Anal. Calcd for $C_8H_6Cl_3NO_3$: C, 35.5; H, 2.2; N, 5.2; Cl, 39.3. Found: C, 35.7; H, 2.3; N, 5.5; Cl, 39.4.

Registry No.—**1a**, 109-92-2; **1b**, 110-87-2; **1c**, 927-61-7; **1d**, 4696-25-7; **1e**, 4696-26-8; **1g**, 2678-54-8; **2b**, 29669-00-9; **2c**, 29669-01-0; **2d**, 29669-02-1; **2e**, 29669-03-2; **3a**, 29669-04-3; **3b**, 29669-05-4; **3c**, 29784-75-6; **3d**, 29669-06-5; **3e**, 29669-07-6; **3f**, 29669-08-7; **4a**, 29669-09-8; **4b**, 29784-76-7; **4g**, 29669-10-1; **6**, 29669-11-2; **7a**, 29669-12-3; **7b**, 29669-13-4; **8a**, 29784-77-8; **9**, 29689-63-2; **10**, 29689-64-3; trichloroacetyl isocyanate, 3019-71-4; *N*-(3-ethoxyacryloyl)benzamide, 29689-66-5.

Acknowledgment.—The authors thank Professors Glenn Berchtold and Roald Hoffmann for helpful discussions.

Synthesis of 3-Alkoxyoxetanes

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Received August 20, 1970

3-Alkoxyoxetanes are prepared by chlorination of allyl alcohol in the presence of an excess of an aliphatic alcohol (including allyl alcohol) followed by ring closure with hot aqueous NaOH. The product distribution during chlorination is consistent with a carbonium ion mechanism, yielding 2,3-dichloropropanol and the isomers 2-alkoxy-3-chloropropanol and 3-alkoxy-2-chloropropanol in the ratio of about 65:35. Side reactions include oxidation and ether formation by reaction of the three main chlorination products with the intermediate carbonium ion. The yield of the three major chlorination products is 65–80%. Yields of alkoxyoxetane based on 2-alkoxy-3-chloropropanol are in the range of 55–75%. A series of alkoxyoxetanes, $\overline{OCH_2CH(OR)CH_2}$, were prepared where R = methyl, ethyl, allyl, *n*-butyl, cyclohexyl, and *n*-dodecyl. These were treated with anhydrous HCl to form the pure precursor 2-alkoxy-3-chloropropanol.

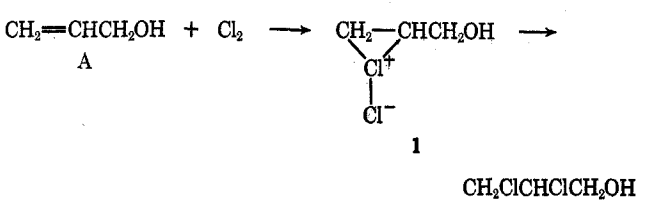
The halogenation of olefins in reactive (nucleophilic) solvents has been studied extensively. The reaction proceeds *via* a carbonium ion mechanism involving intermediate halonium ions. In alcoholic media, the main products are ethers and dihalides.[2-4]

We have studied the chlorination of allyl alcohol since the dichloropropanol and 1,2- and 1,3-chlorohydrin ethers produced offer a route to alkoxyoxetanes as well as epichlorohydin and alkyl glycidyl ethers.

The present work deals with the synthesis of a series of 3-alkoxyoxetanes[5] and their reaction with anhydrous hydrogen chloride to produce pure 2-alkoxy-3-chloropropanols.

Discussion

Chlorination of allyl alcohol in the absence of water leads mainly to chlorohydrin ethers, dichloropropanol, and oxidation products. Dichloropropanol formation



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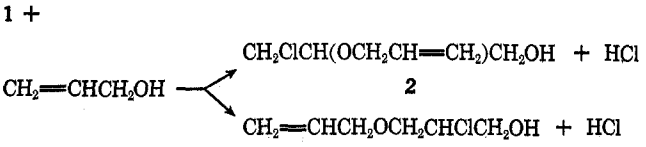
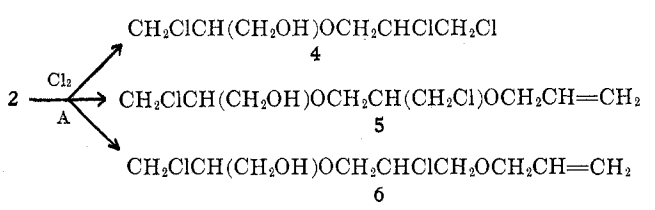


$$CH_2{=}CHCH_2OH + Cl_2 \longrightarrow CH_2{=}CHCHO + 2HCl$$

is initially competitive with ether formation; the respective rates of formation remain approximately the same over the first 20% reaction. At higher conversion, it is expected that dichloropropanol formation would increase relative to ether formation due to the increased HCl concentration (**1** + $Cl^- \rightarrow CH_2ClCHClCH_2OH$). The isomeric allyloxychloropropanols (**2** and **3**) are formed in the ratio of about 65:35.

The initial oxidation product is probably acrolein but it rapidly undergoes further reaction producing an acetal containing a labile chlorine. Acrolein can add HCl and form acetals of β-chloropropionaldehyde.[6] Chlorination followed by acetal formation would give $CH_2ClCHClCH(OR)_2$, $CH_2{=}CHCH_2OCH_2CHClCH(OR)_2$, and $CH_2ClCH(OCH_2CH{=}CH_2)CH(OR)_2$.

The conversion of allyl alcohol was kept low (about 20%) to minimize formation of polyethers resulting from chlorination of the allyloxychloropropanols. A



similar reaction can be written for the linear ether **3**. The same products can be formed by reaction of the intermediate carbonium ion **1** with 2,3-dichloropropanol and with **2** and **3**.

Hennion[7] reported the preparation of 2-allyloxy-3-chloropropanol (but not the linear isomer) in 36% yield by reaction of *tert*-butyl hypochlorite with allyl alcohol but did not study its reaction with base. Later work has shown that reaction of *tert*-BuOCl with allyl alcohol

(1) To whom correspondence should be addressed.
(2) E. L. Jackson, *J. Amer. Chem. Soc.*, **48**, 2166 (1926).
(3) P. D. Bartlett and D. S. Tarbell, *ibid.*, **58**, 466 (1936).
(4) C. F. Erwin and G. F. Hennion, *ibid.*, **63**, 858 (1941).
(5) R. J. Polak, J. A. Wojtowicz, and J. A. Zaslowsky, U. S. Patent 3,400,135 (1968).
(6) A. Kirrmann, M. Goudard, and M. Chahidzadeh, *Bull. Soc. Chim.*, **2**, 2147 (1935).
(7) B. L. Emling, R. R. Vogt, and C. F. Hennion, *J. Amer. Chem. Soc.*, **63**, 1624 (1941).

TABLE I

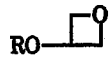
PREPARATION OF 3-ALKOXYOXETANES

Allyl alcohol, mol	Chlorine, mol	Solvent, mol	2,3-Dichloropropanol, mol	Alkoxychloropropanol,[a] mol	Dehydrochlorination: Time, hr	Dehydrochlorination: Conversion,[b] %	Dehydrochlorination: Alkoxyoxetane, mol	Dehydrochlorination: % yield[c]
5.0	5.05	CH_3OH, 74	0.85	3.34	2	98	1.18	55
5.0	5.05	C_2H_5OH, 51	1.17	2.46	4	98	1.16	74
0.5	0.5	HOC_2H_4OH, 2.5	*d*	0.17	6	100	*e*	
250[f]	45.6		12.0	12.0	10.5	86	4.1	63
2.0	2.1	*n*-C_4H_9OH, 4.7	0.6	0.9	14	98	0.40	70
2.0	1.01	*n*-$C_{12}H_{25}OH$, 2.5	0.45	0.40	20	13	0.019	56
2.0	2.04	$C_6H_{11}OH$, 10.7	0.62	0.68	25	82	0.23	60

[a] Sum of 2-alkoxy-3-chloropropanol and 3-alkoxy-2-chloropropanol which are formed in a ratio of about 65:35. [b] Based on chromatographic analysis. [c] Based on 2-alkoxy-3-chloropropanol. [d] Not determined. [e] No oxetane formed; isolated 10.5 g, 0.89 mol of 2-hydroxymethyl-1,4-dioxane. [f] Conversion of allyl alcohol was 22%.

TABLE II

PHYSICAL PROPERTIES OF 3-ALKOXYOXETANES[a]



R	Registry no.	Bp, °C (mm)	d^{25}	$n^{25}D$	MR: Calcd	MR: Found
Methyl	1872-45-3	43 (50)	0.9801	1.4068	22.2	22.1
Ethyl	6777-01-1	42 (25)	0.9578	1.4098	26.8	26.4
Allyl	6777-00-0	64 (25)	0.9788	1.4372	31.0	30.6
n-Butyl	6776-84-7	90 (50)	0.9231	1.4215	36.1	35.7
Cyclohexyl	6777-02-2	93 (9)	1.000	1.4640	43.1	43.1
n-Dodecyl	6776-85-8	92 (0.03)	0.875	1.4420	73.3	73.2

[a] Satisfactory analyses (±0.3% in C and H) were reported for all compounds in the table: Ed.

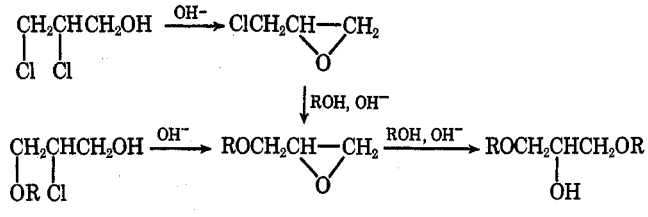
in the presence of $BF_3 \cdot Et_2O$ as catalyst yields both isomers of allyloxychloropropanol.[8]

Other alkoxychloropropanols were prepared using an excess of aliphatic alcohol and incremental addition of allyl alcohol to minimize competitive reaction of allyl alcohol and the main chlorination products with the carbonium ion **1**. In methanol the latter reaction gives the following products: **4**, $CH_2ClCH[OCH_2CH(OCH_3)CH_2Cl]CH_2OH$, and $CH_2ClCH(OCH_2CHClCH_2OCH_3)CH_2OH$. Three additional isomeric products are also possible. The yield of the three main chlorination products was between 65 and 80%. The data are summarized in Table I.

The preparation of methoxy-[9] and *n*-butoxychloropropanols[10] by chlorination of allyl alcohol in methanol and in 1-butanol has been reported.

The susceptibility of the solvent to chlorination must be considered. For example, chlorination of allyl alcohol in excess phenol resulted in formation of *p*-chlorophenol (no phenoxychloropropanols were detected). When dichlorophenol was used, only dichloropropanol and allyloxychloropropanols were observed. 2-Phenoxy-3-chloropropanol and 3-phenoxyoxetane have been synthesized from $CH_2OHCH(OPh)CH_2OSO_2C_6H_4Br$.[11]

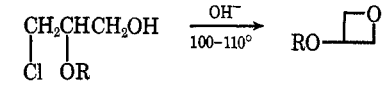
Treating crude reaction mixtures (after removal of solvent) with aqueous NaOH at room temperature produced epichlorohydrin and alkyl glyceryl ethers. The epoxides were formed in high yield and could be readily removed by distillation of the organic layer. When the dehydrochlorination is conducted without prior removal of the excess alcohol solvent, 1,3-dialkyl glyceryl ethers are obtained in good yield. In the presence of excess



allyl alcohol, an 84% yield of 1,3-diallyloxy-2-propanol was obtained. Zunino[12] prepared a series of 1,3-dialkyl glyceryl ethers by reacting epichlorohydrin with alcohols (methyl, ethyl, *n*-propyl, allyl, and isoamyl) in the presence of KOH. Fairborne[13] prepared glycerol diethers in 70% yields by reaction of dichloropropanol with alcohols in the presence of base.

Instead of dehydrochlorinating the crude chlorohydrins batchwise with caustic, distillation from lime slurry was used. This technique gave good yields of epichlorohydrin and allyl glycidyl ether. The oxetane precursor steam distils unreacted in this procedure.

Dehydrochlorination of 1,3-chlorohydrins to oxetanes requires more vigorous thermal conditions than the corresponding formation of epoxides from 1,2-chlorohydrins. Higher 1,3-chlorohydrins required longer reac-



tion times due primarily to their low solubility in aqueous base. Oxetane yields based on chlorohydrin were in the 55–75% range (see Table I). Physical properties of the 3-alkoxyoxetanes prepared are tabulated in Table II. Ethoxy-, allyloxy-, *n*-butoxy-, cyclohexoxy-,

(8) H. L. Plant, unpublished data.
(9) J. A. Flint and G. T. Merrall, British Patent 988,116 (1965).
(10) K. B. Cofer and R. W. Fourie, U. S. Patent 3,093,689 (1963).
(11) G. L. Brode and J. Wynstra, 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964, No. W 041.
(12) V. Zunino, *J. Chem. Soc., London*, 410 (1899).
(13) A. Fairborne, G. P. Gibson, and D. W. Stephens, *Chem. Ind. (London)*, **49**, 1021 (1930).

TABLE III

PHYSICAL PROPERTIES OF 2-ALKOXY-3-CHLOROPROPANOLS[a]

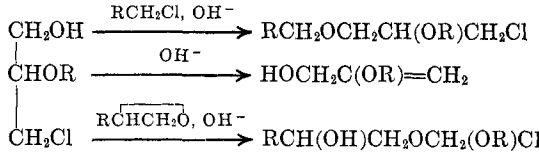
$ClCH_2CH(OR)CH_2OH$

R	Registry no.	Bp, °C (mm)	d^{25}	$n^{25}D$	MR Calcd	MR Found
Methyl	2858-55-1	96 (25)	1.156	1.4472	28.7	28.8
Ethyl	6798-40-9	101 (25)	1.098	1.4440	33.3	33.5
Allyl	10433-29-1	98 (11)	1.121	1.4650	37.4	37.1
n-Butyl	6776-89-2	99 (2)	1.043	1.4460	42.6	42.6
Cyclohexyl	6776-87-0	67 (0.03)	1.112	1.4780	49.5	49.0
n-Dodecyl	29908-08-5	115 (0.03)	0.947	1.4545	79.5	79.7

[a] Satisfactory analyses (±0.3% in C and H) were reported for all compounds in the table: Ed.

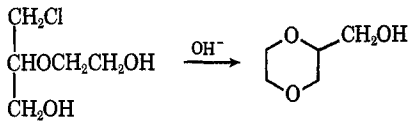
and *n*-dodecoxyoxetanes have not been previously reported. 3-Methoxyoxetane has been prepared in 65% yield by a similar route.[14]

Possible side reactions in the dehydrochlorination of 1,3-chlorohydrins are ether formation (intermolecular Williamson reaction), olefin formation (by HCl elimination), and oxyalkylation. Intermolecular ether



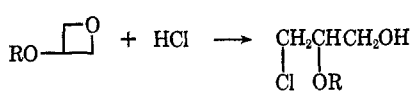
formation is an important side reaction in the dehydrochlorination of bis(2-chloroethyl) acetals to divinyl acetals with alcoholic alkali.[15] Olefin formation in preparation of oxetanes from 1,3-chlorohydrins is a common competing reaction.[16] The oxyalkylation reaction would occur during formation and destruction of epichlorohydrin and alkyl glycidyl ethers. Glycol or ether formation from the oxetane product would not be significant since oxetanes are stable to base at moderate temperatures. Searles[17] has shown that oxetane reacts on prolonged heating at elevated temperatures (175°) with alcohols in the presence of alkoxides to form monoalkyl ethers of trimethylene glycol.

No oxetane was obtained from 2(2′-hydroxyethyl)-3-chloropropanol; dioxane ring formation occurred ex-



clusively. The linear isomer $HOCH_2CH_2OCH_2CHCl$-CH_2OH[18] is also capable of forming methyloldioxane. The same product was obtained by dehydrochlorination of $CH_2ClCHOHCH_2OCH_2CH_2OH$ as well as CH_2-$ClCHOHCH_2OCH_2CH_2Cl$.[19]

Although 3-alkoxyoxetanes are stable at moderate temperatures (100–110°) to base and chloride ion (unlike epoxides), they react readily with anhydrous HCl (like epoxides) to form the precursor 2-alkoxy-3-chloropropanol. Yields are in the vicinity of 85–90% (see Table III). Reaction with concentrated HCl gives mainly chlorohydrin and some 1,3-diol while dilute aqueous HCl (or H_2SO_4)[20] favors 1,3-diol formation.



The epoxide precursors $ROCH_2CHClCH_2OH$, which were formed in yields as high as 24%, are formed in only minor amounts by the reaction of alkyl glycidyl ethers with anhydrous HCl.

Experimental Section

Materials.—Allyl alcohol was from Olin Corp., assaying 97–98% by bromate–bromide analysis. Other chemicals were commercially available reagent grade.

Analyses.—Product distributions were determined by gas–liquid chromatography (glc). Quantitative analyses were obtained using standards of approximately the same concentration as the sample. Normally a 5-ft silicone SF-96 (20% on 80–100 firebrick) column was employed, operating isothermally from 125 to 200° with a He flow of 40 cc/min at 20 psig. The dodecyl compounds were analyzed using a 1-ft silicone SE-30 (15% on 80–100 Chromosorb) column programming from 100 to 350°. The ratio of the isomeric alkoxychloropropanols was determined using a 3-ft Igepal (5% on Fluoropak) column programming from 100 to 200°. The ratio of 2-alkoxy-3-chloropropanol/3-alkoxy-2-chloropropanol was about 65:35. Allyl alcohol was analyzed using a 3-ft polyethylene glycol 400 (15% on 80–100 mesh Chromosorb) column operating at 70°.

Infrared spectra of liquid samples between salt plates were recorded with a Perkin-Elmer Infracord. Absorption bands reported by Searles[21] were used in interpreting the spectra of the oxetanes. The ring C–O–C is characterized by a strong broad band in the region of 10.2–10.3 μ.

^1H nmr spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal standard.

The pyridinium chloride method[22] was used to assay alkoxyoxetanes *via* the oxetane ring. Redistilled products analyzed above 99%.

Attempts to assay alkoxyoxetanes with aqueous $Na_2S_2O_3$ were unsuccessful due to the very slow and incomplete reaction even at reflux temperature. For methoxyoxetane, the initial rate constant was $k^{100} = \sim 2 \times 10^{-4}$ min^{-1}. In contrast, simple epoxides such as ethylene and propylene oxides exhibit rate constants at 64° of 0.67 and 0.36 min^{-1}, respectively.[23]

Searles[24] reports a value of $k^{35} = 0.013$ min^{-1} for oxetane (at pH 8). We observed no base release at 35° and found a measurable reaction rate only at reflux temperature. The initial rate constant was similar to that found for methoxyoxetane; $k^{100} = \sim 2 \times 10^{-4}$ min^{-1}.

Apparatus.—Chlorinations were conducted in a three-neck round-bottom flask fitted with stirrer, thermometer, and chlorine sparger. In the case of methanol and ethanol, the end point (presence of excess Cl_2) was determined potentiometrically (Beckman pH meter) using calomel as reference and platinum as indicating electrodes. This technique was not adaptable to the higher alcohols. Reaction temperature was usually maintained between 30 and 40° by external cooling.

(14) J. A. Flint and G. T. Merrall, British Patent 988,117 (1965).
(15) J. A. Wojtowicz, unpublished data.
(16) N. C. Gaylord, *et al.*, *J. Amer. Chem. Soc.*, **76**, 59 (1954).
(17) S. Searles and C. F. Butler, *ibid.*, **76**, 56 (1954).
(18) M. S. Kharasch and W. Nudenberg, *J. Org. Chem.*, **8**, 189 (1943).
(19) French Patent, 1,084,038 (1955).
(20) J. A. Flint and G. T. Merral, British Patent 991,232 (1965).
(21) G. M. Barrow and S. Searles, *J. Amer. Chem. Soc.*, **75**, 1175 (1953).
(22) R. T. Keen, *Anal. Chem.*, **29**, 1041 (1957).
(23) W. C. J. Ross, *J. Chem. Soc.*, London, 2257 (1950).
(24) S. Searles, *J. Amer. Chem. Soc.*, **73**, 4515 (1951).

Dehydrochlorinations were carried out using an excess of aqueous NaOH at reflux (100–110°) in a three-neck, round-bottom flask equipped with stirrer, thermometer, condenser, and addition funnel.

Reaction of anhydrous HCl with alkoxyoxetanes was run in a three-neck, round-bottom flask fitted with stirrer, thermometer, and sparger. Reaction temperature was maintained between 20 and 30° by external cooling.

Yields.—Yields of chlorination products are based on allyl alcohol while yields of oxetanes are based on 3-chloro-2-alkoxypropanol.

3-Allyloxyoxetane.—Chlorine (3.242 kg, 45.6 mol) was introduced at about 4 g/min into allyl alcohol (145 kg, 250 mol). The following products were identified: 2,3-dichloropropanol (12.0 mol, 21% yield), 3-allyloxy-2-chloropropanol (4.2 mol, 15% yield), 2-allyloxy-3-chloropropanol (7.6 mol, 28% yield), and a chloro acetal (5.3 mol). The latter (determind by the oxime method) released an equimolar amount of HCl on hydrolysis which indicates that its structure is either $CH_2ClCH_2CH(OR)_2$ or $CH_2ClCHClCH(OR)_2$. The conversion of allyl alcohol was 22%. The unreacted allyl alcohol was removed by distillation leaving a crude product of 4.643 kg. Aqueous NaOH (1550 g in 2775 cc of H_2O) was added to the crude product over a 0.5-hr period maintaining the temperature below 30°. The well-stirred mixture was then heated to 100–110° and maintained for 10.5 hr (conversion of 2-allyloxy-3-chloropropanol was 86%). As the temperature was raised (from room temperature), the formation and disappearance of epichlorohydrin and allyl glycidyl ether was observed. Sufficient water to dissolve the salt was added. After separating layers, the aqueous layer was extracted three times with 500-cc portions of CCl_4. The CCl_4 was removed by distillation and the residue combined with the main organic layer. Distillation through a 12-in. glass helices packed column gave 435 g (59% yield) of 3-allyloxyoxetane: bp 64° (25 mm); d^{25} 0.9788; $n^{25}D$ 1.4372; ir 1.633 and 2.113 (terminal CH_2), 6.07 (C=C), 8.9 (COC), 10.2 (oxetane ring), and 10.7 μ (CH out of plane bending); nmr ($CDCl_3$) multiplet at 3.9 ppm (intensity 2) assigned to CH_2O of the allyloxy group, multiplet at 5.2 ppm (intensity 2) and 5.9 ppm (intensity 1) assigned to CH_2 and CH of the vinyl group, and a multiplet at 4.6 ppm (intensity 5) assigned to CH and CH_2 of the oxetane ring. Mass spectral analysis gave no parent peak but the cracking pattern was consistent with the proposed structure. Observed molecular weight (cryoscopic) was 114. Assay by pyridinium chloride or bromination (bromate–bromide reagent) indicated a purity of >98%.

Anal. Calcd for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found: C, 63.2; H, 8.8.

The solubility of allyloxyoxetane in water is about 15% and is similar to that of allyl glycidyl ether.

3-Methoxyoxetane.—Chlorine (359 g, 5.05 mol) and allyl alcohol (265 g, 4.57 mol) were introduced at about 30 mmol/min into a solution of allyl alcohol (25 g, 0.43 mol) in methanol (2.336 kg, 74 mol). The excess methanol was removed by distillation leaving a residue of 622 g consisting of 2-chloro-3-methoxypropanol (1.17 mol, 23% yield), 2-methoxy-3-chloropropanol (2.17 mol, 43% yield), and 2,3-dichloropropanol (0.85 mol, 17% yield). The crude product was added to 2 l. of 10% NaOH solution and stirred for 2 hr at 25° and then at 105° for 2 hr (conversion of 2-methoxy-3-chloropropanol was 98%). The mixture was extracted twice with 2-l. portions of methyl ethyl ketone. After stripping off of the solvent, the product was vacuum distilled through a 24-in. Berl saddles packed column providing 93 g (50% yield) 3-methoxyoxetane, bp 43° (53 mm). A redistilled sample analyzed 99.9% and had the following physical properties: bp 110.5°; d^{25} 0.9801; $n^{25}D$ 1.4068; ir 7.25 (CH_3), 8.85 (C–O–C), and 10.25 μ (oxetane ring). The nmr spectrum in benzene showed three absorptions in the ratio 3:1:4; singlet at δ 2.85 (OCH_3), triplet of triplets at δ 3.93 (OCH), and a doublet at δ 4.42 (OCH_2). A first-order spectrum was not obtained.

Anal. Calcd for $C_4H_8O_2$: C, 54.5; H, 9.1. Found: C, 54.6; H, 9.1.

Experimental and physical data on the preparation of other alkoxyoxetanes are shown in Tables I and II.

2-Allyloxy-3-chloropropanol.—Anhydrous HCl (15.3 g, 0.42 mol) was introduced slowly into 3-allyloxyoxetane (49 g, 0.43 mol) over a 1-hr period. Analysis (glc) indicated a yield of about 90%. Vacuum distillation through a 12-in. glass helices packed column gave 38 g of a heart cut: bp 98–100° (11–11.5 mm); d^{25} 1.121; $n^{25}D$ 1.4650; assay for unsaturation by bromate–bromide reagent showed a purity of 98%; ir 2.9 (COH), 6.07 (C=C), 9.0 (COC), 10.7 (CH out-of-plane bending), and 13.4 μ (CCl).

Anal. Calcd for $C_6H_{11}O_2Cl$: C, 47.8; H, 7.3; Cl, 23.5. Found: C, 47.5; H, 7.3; Cl, 23.7.

Data on the preparation of other 2-alkoxy-3-chloropropanols are given in Table III.

Hydroxyethylchloropropanol.—Chlorine (106 g, 1.5 mol) and allyl alcohol (87 g, 1.5 mol) were added at about 14 mmol/min to ethylene glycol (393.5 g, 6.35 mol). The excess glycol was distilled out under vacuum (25 mm) through a 12-in. glass helices packed column. The residue (134 g) was further distilled yielding 77 g of isomeric hydroxyethylchloropropanols: bp 140–145° (5 mm); d^{25} 1.235; $n^{25}D$ 1.4697; ir 3.0 (COH), 8.9 (COC), and 13.4 μ (CCl).

Anal. Calcd for $C_5H_{11}O_3Cl$: C, 38.9; H, 7.1; Cl, 23.0. Found: C, 38.5; H, 7.1; Cl, 22.6.

2-Hydroxymethyl-1,4-dioxane.—Chlorine (35 g, 0.5 mol) and allyl alcohol (29 g, 0.5 mol) were added at 14 mmol/min to ethylene glycol (155 g, 2.5 mol). Excess glycol was removed under vacuum (30 mm). The residue (50 g containing 0.17 mol of hydroxyethylchloropropanol) was stirred at reflux with excess NaOH for 6 hr. The reaction mixture was extracted three times with 150-cc portions of methyl ethyl ketone. The solvent was removed by distillation at atmospheric pressure, and the residue vacuum distilled yielding 10.5 g of distillate: bp 100–105° (18 mm); d^{20} 1.159; $n^{25}D$ 1.4555. The product was identified as 2-hydroxymethyl-1,4-dioxane by ir and mass spectral analysis.

Anal. Calcd for $C_5H_{10}O_3$: C, 50.8; H, 8.5. Found: C, 50.8; H, 8.4.

1,3-Diallyloxy-2-propanol.—Chlorinated allyl alcohol solution (405 g) containing dichloropropanol (0.142 mol) and allyloxychloropropanols (0.136 mol) was vigorously stirred at reflux (~90°) with excess 30% aqueous NaOH for 6 hr. Water was added to dissolve salt, the layers were separated, and the aqueous phase was extracted three times with 50-cc portions of CCl_4. The stripped extract was combined with the main organic layer. Chromatographic analysis showed the presence of some unreacted 2-allyloxy-3-chloropropanol (0.014 mol) and 3-allyloxyoxetane (0.043 mol, 59% yield) as well as 1,3-diallyloxy-2-propanol (0.160 mol, 84% yield). The ir of chromatographically trapped product was identical with the ir of that from reaction of epichlorohydrin with excess allyl alcohol in the presence of KOH.

Epichlorohydrin and Allyl Glycidyl Ether.—Steam was passed into a lime slurry [10 g $Ca(OH)_2$ in 200 g H_2O] in a 500-cc, three-neck flask fitted with stirrer, thermometer, addition funnel, and take-off condenser. A crude chlorohydrin mixture (20 g), stripped of excess allyl alcohol, containing dichloropropanol (52 mmol), 3-allyloxy-2-chloropropanol (18 mmol), and 2-allyloxy-3-chloropropanol (34 mmol) was added dropwise over a 30-min period. The distillate was saturated with salt and extracted with methyl ethyl ketone. Oxirane analysis (thiosulfate method) of the extract indicated the presence of 58.5 mmol of epoxide. Chromatographic analysis showed epichlorohydrin (44 mmol, 85% yield), allyl glycidyl ether (13 mmol, 72% yield), and unreacted 2-allyloxy-3-chloropropanol (32 mmol, 94% recovery).

Reactivity of Alkoxyoxetanes.—A 3% solution of allyloxyoxetane exhibited no decomposition when refluxed for several hours in 1 *N* NaOH, 1 *N* NaOH saturated with NaCl, or in saturated aqueous NaCl.

Refluxing methoxyoxetane in 0.1 *N* HCl resulted in 21% conversion to chlorohydrin and the balance to 1,3-glycol. In 1 *N* HCl the conversion to chlorohydrin was 59%. In concentrated HCl (11 *N*) cyclohexoxyoxetane was converted in about 90% yield to chlorohydrin.

Methoxyoxetane (1.07 mmol) in 25 cc of H_2O containing 5 g of $Na_2S_2O_3 \cdot 5H_2O$ was refluxed and the liberated base titrated periodically with 0.1 *N* HCl. After 67.3 hr the extent of reaction was 45.3%. The initial rate constant was $k^{100} = \sim 2 \times 10^{-4}$ min^{-1}. With oxetane, an identical initial rate was obtained.

3-Methoxy-2-chloropropanol.—The reaction mixture from chlorination of allyl alcohol in excess methanol was neutralized with $NaHCO_3$ and stripped of solvent. 3-Methoxy-2-chloropropanol was isolated from the residue by chromatographic trapping using a 5-ft column (15% Igepal on 90–100 Anakrom ABS) at 135°. The product had $n^{20}D$ 1.4494.

Anal. Calcd for $C_4H_9O_2Cl$: C, 38.6; H, 7.3; Cl, 28.5. Found: C, 38.5; H, 7.3; Cl, 28.4.

Chloromethoxypropoxychloropropanols.—The reaction mixture from chlorination of allyl alcohol (1.0 mol) in methanol (10 mol) containing Na_2CO_3 (0.5 mol) was filtered and stripped of solvent. The residue was vacuum distilled through a 12-in. glass helices packed column giving 96 g of a mixture of chloromethoxypropanols and dichloropropanol [bp 65° (5 mm)–45° (0.5 mm)]. The pot residue was extracted with ether to eliminate salt. After stripping, it was refluxed in acidified 1:1 MeOH–H_2O to hydrolyze acetals. The mixture was stripped of solvent and the residue vacuum distilled giving an additional 5 g of chlorohydrins and 8 g of a higher boiling fraction (140–145° at 0.5 mm). Chromatographic analysis (220°, 5-ft 15% CW20M/Anakrom ABS) showed two peaks in the ratio 9:1 at retention times of 8 and 12.5 min. The first (major) peak was trapped and identified (ir, mass spectrum, and nmr) as an isomeric mixture of chloromethoxypropoxychloropropanol. The four possible isomers are: $CH_2ClCH[OCH_2CH(OCH_3)CH_2Cl]CH_2OH$, $CH_2ClCH(OCH_2CHClCH_2OCH_3)CH_2OH$, $CH_2ClCH(OCH_3)CH_2OCH_2CHClCH_2OH$, and $CH_3OCH_2CHClCH_2OCH_2CHClCH_2OH$. Mass spectral analysis showed a molecular ion at mass 216 and indicated a compound containing two chlorine atoms. The cracking pattern was consistent with the proposed structures. Nmr (60 MHz) showed a complex region (3.50–4.30 ppm) assigned to the methylene and methine protons, two singlets for methoxy at 3.48 and 3.43 ppm, and a broad absorption due to hydroxyl at 2.88 ppm. At 90 MHz the methoxy protons were resolved into six singlets (3.478, 3.474, 3.467, and 3.417, 3.408, 3.404 ppm). Since each positional isomer contains two asymmetric centers a total of eight singlets is possible. Assigning the higher field group to primary methoxy and the lower field group to secondary methoxy gives values of 73% primary and 27% secondary.

Anal. Calcd for $C_7H_{14}O_3Cl_2$: C, 38.7; H, 6.5; Cl, 32.7. Found: C, 38.9; H, 6.4; Cl, 32.7.

Dichloropropoxychloropropanols.—Peak number two from the higher boiling fraction in the isolation of chloromethoxypropoxychloropropanols was trapped and identified (ir, mass spectrum, and nmr) as an isomeric mixture of $CH_2ClCH(OCH_2CHClCH_2Cl)CH_2OH$ and $CH_2ClCHClCH_2OCH_2CHClCH_2OH$.

Anal. Calcd for $C_6H_{11}O_2Cl_3$: C, 32.5; H, 5.0; Cl, 48.0. Found: C, 32.5; H, 5.0; Cl, 47.6.

Registry No.—3-Chloro-2-(2-hydroxyethoxy)propanol, 15045-14-4; 2-chloro-3-(2-hydroxyethoxy)propanol, 29908-10-9; 2-hydroxymethyl-1,4-dioxane, 29908-11-0; 3-methoxy-2-chloropropanol, 26438-92-6; $H_2CClCH[OCH_2CH(OCH_3)CH_2Cl]CH_2OH$, 29908-13-2; $CH_2ClCH(OCH_2CHClCH_2OCH_3)CH_2OH$, 29908-14-3; $CH_2ClCH(OCH_3)CH_2OCH_2CHClCH_2OH$, 29908-15-4; $CH_3OCH_2CHClCH_2OCH_2CHClCH_2OH$, 29908-16-5.

Acknowledgment.—The author are indebted to Dr. R. C. Rittner, Mr. J. Culmo, and Mr. J. Giunta for microanalyses; to Mr. H. Hoberecht and Dr. F. J. Preston for mass spectral analyses; to Mr. G. D. Vickers and Dr. T. Groom for nmr analyses; and to Mr. W. A. Nichols for performing some of the chromatographic analyses.

Cyclopropylthiophenes. Syntheses, Reactions, and Ultraviolet Spectra

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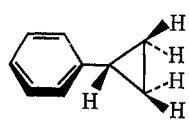
Received November 16, 1970

Synthetic routes to 2- and 3-cyclopropylthiophenes are described. Electrophilic deuteration, bromination, formylation, and iodination occur exclusively at the 5 position of 2-cyclopropylthiophene and at the 2 position of 3-cyclopropylthiophene. Nitration is less selective, proceeding at the 3 and 5 positions of 2-cyclopropylthiophene (40 and 60%, respectively) and at the 2 and 5 positions of 3-cyclopropylthiophene (88 and 12%, respectively). The cyclopropyl ring does not open during electrophilic substitution. Upon irradiation in benzene the iodo substituents of 2-cyclopropyl-5-iodothiophene and 3-cyclopropyl-2-iodothiophene are replaced by phenyl. The effect of cyclopropyl on the uv spectra approximates that of phenyl contrasting strongly the behavior of simple cyclopropyl-substituted aryl systems where only modest bathochromic shifts are found. The larger effect in thiophenes is attributed to a relatively larger decrease in electron density upon excitation at the carbon to which cyclopropyl is attached thereby making a greater demand upon the conjugative abilities of cyclopropyl. Comparisons with literature data are made.

Discussions of the effect of a cyclopropyl group on an aromatic ring have generally concentrated on the degree and type of conjugative interaction existing between the two bonded rings. Strong *ground-state* conjugative interaction in cyclopropyl aromatics may occur[2] providing that significant electronic demands are made on the cyclopropyl group[3] and providing that a conformation can be attained allowing maximum overlap between



the Walsh[4] orbitals for cyclopropyl and the aryl π system. The latter condition is best satisfied with the bisected conformation illustrated for cyclopropylbenzene.

Evidence for conjugative interaction in the excited state is less clear-cut. A modest bathochromic shift of 5 mμ (740 cm^{-1}) of the 0–0 band of cyclopropylbenzene over that for isopropyl benzene is indeed found,[5,6] but, as judged from bathochromic shifts, the degree of interaction seems not to be a sensitive function of cyclopropane geometry.[7] The reasonable suggestion has been made recently that significant conjugative interaction (and thereby geometrical influence) in the excited state (as in the ground state) will only occur if the aromatic moiety has "sufficient electron-attracting power to make .....demand on the conjugative ability of the cyclo-

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