

methyl) ether (II) with sodium methoxide. Neither conditions nor yield are recorded. The preparation of I by reaction of paraformaldehyde, methanol, and methylal is reported⁶ in 26% yield.

Bis(ethoxymethyl) ether (III) was prepared by Descudé⁴ in 25% yield from II and sodium ethoxide. Ali-Zabe *et al.*⁶ report the preparation of III from ethanol, sodium hydroxide, and bis(bromomethyl) ether. No yield is given. Diethyl formal and paraformaldehyde react catalytically to form III in 43% yield.⁵

Our results indicate that neither I nor III can readily be prepared from II and the corresponding sodium alkoxide in inert solvents. The reaction between II and the alcohols occurs readily, but in the absence of a base the principal products are methylal or diethyl formal and formaldehyde.

The reaction between II and methanol in the presence of sodium methoxide at 55–60° produced I in 32% yield. The yield of I was only 15% and isolation was complicated by substituting sodium hydroxide for sodium methoxide.

When II was treated with ethanol at 55–60° in the presence of sodium hydroxide, III was formed in 60% yield. No improvement in yield was obtained by using sodium ethoxide in place of sodium hydroxide. The yield of III was 41% when II was treated with ethanol in the presence of sodium methoxide. No I could be isolated from the reaction mixture.

EXPERIMENTAL

Bis(methoxymethyl) ether (I). A one-liter, three-necked flask, equipped with a thermometer, condenser, dropping funnel, and magnetic stirring bar, was charged with 4 moles sodium methoxide and 500 ml. methanol. A temperature of 55–60° was maintained by cooling while 2 moles of II was added dropwise over a period of 6 hr. The filtrate from the reaction mixture was fractionated in a 12-plate column to remove methanol. The pot residue was filtered to remove salt. When the upper layer from the filtrate was fractionated, 0.63 mole (32% yield) of I was obtained, b.p. 64.5–65°/200 mm., n_D^{25} 1.3769, d_4^{25} 0.945.

Anal. Calcd. for $C_4H_{10}O_3$: mol. wt., 106.1; C, 45.27; H, 9.60. Found: mol. wt., 107; C, 44.83; H, 9.74.

When conditions essentially the same as just described were employed except that carbon tetrachloride or 1,4-dioxane was substituted for methanol, no I was isolated. When II and methanol were reacted in the absence of a base, methylal and formaldehyde were formed, but no I. Small yields (about 15%) of I were obtained when sodium hydroxide or calcium oxide was substituted for sodium methoxide in the reaction between methanol and II.

Bis(ethoxymethyl) ether (III). The equipment described under the preparation of I was charged with 1.25 moles so-

(2) A portion of this study was conducted under contract No. AF 33(616)-455 sponsored by the U.S. Air Force and is contained in AF Technical Report No. 43-434.

(3) Present address: El Paso Natural Gas Co., Farmington, N. M.

(4) M. Descudé, *Compt. rend.*, **138**, 1704 (1904).

(5) Imperial Chemical Industries, Ltd., British Patent **603,872** (June 24, 1948).

(6) G. Ali-Zabe, K. C. Aleva, and L. M. Kosheleba, *J. Gen. Chem. (U.S.S.R.)*, **19**, 1475 (1949).

dium hydroxide and 4.3 moles ethanol. The temperature was maintained at 50–60° while 0.5 mole of II was added over a period of 3 hr. The product was filtered and the filtrate fractionated to yield 0.3 mole of III, b.p. 67–67.5°/60 mm., d_4^{25} 0.903, n_D^{25} 1.3861.

Anal. Calcd. for $C_6H_{14}O_3$: mol. wt., 134.2; C, 53.71; H, 10.52. Found: mol. wt., 132; C, 52.68; H, 11.25.

Under similar conditions ethanol and II react in the absence of a base, but the products are diethyl formal and formaldehyde rather than III.

When a reaction was conducted using 4.3 moles ethanol, 1.25 moles sodium methoxide, and 0.5 mole II, a 41% yield of III was obtained, but no I was isolated.

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Preparation of Certain Polychlorodimethyl Ethers¹

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The liquid-phase chlorination of chloromethyl methyl ether yields bis(chloromethyl) ether (I) and methyl dichloromethyl ether (II). The ratio of I:II is approximately 7. In the vapor-phase chlorination of dimethyl ether with excess chlorine,³ the ratio of I:II varies from 1.6 to 3.0 based on contact time, temperature, and ratio of reactants. Salzberg and Wertz⁴ prepared I and II by chlorinating dimethyl ether with excess chlorine in an inert solvent, but reported no data on the relative amounts of the two compounds.

When I is further chlorinated, chloromethyl dichloromethyl ether III is formed. The properties of our product are in agreement with those of Sonay who reported the preparation of III by a similar process.⁵

Chlorination of II in a similar manner also yields III but no methyl trichloromethyl ether (IV) was isolated. Compound IV has been prepared by the chlorination of bis(methoxythiocarbonyl) disulfide.⁶

The monochlorination of III also forms only one product although two products are possible. This product was identified as bis(dichloromethyl)

(1) Taken in part from the thesis submitted by R. A. Gray to the Graduate Committee of New Mexico A&M in partial fulfillment of the requirements for the degree of Master of Science, August 1952.

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(3) L. R. Evans, U. S. Patent **2,811,485** (1957). The results of this study by L. R. Evans and R. E. Neligan are to be published soon.

(4) P. L. Salzberg, and J. H. Wertz, U. S. Patent **2,065,400** (1937); *Chem. Abstr.*, **31**, 1046 (1937).

(5) A. de Sonay, *Bull. Acad. Roy. Belg.*, [3] **26**, 629 (1893).

(6) I. B. Douglass and G. H. Warner, *J. Am. Chem. Soc.*, **78**, 6070 (1956).

ether (V) by both chemical and instrumental analysis.

Attempts to prepare more highly chlorinated dimethyl ethers by the chlorination of V were unsuccessful. The reaction with chlorine was very sluggish and no products boiling higher than V could be isolated.

Both pentachlorodimethyl ether⁷ (VI) and hexachlorodimethyl ether^{5,8} (VII) have been reported. However, Regnault's and Sonay's values for the boiling point and density of VII are not in agreement with the values to be expected based on the other chlorinated dimethyl ethers.

EXPERIMENTAL

Chlorination of chloromethyl methyl ether. A 2-liter, 3-necked flask which was equipped with a mechanical stirrer, condenser and ice trap, thermometer, and sintered-glass disk inlet tube was charged with 322 g. (4.0 moles) of chloromethyl methyl ether and 1232 g. (8.0 moles) carbon tetrachloride. The flask was illuminated with a 275-watt ultraviolet bulb. Chlorine was admitted through the sintered disk at a rate of 200 ml./min. until 142 g. (2.0 moles) had been introduced. The heat of reaction maintained the system at reflux. Fractionation of the product produced 163 g. (1.4 moles) bis(chloromethyl) ether (I); b.p. 103–105°, n_D^{20} 1.4421 and 24 g. (0.2 mole) dichloromethyl methyl ether (II); b.p. 82–84°, n_D^{20} 1.4353.

Anal. Calcd. for $\text{ClCH}_2\text{OCH}_2\text{Cl}$: Sapon. Equiv., 57.5; Cl, 61.68. Found: Sapon. Equiv., 57.3; Cl, 61.81.

Calcd. for $\text{CH}_2\text{OCHCl}_2$: Sapon. Equiv., 38.3; Cl, 61.68. Found: Sapon. Equiv., 38.4; Cl, 61.77.

Chlorination of bis(chloromethyl) ether (I). The equipment described under chlorination of chloromethyl methyl ether was charged with 460 g. (4.0 moles) (I) and 1232 g. (8.0 moles) carbon tetrachloride. After heating to reflux, chlorine was passed in at a rate of 407 ml./min. until 212 g. (2.98 moles) had been introduced. The heat of reaction maintained the system at reflux. Fractionation of the product yielded 190 g. (1.27 moles) (42.6% yield) of (III) with b.p. 129°, n_D^{20} 1.4622 and d_4^{20} 1.464.

Anal. Calcd. for $\text{ClCH}_2\text{OCHCl}_2$: mol. wt., 149.4; Cl, 71.19. Found: mol. wt., 150; Cl, 70.5.

Chlorination of dichloromethyl methyl ether (II). The equipment described under chlorination of chloromethyl methyl ether was charged with 196 g. (1.7 moles) (II) and 616 g. (4.0 moles) carbon tetrachloride. After heating to reflux, chlorine was admitted at a rate of 275 ml./min. until 64 g. (0.90 mole) had been introduced. Only initial heating was necessary to hold the temperature at reflux. Upon fractionation, 109 g. (0.73 mole) (81.1% yield) of chloromethyl dichloromethyl ether (III) was obtained with b.p. 128–129°, n_D^{20} 1.4630, and d_4^{20} 1.464. No methyl trichloromethyl ether was isolated. The physical constants and analysis of this product agreed well with those obtained by the chlorination of bis(chloromethyl) ether.

Chlorination of dichloromethyl chloromethyl ether (III). The equipment described under chlorination of chloromethyl methyl ether was charged with 284 g. (1.9 moles) (III) and 616 g. (4.0 moles) carbon tetrachloride. The solution was heated to reflux and chlorine was bubbled in at a rate of 114 ml./min. until 81g. (1.15 moles) had been introduced. The heat of reaction maintained the system at reflux. By fractionation at reduced pressures, 63 g. (0.34 mole)

(29.6% yield) of bis(dichloromethyl) ether (V) was obtained having b.p. 143°, n_D^{20} 1.4728 and d_4^{20} 1.558.

Anal. Calcd. for $\text{CHCl}_2\text{OCHCl}_2$: mol. wt., 183.9; Cl, 77.13. Found: mol. wt., 190; Cl, 76.4.

Only one product resulted from this reaction whereas two products are possible. Since neither of the two expected products is reported in the literature, the identity of the product was confirmed by mass spectrometer and infrared patterns.⁹ The mass pattern showed relative peak heights at 83, 85, and 87 of 1.00:0.64:0.116 which is in good agreement with the values expected for CHCl_2 based on the relative abundance of the chlorine isotopes. The ratios of the heights of the 117, 119, 121, and 123 peaks are 1.00:4.67:4.00:1.17. These values are not in agreement with the heights expected for a CCl_3 group which should be 1.0:1.0:0.3:0.04. The infrared pattern as interpreted by Dr. W. H. Calkins is in agreement with the pattern to be expected for the *sym*-tetrachloro derivative. Furthermore, the relative areas from a gas chromatogram indicated that the sample was about 95% pure.

Chlorination of bis(dichloromethyl) ether (V). The equipment described under chlorination of chloromethyl methyl ether was charged with 616 g. (4.0 moles) carbon tetrachloride and 368 g. (2.0 moles) (V). The solution was heated to reflux and chlorine was introduced at a rate of 142 ml./min. until 43 g. (0.6 mole) had been admitted. It was necessary to apply external heat to maintain reflux. Fractionation of the product at reduced pressures resulted in the recovery of phosgene, unreacted (V) and 709 g. (4.6 moles) carbon tetrachloride. The excess carbon tetrachloride over that charged presumably resulted from the same decomposition which produced phosgene. No chloroform or more highly chlorinated ether was recovered.

This experiment was repeated reducing the temperature to 50° and the chlorine flow to 100 ml./min. Again phosgene, unreacted V, and 115% of the charged carbon tetrachloride were obtained by fractionation at reduced pressures.

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Preparation of 1,5-Dibromo-4,8-diiodonaphthalene¹

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We have recently prepared 1,5-dibromo-4,8-diiodonaphthalene according to the method of Whitehurst.² Some observations upon this synthesis are pertinent.

(1) Abstracted from a thesis presented to the Graduate School, University of North Dakota, by Robert W. Bayer in partial fulfillment of the requirements for the Master of Science degree in chemistry.

(2) J. S. Whitehurst, *J. Chem. Soc.* 222 (1951).

(7) I. Rabcewicz-Zabkowski, and S. Chwalinski, *Roczniki Chem.*, **10**, 686 (1930).

(8) V. Regnault, *Ann.*, **34**, 24 (1840).