tained by the addition of the other half of the solution of the halide. The suspension was heated for one hour at reflux under a positive nitrogen pressure, then cooled, and 65 ml. of dry pentane added. Carbon dioxide, dried by passage through concentrated sulfuric acid, was passed over the vigorously stirred suspension for two hours. The excess lithium was removed by the addition of 20 ml. of absolute ethanol, followed by 60 ml. of water. Following the addition of 50 ml. of ether, the aqueous phase was acidified with concd. hydrochloric acid. The phases were separated, and the aqueous phase, after saturation with salt, was extracted with 3 100-ml. portions of ether. The combined ethereal extracts were extracted with 3 100-ml. portions of aqueous sodium carbonate, the sodium carbonate phase acidified with 12*N* hydrochloric acid, saturated with salt, and extracted with 3 100-ml. portions of ether. The ethereal extracts were dried and the solvent removed by distillation through a 12-inch column. The product was sublimed at 10 mm. and 80° to give 5.48 g. (51%) of 1-carboxybicycloheptane, m.p. 113.8-115.5°.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.5; H, 8.5.

The reported melting points for *exo*- and *endo*-2-carboxybicycloheptane are 48°[19] and 65°,[20] respectively. The acid has an odor similar to that of butyric acid.

1-Hydroxymethylbicycloheptane. The above acid, 2.19 g. (0.0156 mole), was reduced in 130 ml. of ether with 3.0 g. (0.0790 mole) lithium aluminum hydride. The excess hydride was destroyed by addition of water and the contents of the flask poured into 100 ml. of 10% aqueous sulfuric acid. The phases were separated, and the aqueous phase extracted with 2 25-ml. portions of ether. The combined ethereal extracts were washed with water, saturated aqueous sodium bicarbonate and water and dried over magnesium sulfate. The solvent was removed by distillation through a 12-inch Vigreux column to yield an oily residue. The residue was sublimed at 6 mm. and 65° to give 1.76 g. (91%) of product, m.p. 59.0-60.2°, soft waxy needles.

Anal. Calcd. for $C_8H_{14}O$: C, 76.1; H, 11.2. Found: C, 75.9; H, 11.3.

1-Bicycloheptylmethyl tosylate. To an ice cold solution of 0.70 g. (5.56 mole) of the above alcohol dissolved in 6 ml. of dry pyridine was added 1.06 g. (5.56 mole) of tosyl chloride. The solution was allowed to stand overnight at 4° and then added to 12 ml. of ice cold 6*N* hydrochloric acid. An oil formed and began to crystallize whereupon the mixture was stirred with 25 ml. of carbon tetrachloride until all of the solid had dissolved. The phases were separated and the aqueous phase extracted with 15 ml. of carbon tetrachloride. The organic phases were combined and dried. The solvent removed by evaporation and the residue was recrystallized from 6 ml. of hexane to give 1.33 g. (86%) of tosyl derivative, m.p. 78.9-80.0°.

Anal. Calcd. for $C_{15}H_{20}O_3S$: C, 64.3; H, 7.2. Found: C, 64.2: H, 7.2.

Rate of acetolysis of 1-bicycloheptylmethyl tosylate. The acetolysis was conducted in anhydrous acetic acid, according to the method of Winstein, Grunwald, and Ingraham.[12] Anhydrous acetic acid was prepared by adding sufficient acetic anhydride to react with the water present in glacial acetic acid as determined by its freezing point, allowing the mixture to reflux for 3 hr. and then distilling. The distillate was made approximately 0.5% in acetic anhydride, held at reflux for 3 hr., cooled, and then stored in sealed containers.

Approximately 0.05*N* perchloric acid in acetic acid was prepared by dilution of a 9*N* aqueous solution with the anhydrous acid. This solution was standardized against potassium acid phthalate to a brom phenol blue end point.[21] Approximately 0.10*N* sodium acetate in acetic acid was prepared by the addition of anhydrous sodium carbonate to the anhydrous acid and was standardized against the perchloric acid solution. The acetic anhydride in the anhydrous acid was determined to be 0.50% by the method of Kilpi,[22] *i.e.*, the addition of anthranilic acid to the anhydrous acid and titration with perchloric acid. In all titrations, 8 drops of 1% brom phenol blue indicator in the anhydrous acid were used per 5 ml. of solution.

The acetolysis was conducted as follows: 6-ml. aliquots of a 0.03547*M* solution of the tosyl derivative in the anhydrous acid were placed in ampoules, the ampoules sealed, placed in an oil bath at 99.66 ± 0.02°, single ampoules removed at selected time intervals, immediately cooled, opened, 5.00-ml. aliquots removed, and titrated with the sodium acetate solution. The time was computed from the time of opening the ampoules. The aliquots were titrated with the aid of a syringe buret,[23] previously calibrated by titration of the perchloric acid solution with the sodium acetate solution. The first order rate constants were calculated from the expression $kt = \ln(a/a - x)$. The hydrolysis was followed to 64%. The results are summarized in Table I.

TABLE I

RATE OF ACETOLYSIS OF 1-BICYCLOHEPTYLMETHYL TOSYLATE[a]

Time, Sec.	Base,[b] Ml.	$(a - x)$ (M)	$k \times 10^6$ Sec.$^{-1}$
0[c]	0.1933	0.03147	...
9549	0.3529	0.02816	11.63
21860	0.5435	0.02472	11.97
34676	0.7000	0.02098	11.70
44576	0.8213	0.01847	11.95
74040	1.0938	0.01283	12.13
86384	1.1129	0.01243	10.76
95565	1.2147	0.01033	11.66[d]

[a] In an hydrous acetic acid containing 0.50% acetic anhydride at 99.66 ± 0.02°. [b] 0.1035*N* sodium acetate per 5.00-ml. aliquot. [c] $a_0 = 0.03547$ *M*. [d] $k_{\text{mean}} = 11.69 \pm 0.29 \times 10^{-6}$ sec.$^{-1}$

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[19] K. Alder and G. Stein, *Ann.*, **514**, 211 (1934).

[20] K. Alder and G. Stein, *Ann.*, **514**, 197 (1934).

[21] Because of the high temperature coefficient of expansion of acetic acid, all solutions were maintained at 25.00° prior to standardization, or any volumetric measurement.

[22] S. Kilpi, *Suomen Kemistilehti*, **13B**, 19 (1940); *Chem. Abstr.*, **35**, 2445 (1941).

[23] P. A. Shaffer, P. S. Farrington, and C. Niemann, *Ind. Eng. Chem., Anal. Ed.*, **19**, 492 (1947).

Reaction of Bis(chloromethyl) Ether with Methanol and with Ethanol[1,2]

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Bis(methoxymethyl) ether (I) was first prepared by Descudé[4] in 1904 by reaction of bis(chloro-

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methyl) ether (II) with sodium methoxide. Neither conditions nor yield are recorded. The preparation of I by reaction of paraformaldehyde, methanol, and methylal is reported[5] in 26% yield.

Bis(ethoxymethyl) ether (III) was prepared by Descudé[4] 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 sodium 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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[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).

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Preparation of Certain Polychlorodimethyl Ethers[1]

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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 Werntz[4] 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)

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[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.

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