

coholic solution; m. p., 210–211° with decomposition. This compound is less soluble in water and alcohol than is the corresponding compound containing two molecules of the hydroxide. It is insoluble in benzene.

Anal. Subs., 0.1933, 0.2317, 0.2213: AgBr, 0.0846, 0.0995, 0.0945. Calcd. for $C_6H_{19}OSn_2Br_2 \cdot H_2O$: Br, 18.06. Found: 18.63, 18.27, 18.17.

$(CH_3)_3SnOH \cdot (CH_3)_3SnCl \cdot H_2O$.—This compound was prepared as was the corresponding iodide and bromide. The crystals are more difficultly soluble in water than are those of the corresponding compound containing two molecules of hydroxide. They melt at approximately 90°, where decomposition takes place only slowly.

Anal. Subs., 0.4550, 0.2065: AgCl, 0.1972, 0.0473. Calcd. for $C_6H_{19}OSn_2Cl \cdot H_2O$: Cl, 8.90. Found: 8.95, 8.90.

Summary

1. Compounds corresponding to the empirical formula $[(CH_3)_3SnOH]_2 \cdot (CH_3)_3SnX$ have been prepared by the following methods: (1) by subjecting trimethyltin iodide to the action of sunlight in the presence of air; (2) by oxidizing a solution of the free trimethyltin group in moist benzene in the presence of trimethyltin iodide; and (3) by treating trimethyltin halide with 2 molecular proportions of trimethyltin hydroxide in benzene solution. The three preparations yield identical products. The compounds exhibit salt-like properties, being readily soluble in water and alcohol and difficultly soluble in non-ionizing solvents. They melt with decomposition at temperatures above 100°.

2. Compounds of the type $(CH_3)_3SnOH \cdot (CH_3)_3SnX \cdot H_2O$ have been prepared by treating 1 molecular proportion of trimethyltin hydroxide with 1 molecular proportion of the corresponding halide in alcoholic solution. The compounds are salt-like in properties, are soluble in alcohol and water and insoluble in non-ionizing solvents.

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CHLORO ETHERS. II. PREPARATION OF SOME NEW CHLORO ETHERS AND ALKOXYMETHYL ESTERS

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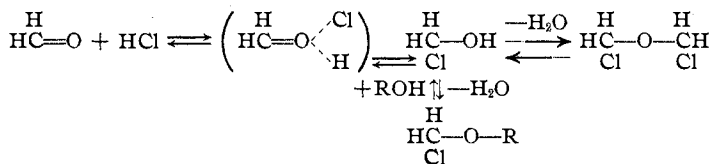
In a previous article² from this Laboratory Clark, Cox and Mack have described a series of esters prepared by the action of chlorodimethyl ether on the salts of formic, acetic, propionic and butyric acids. A continuation of this work has led to a study of other chloro ethers of this same series of

¹ This article is an abstract from theses submitted by J. W. Farren and H. R. Fife for degrees of Master of Science at West Virginia University. A preliminary paper was presented before the Organic Division at the 69th Meeting of the American Chemical Society, April 6–10, 1925 (by F. E. Clark).

² Clark, Cox and Mack, *THIS JOURNAL*, **39**, 712 (1917).

acids, in addition to the preparation of some new chloromethyl ethers which include those of secondary as well as primary alcohols. Gaspari³ studied the action of chloromethylethyl ether on fused sodium acetate and recorded the properties of the compounds formed. Wedekind⁴ has also studied the action of chloromethylethyl ether on potassium acetate and lead formate but no physical properties of these products were reported. This work was furthered by W. H. Moran in this Laboratory and a study made of the ethers from the salts of formic, acetic, propionic and butyric acids, but the incompleteness of data and lack of analyses have necessitated its duplication. A search of the literature indicated that only one secondary alcohol has been used in the preparation of a chloro ether. Stappers⁵ prepared chloromethylisopropyl ether and reported some of its constants.

In this investigation a modification of the methods of Wedekind and Henry was used in preparing the chloro ethers. In general it consists in treating molecular equivalent quantities of an alcohol and aldehyde, in the form of trioxymethylene, with dry hydrogen chloride. We propose to represent the reaction mechanism as follows.



It is known that aldehydes tend to add hydrogen chloride, and in the case of formaldehyde one of the products is chloromethyl alcohol, which may possibly be formed through the intermediate development of an oxonium compound. The chloromethyl alcohol unites with the alcohol used in the reaction with the elimination of a molecule of water to form the monochloromethyl-alkyl ether. There is also formed some of the symmetrical dichlorodimethyl ether, which, since it resembles α -chloro ethers tends to revert to chloromethyl alcohol. This general tendency is well known in the case of α -chloro ethers which tend to hydrolyze readily with the formation of the corresponding chloro alcohol, this in turn breaking up to give the aldehyde and hydrogen chloride. For example, α -chlorodiethyl ether yields ethyl alcohol, acetaldehyde and hydrogen chloride. The ease of hydrolysis of chloromethyl-alkyl ethers may, then, be considered as due to the fact that a substitution of chlorine for hydrogen renders the methyl radical more negative, thereby allowing the bond between it and the ether oxygen to be more readily broken.

³ Gaspari, *Gazz. chim. ital.*, [II] 27, 297 (1897).

⁴ Wedekind, *Ber.*, 36, 1383 (1903).

⁵ Stappers, *Bull. Acad. Roy. Belgique*, 1161-70 (1904); *Chem. Centr.*, 76, 921 (1905).

Experimental Part

Preparation of Chloro Ethers.—In the modification of the methods of Wedekind and Henry equivalent quantities of alcohol and trioxymethylene were treated with dry hydrogen chloride in a reaction flask surrounded with an ice-bath in order to remove the heat liberated and at the same time to increase the solubility of the hydrogen chloride. After a state of saturation had been reached the product was separated from the aqueous hydrochloric layer and dried over fused calcium chloride. After the product was thoroughly dried, a stream of dry hydrogen was passed through it in order to remove any free hydrogen chloride and also any which might be retained as an oxonium compound of the ether. The material was then further distilled in a current of dry hydrogen which practically eliminated decomposition at this point. Previous fractionation without the use of hydrogen always resulted in a large amount of decomposition together with deposition of trioxymethylene in the condenser. After being distilled twice in a current of hydrogen the product was fractionated, and an average yield of 90% of constant-boiling ether was obtained. With the alcohols used in these syntheses, the same amount of care being taken to insure against moisture, there is no marked tendency toward decomposition of one product as compared with another.

New chloromethyl ethers have been prepared from the following alcohols: *sec.*-butyl, cyclohexanol, ethylene chlorohydrin and *isopropyl* alcohols. However, the last has previously been prepared by Stappers, but some additional data are given on this and the ether from ethyl alcohol as well. Reactions were carried out using ethylene glycol and glycerol respectively, in an attempt to form the corresponding chloromethyl ethers. In each case the reaction took place very readily, all of the solid trioxy-

TABLE I
CHLORO ETHERS. GENERAL FORMULA: R—O—CH₂—Cl

R	B. p. °C.	d ₄ ⁰	d ₄ ²⁰	n _D	Molecular refraction	
					Calcd.	Obs.
1. C ₂ H ₅ —	81–82	1.0463	1.0263	1.0282 (12°)	22.49	22.55
2. (CH ₃) ₂ CH—	97–98	1.0000	0.9790	1.4592 (16°)	27.05	26.85
3. CH ₃ — C ₂ H ₅ —	121–123	0.9947	0.9751	1.4205 (16°)	31.62	32.08
CH—						
4. (R)C ₆ H ₁₁ —	183–185	1.0712	1.0432	1.4713 (9°)	38.56	39.02
5. Cl—CH ₂ CH ₂ —	145–147	1.3157	1.2817	1.4952(11°)	27.39	27.23
Formula	Mol. wt.		Analysis for Cl, %		Yield, %	
	Calcd.	Obs.	Calcd.	Found		
1. C ₃ H ₇ OCl	94.5	95.7	37.53	37.42	85	
2. C ₄ H ₉ OCl	108.5	107.8	32.67	32.02	85	
3. C ₅ H ₁₁ OCl	122.5	122.2	28.90	29.56	70	
4. C ₇ H ₁₃ OCl	148.5	149.2	23.86	23.01	50	
5. C ₃ H ₅ OCl ₂	128.9	130.1	54.98	54.32	65	

methylene disappearing from the mixture, but as yet we have been unable to separate and purify the products formed.

Esters by Reaction of Chloro Ethers with Salts of Aliphatic Acids

The reaction of chloro ethers with salts of organic acids has been described in a previous article published from this Laboratory. In the present investigation the technique has been modified so as to warrant a detailed description here, changes having been introduced so that yields of 80–90% may be obtained. All sodium salts of the acids were carefully fused, with the exception of the formate, which was dried in a desiccator over sulfuric acid. The salts were placed in a reaction flask which was fitted with a mercury-sealed mechanical stirrer, reflux condenser, dropping funnel, inlet and exit tubes. The flask was then immersed in an ice-bath and the contents were stirred rapidly while the ether was slowly introduced. It was found advantageous to continue the stirring to completion of the reaction by refluxing on a water-bath as had previously been done. On completion of the reaction the ester was distilled from the reaction flask in a current of dry hydrogen to a second flask, and redistilled to a third in a stream of hydrogen before final fractionation. Before beginning the preparation, the three flasks with condensers in series between were carefully dried by passing dry heated air for several hours through the entire system. This was done in order to carry out the preparation and purification of the material without having it come at any time into contact with the moisture of the air.

The series of esters prepared includes the formates, acetates, propionates and butyrates from the following ethers: chloromethylethyl, chloromethylisopropyl, chloromethyl-*sec.*-butyl. A formic ester, which boiled at 184–188°, was prepared from β -chloro-ethyl-chloromethyl ether. This was not purified sufficiently to allow us to report its properties. An anal-

TABLE II

ESTERS PREPARED FROM CHLORO ETHERS. GENERAL FORMULA: $\text{RCOOCH}_2\text{OR}'$

R.	R'	B_{C} , p.	d_4^{20}	d_4^{20}	n	Molecular refraction	
						Calcd.	Obs.
1. H-	ethyl	114–116	1.0537	1.0343	1.3900 (12°)	23.77	23.55
2. Methyl	ethyl	128–129	1.0081	0.9932	1.3903 (12°)	28.30	27.87
3. Ethyl	ethyl	145–146	0.9931	.9711	1.4000 (12°)	32.91	32.75
4. Propyl	ethyl	160–162	.9816	.9656	1.4050 (16°)	37.52	38.33
5. H-	isopropyl	124–126	1.0270	1.0000	1.3910 (25°)	28.30	27.70
6. Methyl	isopropyl	133–135	0.9761	0.9502	1.3890 (16°)	32.91	32.50
7. Ethyl	isopropyl	147–149	.9626	.9444	1.3980 (18°)	37.52	37.30
8. Propyl	isopropyl	164–166	.9617	.9432	1.4001 (16°)	42.05	41.92
9. H-	<i>sec.</i> -butyl	147–148	.9683	.9477	1.4020 (17°)	32.91	33.51
10. Methyl	<i>sec.</i> -butyl	156–158	.9574	.9319	1.4035 (19°)	37.52	37.38
11. Ethyl	<i>sec.</i> -butyl	164–166	.9519	.9291	1.4075 (18°)	42.05	42.38
12. Propyl	<i>sec.</i> -butyl	177–178	.9492	.9283	1.4085 (20°)	46.62	46.00

TABLE II (Concluded)

Empirical formula	Mol. wt.		Analyses				Yield %
	Calcd.	Obs.	Carbon, %		Hydrogen, %		
			Calcd.	Found	Calcd.	Found	
1. C ₄ H ₈ O ₃	104.0	105.2	46.15	46.25	7.70	7.98	70
2. C ₅ H ₁₀ O ₃	118.0	117.8	50.80	50.99	8.53	8.27	85
3. C ₆ H ₁₂ O ₃	132.0	133.4	54.54	54.35	9.15	9.32	85
4. C ₇ H ₁₄ O ₃	146.1	145.7	57.51	57.30	9.60	9.61	90
5. C ₅ H ₁₀ O ₃	118.0	120.1	50.80	50.71	8.53	8.56	60
6. C ₆ H ₁₂ O ₃	132.0	133.0	54.54	54.36	9.15	9.05	66
7. C ₇ H ₁₄ O ₃	146.1	145.2	57.51	57.40	9.60	9.66	75
8. C ₈ H ₁₆ O ₃	160.1	158.4	60.00	59.90	10.00	9.78	85
9. C ₆ H ₁₂ O ₃	132.0	132.4	54.54	54.05	9.15	9.09	65
10. C ₇ H ₁₄ O ₃	146.1	146.7	57.51	57.61	9.60	9.54	75
11. C ₈ H ₁₆ O ₃	160.1	158.0	60.00	59.60	10.00	9.91	80
12. C ₉ H ₁₈ O ₃	174.1	173.0	62.05	61.80	10.34	9.96	65

ysis of this product shows that only one chloride has reacted with the sodium salt of the acid. A further study is being made of this reaction.

Carbon and hydrogen were determined by the usual method of combustion, samples being sealed in small weighed bulbs and the tips broken before introduction into the furnace. Chlorine was determined by the Parr bomb method. In this case samples were sealed in small vials as in the combustion method. The difficulty of filling these vials without causing traces of hydrolysis probably accounts for the fact that the chlorine values tend to run consistently low. For molecular-weight determinations the freezing-point method was employed, benzene being used as a solvent.

Summary

1. Some new chloromethyl ethers have been prepared from primary and secondary alcohols and their physical properties and reactions with sodium salts of aliphatic acids studied.

2. Three series of four esters each, which include the formates, acetates, propionates and butyrates, have been prepared from the chloromethyl ethers of ethyl, *isopropyl* and *sec.*-butyl alcohols.

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