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NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Reactions of 2-Chlorodioxene with Alcohols, Phenols, and Acids

MELVIN J. ASTLE AND JOHN D. WELKS[1,2]

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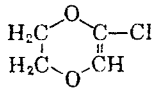
2-Chlorodioxene being an α-chloro and a vinyl ether may react with alcohols by replacement of the chlorine or by addition to the olefinic double bond. The products obtained can be accounted for if the first step involves addition to the double bond.

The olefinic bond in 2-chlorodioxene was found to possess unusual reactivity, adding alcohols, acids and phenols under mild conditions in the absence of added catalysts.

The products obtained from the reactions with alcohols were found to depend upon the general type of alcohol employed. Primary alcohols gave esters of 2-chloroethoxyacetic acid. Secondary alcohols gave a mixture of the ester, an alkyl chloride and p-dioxanone, while tertiary alcohols gave exclusively the corresponding alkyl chloride and p-dioxanone. Phenols reacted in the same manner as primary alcohols.

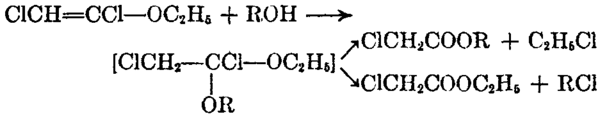
Acids were found to yield the corresponding acyl halide and p-dioxanone.

The chlorodioxene was obtained according to the method of Astle and Gergel[3] by the thermal dehydrohalogenation of 2,3-dichlorodioxane. It is a water-white liquid boiling at 145–147° at atmospheric pressure.



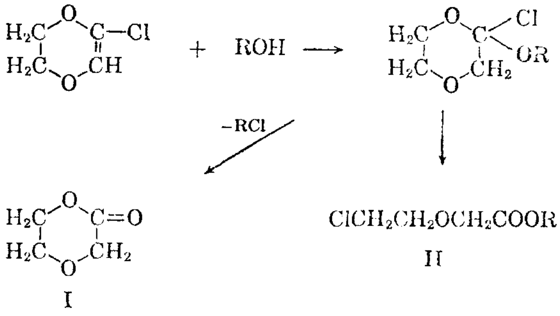
2-Chlorodioxene is an α-chloro ether as well as a vinyl ether. Although the chlorine would not be expected to have quite the activity found in most α-chloro ethers because of the inactivating effect of the double bond, the primary reaction may well involve replacement of this chlorine as the first step. As a vinyl ether the predominant reaction of active hydrogen compounds might be the addition to the double bond. Because of the difunctionality of this compound it was interesting to determine the nature of the reaction with a number of alcohols and acids.

Very little is found in the literature concerning the reactions of α-halovinyl ethers. Imbert[4] reports that reactions of α-halovinyl ethers with alcohols and acids give esters and acyl halides respectively. Cromptom and Vanderstichele[5] prepared chloro acetates and acid halides from α,β-dichlorovinyl ethyl ether. The reaction gives two distinct sets of products from a common intermediate formed by the addition of an alcohol to the double bond.



$$ClCH{=}CCl{-}OC_2H_5 + ROH \longrightarrow [ClCH_2{-}\underset{\displaystyle \overset{|}{OR}}{CCl}{-}OC_2H_5] \begin{matrix} \nearrow ClCH_2COOR + C_2H_5Cl \\ \searrow ClCH_2COOC_2H_5 + RCl \end{matrix}$$

Applying this reaction sequence to chlorodioxene the products should be an alkyl chloride and dioxanone (I), or an ester of 2-chloroethoxyacetic acid (II).



EXPERIMENTAL

Four methods of reaction were employed in this investigation. Each method is illustrated.

Method A. This method involves simply refluxing the reactants in a suitable solvent for an appropriate length of time.

Chlorodioxene (120.5 g., 1.0 mole), 74.1 g. (1.0 mole) of butanol and 200 ml. of 1,4-dioxane were charged into a 500-ml. thermowell flask equipped with a thermometer and reflux condenser to which was attached a drying tube. The mixture was refluxed for 16 hr. with a pot temperature of 112°. A slight evolution of hydrogen chloride was noticed during this heating period. The reaction mixture was frac-

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(1) From the M.S. thesis of John D. Welks.

(2) Present address: American Can Co., Barrington, Ill.

(3) M. J. Astle and W. C. Gergel, U. S. Patent 2,756,240 (July 4, 1956).

(4) G. Imbert, Ger. Patent 212,592 (Oct. 4, 1906).

(5) H. Crompton and P. L. Vanderstichele, *J. Chem. Soc.*, 691 (1920).

tionated at atmospheric pressure to remove low-boiling compounds, then at 102 mm. to remove the dioxane and excess butanol, and finally at 19 mm. to yield 156.8 g. of the *n*-butyl ester of 2-chloroethoxyacetic acid. (b.p. 132–134 at 19 mm.) The yield was 81%.

Method B. This method involves preheating the pure chlorodioxene to the desired temperature and then introducing the alcohol or acid dropwise. Thus, chlorodioxene (30 g., 0.25 mole) was charged into a 200-ml. three-neck flask equipped with a thermometer, dropping funnel and a reflux condenser capped by a drying tube. The chlorodioxene was heated to 40° and 20 g. (0.2 mole) of glacial acetic acid was added dropwise over a period of 1.5 hr. The temperature was then increased to 100° to insure total reaction. The mixture was distilled to yield 13.0 g. of acetyl chloride 0.166 mole) and 15.0 g. of *p*-dioxanone (0.167 mole) (b.p. 109–110° at 37.5 mm.; m.p. 26–27°).

Method C. This procedure is essentially the same as Method B except that solid reactants were added by portions through the neck of the flask which was then stoppered. A magnetic stirrer was used to effect solution of the reactants.

Method D. Here the reactants were mixed in the reaction flask and cooled or heated to maintain the desired reaction temperature. No solvent was employed in this procedure.

Identification of Compounds. The most frequently encountered compound was *p*-dioxanone which had been prepared previously by other methods. This compound had a marked tendency to undergo reversible polymerization. Palomaa and Jarvenkyla[6] have reported that *p*-dioxanone polymerized on standing; and while its melting point and molecular weight increased, the boiling point remained constant at 213–214° and after distillation of the polymer, the melting point reverted to that for the monomer, which was 26.7°. Salmi, Leimu, and Kallio[7] report the same peculiar behavior and suggest distillation over fused potassium hydroxide to remove traces of the unlactonized acid which they felt catalyzed the polymerization. The *p*-dioxanone isolated from the anhydrous mixture of the acids, melted at 26–27°. These properties were observed in the product obtained from chlorodioxene. Further confirmation was obtained by an infrared analysis.

The 2-chloroethoxyacetates were identified by properties found in the literature, by infrared analysis, and saponification equivalents.

The methyl and ethyl esters of 2-chloroethoxyacetic acid had been prepared previously.[1] There was good agreement with the products prepared from chlorodioxene. It was very difficult to separate the ethyl ester from dioxanone. The compounds prepared from chlorodioxene and acids are all well known.

Methyl-2-chloroethoxy acetate and *p*-dioxanone could not be separated by conventional distillation techniques; however, the tendency of the *p*-dioxanone to polymerize was used to effect the separation. The fraction which contained the ester and *p*-dioxanone was allowed to stand for 2 weeks, during which time the *p*-dioxanone polymer collected on the sides of the vessel. The fraction was then filtered and redistilled to yield the ester. Infrared analysis indicated that the ester obtained in this manner was free from *p*-dioxanone.

DISCUSSION

The reactions of chlorodioxene with primary alcohols, phenols and acids were exothermic following induction periods of varying lengths at room temperature. Reactions with secondary and tertiary alcohols were not appreciably exothermic.

TABLE I

SAPONIFICATION EQUIVALENTS

Ester of 2-Chloroethoxy-Acetic Acid	Mol. Wt.	Sap. Equiv.	
		Calcd.	Found
Methyl	152.5	76.3	77.4
n-Butyl[b]	194.6	97.3	97.8
sec-Butyl	194.6	97.3	88.4[a]
Allyl	178.5	89.3	91.9
p-Methoxyphenyl	244.6	122.3	121.9
$ClCH_2CH_2$—	201.0	67.0	67.3
—(CH_2CH_2)—	303.0	75.8	75.6

[a] Very difficult to hydrolyze, contaminated with *p*-dioxanone. [b] *Anal.* Calcd. for *n*-butyl ester (from Weiler and Strauss): C, 49.36; H, 7.77; Cl, 18.22; O, 24.66. Found: C, 49.95; H, 7.81; Cl, 16.29; O, 25.95.

The results of the reactions of 2-chlorodioxene with alcohols are summarized in Table II. Primary alcohols and phenols, with the exception of methyl and allyl alcohols, yielded only the 2-chloroethoxyacetates when the reactions were carried out at 80–100° in solvents or in the absence of solvents.

Secondary alcohols such as 2-butanol gave a mixture of 2-chlorobutane, *p*-dioxanone, and the chloroethoxy acetate. Methyl and allyl alcohols gave similar results.

The product from the *sec*-butyl alcohol and allyl alcohol runs contained a large fraction, distilling at slightly lower temperature than the ester. Infrared spectra of these fractions indicated a mixture of the ester and *p*-dioxanone. This method was successfully used to separate the allyl ester from the *p*-dioxanone, but the 2-butyl ester–*p*-dioxanone mixture completely solidified and could not be separated. Here, solvent extraction was employed, but the ester obtained was still slightly contaminated with *p*-dioxanone.

tert-Butyl alcohol gave only the alkyl chloride and *p*-dioxanone.

Ethylene glycol reacted to give a mixture of $ClCH_2CH_2OCH_2COOCH_2CH_2Cl$ (III) and $ClCH_2CH_2OCH_2COOCH_2CH_2OOCCH_2OCH_2CH_2Cl$ (IV). Compound III had a saponification equivalent of 67.3 indicating three saponifiable sites. It might have been formed from ethylene chlorohydrin from the intermediate. *p*-Dioxanone, which should be formed in this case, was not isolated. An examination of the infrared spectra indicated the absence of OH groups so that $ClCH_2CH_2OCH_2COOCH_2CH_2OH$ could not have been formed in appreciable amounts.

The behavior of water was somewhat anomalous. When treated with 2-chlorodioxene on a mole-for-mole basis, a viscous, black tar was obtained. However, when a two-fold excess of chlorodioxene was used, a 65% yield of *p*-dioxanone was obtained.

The results of the reaction of 2-chlorodioxene with acids are summarized in Table III. The acids all gave acyl halides and *p*-dioxanone. In the reaction with benzoic acid, the two expected

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(6) M. H. Palomaa and Y. T. Jarvenkyla, *Ber.* **65B**, 923 (1932).

(7) E. J. Salmi, R. Leimu, and H. Kallio, *Suomen Kemistilehti* **17B**, 17 (1944), *Chem. Abstr.* **40**, 6491 (1956).

TABLE II

REACTIONS OF 2-CHLORODIOXENE WITH ALCOHOLS AND PHENOLS

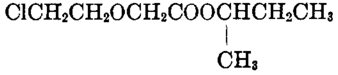
Alcohol or Phenol	Reaction Method and Solvent	Time, Hr.	Temp.	Products	Yield, %	B.P.
Methanol	B	1.5	110	*p*-Dioxanone	2	
				$ClCH_2CH_2OCH_2COOCH_3$	54	92/12 mm.
Ethanol	B	4	80	*p*-Dioxanone	Trace	
				$ClCH_2CH_2OCH_2COOC_2H_5$	71	96/10 mm.
n-Butyl alcohol	A; Dioxane	16	112	*p*-Dioxanone	Trace	
				$ClCH_2CH_2OCH_2COOC_4H_9$	81	129/16.5 mm.
n-Butyl alcohol	B	4	80	*p*-Dioxanone	Trace	
				$ClCH_2CH_2OCH_2COOC_4H_9$	78	
H_2O	D	17	—	*p*-Dioxanone	65	
Allyl alcohol	D	1	50	*p*-Dioxanone	4.7	
				Allyl chloride	46	
				$ClCH_2CH_2OCH_2COOCH_2CH{=}CH_2$	27.8	112/11 mm.
Ethylene glycol	D	1	100	$ClCH_2CH_2OCH_2COOC_2H_4Cl$	18.8	86/0.06 mm.
				$(ClCH_2CH_2OCH_2COO)_2C_2H_4$	13.2	164/0.09 mm.
2-Butanol	D	41	25	2-Chlorobutane	14.2	
				p-Dioxanone	19.4	
				 $ClCH_2CH_2OCH_2COO\underset{\substack{\vert \\ CH_3}}{C}HCH_2CH_3$	4.1	92–94/2.5 mm.
t-Butyl alcohol	A; Dioxane	10.5	81	*t*-Butyl chloride	25.0	
				p-Dioxanone	32.0	
Phenol	A; Dioxane	22	123	*p*-Dioxanone	None	
				$ClCH_2CH_2OCH_2COOC_6H_5$	82	151/4.5 mm.
Phenol	C	1.5	80	*p*-Dioxanone	None	
				$ClCH_2CH_2OCH_2COOC_6H_5$	91.5	
p-Methoxy-phenol	D	2	80	*p*-Dioxanone	None	
				$ClCH_2CH_2OCH_2COOC_6H_4OCH_3$	87	182–5/4.5 mm.

TABLE III

REACTIONS OF 2-CHLORODIOXENE AND ACIDS

Acid	Reaction Method and Solvent	Time, Hr.	Temp.	Products	Yield, %
Acetic acid	B	1.5	40	Acetyl chloride	83.5
				p-Dioxanone	84
Acetic acid	A; Dioxane	11	116	Acetyl chloride	35.8
				p-Dioxanone	66
Chloroacetic acid	D	3	80	Chloroacetyl chloride	96[a]
				p-Dioxanone	102
p-Nitrobenzoic acid	D	4	120	*p*-Nitrobenzoyl chloride	38
				p-Dioxanone	74.5
Benzoic acid	C	3	80–120	Benzoyl chloride	97.5
				p-Dioxanone	62.5

[a] Hydrolysis in excess 2-chlorodioxene.

products were obtained and there was spectral evidence for anhydride; however, it could not be isolated.

In summary, there appears to be a trend in the reactions of primary, secondary and tertiary alcohols in which it is noted that the tendency for the reaction to yield the ester or the alkyl chloride and *p*-dioxanone combination can be related to the stability of the carbonium ion obtainable from the alcohol by cleavage of the carbon-oxygen bonds. The more stable *tert*-butyl carbonium ion would be expected to give only *p*-dioxanone and *tert*-butyl chloride, those with slightly less stability, the *sec*-butyl and allyl carbonium ions should give both the ester and the *p*-dioxanone-alkyl chloride combination, while the least stable primary carbonium ions should give only the ester. The reaction therefore probably proceeds through the formation of intermediate carbonium ions.

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