

TABLE I
 LIST OF DERIVATIVES

Compound	Derivative	M.p., °C.	Element	Calcd., %	Composition Found, %
CF ₃ CH=CHCOCl	N-Methyl amide	110.0	N	9.16	9.07
CF ₃ CHBrCHBrCO ₂ C ₂ H ₅	Benzylamine hydrobromide	220
CF ₃ CH=CHCH ₂ OH	Phenylurethan	63.0	N	5.72	5.71
CH ₃ CH—CHCH ₂ CO ₂ C ₂ H ₅	Hydrazide acid	41.0 ^a	N ^b	14.15	14.29
	anilide	129.0	N	5.41	5.45
CH ₃ CF ₃					
CH ₃ CH ₂ CHCH ₂ CO ₂ C ₂ H ₅	Hydrazide acid	65.0	N	15.2	15.2
	anilide	81.0	N	5.72	5.75
CF ₃					
CF ₃ CH=CHCHO	2,4-Dinitrophenylhydrazone	226.0	C and H	39.5; 2.30	39.6; 2.30
			N	18.4	18.4

^a Apparently this is the m.p. of a hydrate. After drying in an Abderhalden pistol over phosphorus pentoxide the material turned liquid upon exposure to air, then resolidified to the 41.0° material. ^b Analysis performed on the dried material.

Freshly distilled aluminum isopropoxide (5.5 g., 0.027 mole) was placed in the flask and 4,4,4-trifluorocrotyl alcohol (10 g., 0.08 mole) was added to it in one portion. The pressure in the system was reduced to 100 mm. and the flask was heated slowly to 65–70° by means of an oil-bath. After one hour at this temperature, during which time isopropyl alcohol slowly distilled from the reaction flask, the temperature of the flask was raised to 110° to drive off the last traces of isopropyl alcohol, then the pressure was lowered to 20 mm. whereupon 1.3 g. of 4,4,4-trifluorocrotyl alcohol was recovered.

Anisaldehyde (16.3 g., 0.12 mole) was placed in the addition funnel, the flask was warmed to 65° and the pressure was lowered to 100 mm. The anisaldehyde was added dropwise to the white solid in the reaction flask, which started to darken and finally turned into a black, tarry mass. Upon lowering the pressure further and slowly raising the temperature of the oil-bath a clear, water white distillate

was obtained, b.p. 70–76° (70 mm.). This liquid weighed 3.0 g. and was converted into its 2,4-dinitrophenylhydrazone, m.p. 226° (see Table I for analysis).

Preparation of Derivatives.—These were prepared in the usual manner.^{15,16} Note that benzylamine hydrobromide was obtained (instead of the expected benzyl amide) when benzylamine was added to ethyl 2,3-dibromo-4,4,4-trifluorobutyrate. Such a phenomenon is not unusual.¹⁷ The derivatives are listed in Table I.

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, New York, N. Y., 1948.

(16) A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948.

(17) C. A. Buehler and C. A. Mackenzie, *THIS JOURNAL*, **59**, 421 (1937).

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NOTES

A New Synthesis of 1,2-Dialkoxyethanes

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In the course of an investigation involving the behavior of various metals on halogenated ethers, it was observed that chloromethyl alkyl ethers are able to undergo Wurtz coupling in the presence of sodium to give 1,2-dialkoxyethanes. Oda and Teramura¹ state that this reaction with sodium occurs and they report good yields of the 1,2-dialkoxyethanes when metallic copper or iron is used as a condensing agent, but they give no experimental details. Jain, *et al.*,² on the other hand, found that with sodium the 1-chloro-1-alkoxymethanes undergo Wurtz-Fittig coupling with some aromatic compounds having bromine attached to the ring, but not with benzyl bromide, and they report no products which are formed from the condensation of the ether with itself.

(1) R. Oda and K. Teramura, *Bull. Inst. Chem. Res. Kyoto Univ.*, **26**, 88 (1951).

(2) N. C. Jain, R. Kushall and S. Deshapande, *J. Indian Chem. Soc.*, **28**, 49 (1951).

In the present work the reaction of chloromethyl alkyl ethers with sodium is found to proceed in a normal manner except that there is usually a considerable amount of polymerized material left in the reaction flask. It is observed that sodium-toluene dispersions³ seem to give higher yields than sodium shot. No attempt has been made, however, to find optimum conditions for maximum yields.

 TABLE I
 ROCH₂CH₂OR

R	B.p.		n _D ²⁰	d ₄ ²⁰	Yield, %
	°C.	Mm.			
CH ₃	83–85	760	1.3739 ²⁴	0.8602 ³³	27
C ₂ H ₅	120–124	760	1.3886 ²⁵	.8421 ³⁰	32
C ₃ H ₇ ^a	158–165	760	1.3964 ³⁰	.8307 ³⁰	72 ^b
C ₄ H ₉	200–201	760	1.4055 ²⁵	.8351 ²⁸	79 ^b
C ₆ H ₁₁	218–220	755	1.3962 ³²	.8318 ³²	42
<i>i</i> -C ₃ H ₇	42–43	3	1.3945 ³²	.8096 ³²	26
<i>i</i> -C ₄ H ₉	64–67	7	1.3949 ³²	.8189 ³²	42

^a Anal. Calcd. for C₈H₁₈O₂: C, 65.71; H, 12.41. Found: C, 65.73; H, 12.62. ^b Prepared with dispersed sodium.

(3) Furnished through the courtesy of Dr. John Nobis of the National Distillers Products Corp.

The physical properties and yields of the 1,2-dialkoxyethanes prepared are given in Table I. The 1,2-dipropoxyethane has been identified by its physical constants, its stability to acids (showing it not to be an acetal) by cleavage with zinc chloride and acetic acid to give propyl acetate, and by carbon-hydrogen analyses.

Experimental

Halogenated Ethers.—The chloromethyl alkyl ethers prepared by the method of Henry⁴ were dried over phosphorus pentoxide for 20 minutes and distilled immediately before using.

1,2-Dialkoxyethanes.—One mole of the chloromethyl alkyl ether was slowly dropped into 1.2 gram-atoms of sodium shot covered with sodium-dried ether, the rate of addition being such as to maintain a slow reflux. After the addition had been completed, the reaction mixture was stirred overnight, filtered, the solvent removed, and the product distilled. It is interesting to note that this reaction does not occur with 1-chloro-1-alkoxyethane. The results of this latter reaction will be reported later.

Acknowledgment.—This work was performed with the aid of U. S. Navy funds, and under a contract with the Office of Naval Research. We acknowledge also the help of Mr. Bennie Lacy, graduate chemistry student, in preparing some of the above compounds.

(4) L. Henry, *Bull. chim. soc. Belg.*, [2] **44**, 458 (1885).

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Acetyl Bromide as a Possible Intermediate in the Reaction of Acetaldehyde with Bromine in Aqueous Ethanol¹

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Farkas, *et al.*,² have demonstrated that both acetic acid and ethyl acetate are formed when acetaldehyde, formed *in situ* by the oxidation of aqueous ethanol by bromine, is further oxidized by this reagent. They also proved that the ester does not result from esterification of acetic acid and postulated that it arises from oxidation of the hemiacetal of acetaldehyde while the acid is derived from the hydrate. An excellent analogy for this hypothesis is to be found in work of Isbell^{3,4} who assembled compelling evidence that δ -lactones are produced directly on oxidation of several mono- and disaccharides by bromine in aqueous solution buffered with barium carbonate-carbon dioxide, and concluded that the pyranose hemiacetal sugars are the actual reactants. Very recently Mosher and Preiss⁵ have demonstrated that with chromic acid as oxidant hemiacetals are more reactive than the corresponding free aldehydes and yield esters directly.

Both the products and the second-order kinetics

(1) Based upon an A.M. Thesis submitted by Felix Granchelli to the Graduate School of Boston University, June, 1950.

(2) L. Farkas, B. Perlmutter and O. Schächter, *THIS JOURNAL*, **71**, 2829 (1949).

(3) H. S. Isbell, *J. Research Natl. Bureau of Standards*, **8**, 615 (1932).

(4) H. S. Isbell and W. W. Pigman, *ibid.*, **10**, 337 (1933).

(5) W. A. Mosher and D. M. Preiss, *THIS JOURNAL*, **75**, 5605 (1953).

which maintain^{2,6} in the oxidation of acetaldehyde by bromine in aqueous ethanol are, however, consistent with an alternative possibility, namely, that acetaldehyde is converted in the rate-determining step to acetyl bromide which then rapidly undergoes solvolysis to a mixture of acid and ester. Acyl halides have been observed in reactions of aldehydes and bromine or chlorine. Thus, it has been reported that on treatment with dry chlorine in the absence of solvent, acetaldehyde⁷ and benzaldehyde⁸ yield the respective acid chlorides. The latter reacts⁹ with bromine in the absence of solvent to yield α -bromobenzyl benzoate, a compound which was found to form rapidly from the reaction of benzoyl bromide with benzaldehyde.

A direct test of the hypothesis that acetyl bromide is an intermediate in the reaction of acetaldehyde in aqueous ethanol solution is made possible by the work of Farkas, *et al.*,^{2,10} These workers carried out the reaction at 25°, in the presence of bromate, in a solvent containing 41% by weight of ethanol. This reagent removes hydrogen bromide which otherwise catalyzes equilibration of acid and ester. Under these conditions they found that the molar ratio of ester to acid does not change significantly as the reaction proceeds and its value, approximately 2.3, is quite different from that at equilibrium, 0.87. If acetyl bromide is, in fact, an intermediate, its solvolysis in 41% aqueous ethanol at 25° must yield the former ratio provided that equilibration of esterification is slow compared to the rate of solvolysis.

Experimental

Acetyl bromide was distilled as needed from an all-glass rectifying column protected from moisture: b.p. 75.9° at 767 mm., d_{20}^{25} 1.650. On titration with sodium hydroxide, 96.6% of the theoretical amount of acid was found. Solvolysis in aqueous ethanol (approx. 4:1) yielded 99.0% of the theoretical bromide (Mohr titration).

Solvolysis Experiments.—Acetyl bromide was added dropwise with the aid of a dropping funnel protected by a drying tube into the stirred aqueous solvent containing 41% by weight of commercial absolute alcohol. The solvent had been equilibrated with a thermostat maintained at 25° and remained immersed therein during the addition. Enough solvent was used to give a solution 0.1 to 0.5 *M* in HBr prior to dilution. Slow addition (4 g. in 20 minutes) was necessitated by the strongly exothermic character of the reaction. Stirring was continued for several minutes after completion of addition. The solution was then made up to a standard volume and aliquots removed periodically for titration with standard base.

Results

Solvolysis in the absence of added reagents gave a solution which initially (40 minutes after addition was complete) contained 1.63 equivalents of acid per mole of acetyl bromide employed. The acidity slowly decreased so that two hours after addition was complete the ratio was 1.59, presumably because of esterification of acetic acid catalyzed by HBr. Solvolysis in the presence of slightly more than one mole of sodium acetate per mole of acetyl bromide yielded 1.61 equivalents of acid per

(6) S. Burgarszky, *Z. physik. Chem.*, **48**, 74 (1904).

(7) A. Wurtz, *Ann.*, **102**, 93 (1857).

(8) F. Wöhler and J. Liebig, *ibid.*, **3**, 262 (1832).

(9) L. Claisen, *Ber.*, **14**, 2473 (1881).

(10) L. Farkas, B. Perlmutter and O. Schächter, *THIS JOURNAL*, **71**, 2833 (1949).