: C, 63.13; H, 6.41. Found: C, 63.29; H, 6.46. With 0.105 *M* trityl chloride, 0.108 *M* quinoline and 0.107 *M* methanol, the initial rate of methanolysis was increased *less than 25%* by either 0.031 *M* or 0.093 *M* concentrations of the anhydrous salt.[4]

Thus there is no competition between tertiary ammonium chlorides and methanol for any intermediate in the methanolysis in benzene solution.[5]

The foregoing experiments, although sufficient to rule out the existence of such a competition, are not a real test of salt effects in benzene because (1) tertiary ammonium salts are hydrogen bonded

[1] This work was supported by the Office of Naval Research.

[2] Swain, THIS JOURNAL, **70**, 1119 (1948). The kinetics shed light on only the rate determining step, which does not necessarily give the final product directly. It is possible that some methanol molecule other than N may bond covalently with carbon in a subsequent fast step.

[3] This was proposed at the American Chemical Society convention at Atlantic City, September 21, 1949, by Dr. Jack Hine; *cf.* "Abstracts of Papers," p. 83M.

[4] The solubilities of quinolinium chloride were 0.01, 0.015 and 0.033 *M* in the presence of 0.00, 0.031 and 0.093 *M* quinolinium *d*-camphorsulfonate, respectively. The rates fell off less rapidly than usual toward the end in the runs with added sulfonate, suggesting that a quinolinium salt (or the acid in equilibrium with it) may serve as the electrophilic reagent E instead of methanol to a small extent. It should be emphasized that the concentration of tertiary ammonium salts in these experiments was purposely increased to a considerably higher level (0.126 *M*) than was present in any previous work. In the previous work, total salt concentrations as low as 0.0015 *M* were used.

[5] It has occurred to us that a more difficultly discernible kind of reversal may be occurring by a first order *intramolecular* reaction between the carbonium ion and solvated chloride ion of a *single* ion pair. However, until intermediates are demonstrated by successful capture by external reagents other than methanol or by spectral methods, we prefer the simpler original picture of concerted back and front side attack.

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}_{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}_{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}_{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}_{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%)