only a trace of *t*-butyl carbanilate, m.p. 135–137°. By allowing equimolar amounts of the azide and aniline to stand in pyridine solution for two weeks followed by precipitation with water, a 50–60% yield, m.p. 135–137°, was obtained (lit.[36] m.p. 136.3–136.5).

***t*-Butyl Hydrazodiformate**[1c,21]—A solution of 2.86 g. of distilled *t*-butyl azidoformate, 2.64 g. of *t*-butyl carbazate in 6 ml. of pyridine was allowed to stand for one week (if allowed to stand for two weeks the yield was only 3–5% greater) and then diluted with 75 ml. of water. The snow-white solid which precipitated amounted to 3.7 g. (80.1%), m.p. 124–126°. The analytical sample was recrystallized from ligroin (60–90°)-benzene (1:1) as tiny needles, m.p. 124–125.5°.

Anal. Calcd. for $C_{10}H_{20}O_4N_2$: C, 51.71; H, 8.70. Found: C, 52.00; H, 8.77.

AMHERST, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Mechanism of Trimethylene Oxide Formation from 3-Chloropropyl Acetate

BY DONALD C. DITTMER, WALTER R. HERTLER AND HERBERT WINICOV

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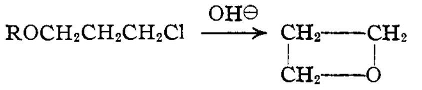
Evidence has been obtained that the better yields of trimethylene oxide from 3-chloropropyl acetate than from 3-chloropropanol may be caused by a protective effect of the acetate group and not by a fundamentally different mechanism. Oxide prepared from carbonyl O^{18}-labeled ester contained no excess O^{18}; this result rules out any mechanism for trimethylene oxide formation in which the two acetate oxygens are equivalent. Trimethylsilyl 3-chloropropyl ether gave as high a yield of oxide as the acetate, and 3-chloropropyl thiolacetate gave only trimethylene sulfide.

Yields of trimethylene oxide obtained by treatment of 3-chloropropyl acetate with strong base have been reported to be much greater than yields from 3-chloropropanol.[1] A similar result has been reported for the preparation of ethylene oxide from 2-chloroethyl acetate.[2]



(1)

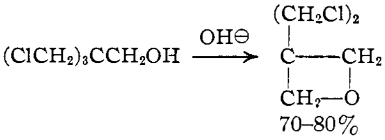
R = H–, CH_3CO–

Since in the concentrated base used the acetate presumably would be hydrolyzed to the same chlorohydrin anion, $^{\ominus}OCH_2CH_2CH_2Cl$, as the one formed from 3-chloropropanol, the yields of trimethylene oxide, if they proceeded from this alkoxide, would not be expected to be as different as they are between acetate and chlorohydrin.

To explain the disparity in yields between chlorohydrin and chloroacetate, a protective effect of the acetate group or a different mechanism may be invoked. The chloroacetate may yield the chlorohydrin anion at a slower rate than it is produced from the chlorohydrin. Since the concentration of alkoxide from chloroacetate at any time would be smaller than from chlorohydrin, conditions might be more favorable for intramolecular cyclization than for intermolecular reaction which would produce a polymeric ether. In other types of ring closure, high dilution of the reactants is necessary to prevent intermolecular reactions since the extent of intermolecular reaction depends on the concentration of the reactants while that of the intramolecular reaction does not.[3]

$$\overset{\ominus}{O}CH_2CH_2CH_2Cl \longrightarrow (OCH_2CH_2CH_2)_x \qquad (2)$$

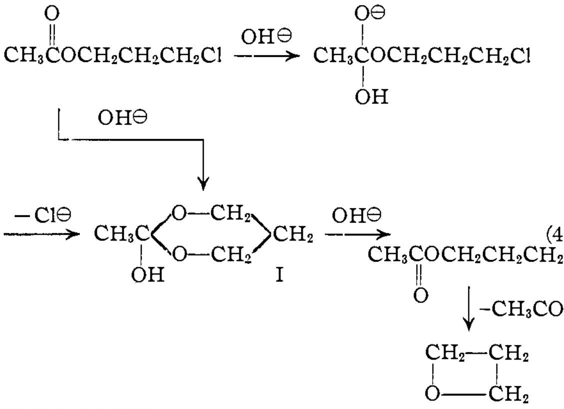
Indeed, a linear polymeric ether, $(C_3H_6O)_x$, has been isolated as a by-product in the preparation of trimethylene oxide from 3-chloropropanol.[4] Excellent yields (70–80%) of 3,3-dichloromethyloxetane have been reported from trichloropentaerythritol and potassium hydroxide.[5] Here, the intermolecular reaction involves a displacement reaction on a neopentyl-type system which would be expected to be very slow.



(3)

Other side products from 3-chloropropanol were said to be allyl alcohol and allyl chloride.[1a] It is not expected that acetylation of the hydroxyl group would have much effect on these olefin-producing side reactions.

If the production of trimethylene oxide from 3-chloropropyl acetate involved a different mechanism other than the straightforward intramolecular displacement of chloride ion by the alkoxide part of the molecule,[6] higher yields of oxide might be expected if the free energy of activation for the new mechanism were less than that for the old



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(1) (a) C. G. Derick and D. W. Bissell, THIS JOURNAL, **38**, 2478 (1916); (b) C. R. Noller, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 835.

(2) E. Demole, *Ann.*, **173**, 125 (1874).

(3) P. Ruggli, *ibid.*, **392**, 92 (1912); G. M. Bennett, *Trans. Faraday Soc.*, **37**, 794 (1941); K. Ziegler, H. Eberle and H. Ohlinger, *Ann.*, **504**, 94 (1933)

(4) M. Reboul, *Ann. chim.*, [5] **14**, 497 (1878).

(5) F. Govaert and M. Beyaert, *Natuur. Tijdschr.*, **22**, 73 (1940); *C. A.*, **37**, 3054 (1943).

(6) S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576 (1939).

mechanism, thereby reducing the importance of side reactions. A possibility exists that the carbonyl group of the ester could displace chloride ion to give an intermediate, I, which decomposes to trimethylene oxide.

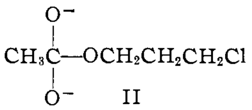
The attack by hydroxide ion on the carbonyl carbon may be concerted with the displacement of chloride ion by the carbonyl oxygen, intermediate I being formed directly. The intermediate I might go to trimethylene oxide by a concerted elimination of acetate with ring closure.

The displacement of chloride ion by the oxygen anion derived from a carbonyl group has an analogy in the Darzens glycidic ester reaction.[7] Participation of acetate carbonyl in displacements of neighboring groups is well known.[8] A displacement of bromide ion by an ester carbonyl oxygen has been suggested to occur in the pyrolysis of γ-bromoesters.[9] A cyclic *ortho* ester analogous to I has been prepared from the monotrichloroacetate of ethylene glycol,[10] and a similar *ortho* ester has been suggested as an intermediate in the preparation of *trans*-2-chlorocyclohexanol from *cis*-1,2-diacetoxycyclohexane.[11] The reaction of the acetate of 3-bromo-2,2-dimethyl-1-propanol with potassium iodide in acetone is 38 times faster than the reaction of neopentyl bromide which indicates a participation by the acetoxy group.[12]

Results

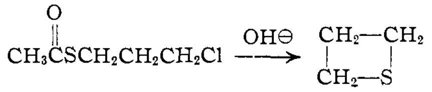
The possibility of a different mechanism of trimethylene oxide formation from 3-chloropropyl acetate was investigated by preparing the oxide from carbonyl O^{18}-labeled 3-chloropropyl acetate which was made by hydrolysis of 3-chloropropyl iminoacetate with H_2O^{18}. If the reaction scheme 4 were correct, excess O^{18} should appear in the trimethylene oxide since in I the two oxygens are equivalent. No excess O^{18} was found in the trimethylene oxide. This result is apparent in Table II in the Experimental section.

Some loss of O^{18} from the ester might occur by the scheme proposed by Bender for ester hydrolysis.[13] The concentration of base used by Bender was 0.001-0.007 *M* while the concentration of base used in the preparation of trimethylene oxide was approximately 200 *M*. The formation of the conjugate acid of the ester-hydroxide ion adduct, $CH_3C(OH)_2OR$, as proposed by Bender would seem to be rather unlikely in such strong base, although the formation of the dianion II is a possibility. Nevertheless, if the dianion were formed, at least 25% of the O^{18} in the original ester should be found in the trimethylene oxide if the latter were formed as shown in equation 4.



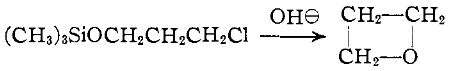
$$CH_3\overset{O^-}{\underset{O^-}{C}}—OCH_2CH_2CH_2Cl \qquad II$$

Only trimethylene sulfide could be isolated from the reaction of 3-chloropropyl thiolacetate with base. Trimethylene sulfide has been prepared in the same way by Bordwell and Hewett.[14]



(5)

Trimethylsilyl 3-chloropropyl ether on treatment with potassium hydroxide gave a yield of trimethylene oxide comparable to the yields from 3-chloropropyl acetate.



41%

Attempts to prepare trimethylene oxide from 3-hydroxypropyl acetate, 3-hydroxypropyl chloroacetate, 3-hydroxypropyl trichloroacetate and 3-hydroxypropyl *p*-toluenesulfonate were not successful.

Trimethylene oxide could be prepared in 24% yield from 3-chloropropyl chloroacetate and potassium hydroxide, but 3-chloropropyl trifluoroacetate and 3-chloropropyl trichloroacetate gave no oxide.

Discussion

The lack of evidence for participation of the ester carbonyl group of 3-chloropropyl acetate in the formation of trimethylene oxide seems to show that the effect of acetylation of chlorohydrins in improving yields of cyclic oxides is not to change the basic mechanism but possibly to minimize side reactions such as the intermolecular Williamson ether synthesis illustrated by equation 2. The fact that the trimethylsilyl ether of 3-chloropropanol gives about the same yield of trimethylene oxide as does the acetate implies that there is nothing special about the function of acetate.

With the silyl ether as with the acetate, the reaction with hydroxide to produce the chlorohydrin anion is slow in comparison with the abstraction of a proton from the chlorohydrin. This slow hydrolysis in both cases decreases the concentration of the anion so that, by this "dilution" effect, the cyclization to trimethylene oxide is favored at the expense of the intermolecular reaction.

Where the intermolecular reaction is hindered as in the reaction of trichloropentaerythritol with base, higher yields of oxide are observed.[5] However, a substituted chlorohydrin also may have a lower free energy of activation for ring closure than its unhindered analog.[15] Steric hindrance in intramolecular reactions has been said to be less than for intermolecular reactions.[16]

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[7] M. S. Newman and J. B. Magerlein, "Organic Reactions," Vol. V, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 413; M. Ballester and P. D. Bartlett, THIS JOURNAL, **75**, 2042 (1953).

[8] S. Winstein, H. V. Hess and R. E. Buckles, *ibid.*, **64**, 2780, 2787 (1942); S. Winstein and R. E. Buckles, *ibid.*, **65**, 613 (1943).

[9] J. Weinstock, *ibid.*, **78**, 4967 (1956).

[10] H. Meerwein and H. Sönke, *J. prakt. Chem.*, **137**, 295 (1933); H. Meerwein and H. Sönke, *Ber.*, **64**, 2375 (1931).

[11] R. Boschan and S. Winstein, THIS JOURNAL, **78**, 4921 (1956).

[12] C. R. Lindegren and S. Winstein, Abstracts of Papers, 123rd Meeting of the American Chemical Society, Los Angeles, Calif., March, 1953, p. 30M.

[13] M. L. Bender, THIS JOURNAL, **73**, 1626 (1951).

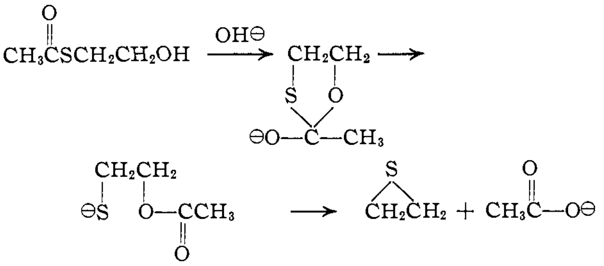
[14] F. G. Bordwell and W. A. Hewett, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, p. 6-O.

[15] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 683 (1956); E. Eliel in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 117-119.

[16] G. Baddeley, *Ann. Repts. on Prog. Chem.*, (*Chem. Soc. London*), **52**, 149 (1955).

Another explanation for the higher yields from 3-chloropropyl acetate and from 3-chloropropyl trimethylsilyl ether is that the attack by hydroxide ion on the carbonyl carbon or on silicon is concerted with ring closure, there being no intermediates involved.

The synthesis of trimethylene sulfide in 24% yield from 3-chloropropyl thiolacetate and the absence of detectable trimethylene oxide did not necessarily rule out a cyclic intermediate, since in the intermediate it might be expected that the carbon–sulfur bond would break preferentially to the carbon–oxygen bond. Ethylene sulfide is prepared in 25% yield from the S-acetate of 2-mercaptoethanol by treatment with base.[17] The analogy to equation 4 is apparent.



Mono-*p*-toluenesulfonates of 1,2-glycols give good yields of epoxides on treatment with base.[18] Our finding that the mono-*p*-toluenesulfonate of 1,3-propanediol gave no trimethylene oxide on treatment with potassium hydroxide agrees with an earlier result.[19]

The failure of monoesters of trimethylene glycol to give trimethylene oxide does not necessarily rule out the mechanism of equation 4 since intermediate I could conceivably go directly to trimethylene oxide by a concerted process. The use of sodium to produce the alkoxides was not very satisfactory since there was evidence of reduction of the ester group.

Experimental

3-Chloropropanol was prepared according to Marvel and Calvery.[20]

3-Chloropropyl Iminoacetate Hydrochloride.—The procedure was based on that by McElvain and Schroeder.[21]

To a mixture of 94.5 g. (1.0 mole) of 3-chloropropanol, 42.2 g. (1.0 mole) of acetonitrile (Eastman Kodak Co. practical grade, redistilled and dried over Drierite) in 50 ml. of anhydrous ether and 5 ml. of reagent-grade chloroform, was added about 40 g. (1.1 moles) of anhydrous hydrogen chloride gas. The reaction mixture was placed in a refrigerator for 12 hr. after which a layer of about 25 ml. of anhydrous ether was placed carefully on top of the viscous solution. The iminoacetate hydrochloride precipitated after 2 to 4 more days in the refrigerator. The crystals were filtered rapidly by reduced pressure and dried in a desiccator over Drierite, potassium hydroxide and paraffin chips. The yield was 158 g. (0.9 mole, 90%), m.p. 75–77° dec. Infrared analysis (potassium bromide disk) showed characteristic bands at 1558 and 1635 cm.$^{-1}$. Ionic chloride was determined by the Volhard method.

Anal. Calcd. for $C_5H_{11}Cl_2NO$: ionic Cl, 20.64. Found: ionic Cl, 20.54.

3-Chloropropyl Acetate (Carbonyl-O^{18}-labeled).—The 3-chloropropyl iminoacetate hydrochloride (120 g., 0.7 mole) was dissolved in 25 g. (1.4 moles) of water containing greater than 1.4% O^{18} (Stuart Oxygen Co., 211 Bay St., San Francisco, Cal.). Heat was evolved and ammonium chloride precipitated. The flask was cooled under a cold water tap until heat was no longer evolved and then was warmed under a hot water tap for 15 to 20 minutes and allowed to stand for 4 hr. at room temperature. About 100 ml. of ether was added and the ammonium chloride removed by filtration and washed several times with ether. The combined ether solutions were dried over anhydrous magnesium sulfate for 24 hr. After the removal of the magnesium sulfate, the ether was evaporated and the crude 3-chloropropyl acetate was distilled through a 25-cm. column packed with glass helices to give 85.4 g. (0.62 mole, 88%) of the carbonyl-O^{18}-labeled ester.

The unlabeled ester was prepared in a similar manner except that ordinary water was used. It also was prepared from 3-chloropropanol and acetyl chloride.

Trimethylene Oxide.—The procedure of Noller was followed,[1b] in which the O^{18}-labeled 3-chloropropyl acetate was treated with hot potassium hydroxide. The trimethylene oxide was distilled as it was formed and was collected in a flask equipped with a Dry Ice condenser. The crude oxide was dried over potassium hydroxide and distilled through a small column to give 10 g. (38%) of material, b.p. 47–48°, $n^{25}\text{D}$ 1.3906. The oxide was dried over sodium metal and redistilled after removal of the sodium. Two fractional distillations of the oxide directly from sodium metal were carried out, followed by a final distillation, b.p. 47.0–47.2°, $n^{25}\text{D}$ 1.3896.

Unlabeled trimethylene oxide was prepared in a similar manner from unlabeled 3-chloropropyl acetate.

Mass Spectrometric Analyses.—Mass spectra of the labeled and unlabeled 3-chloropropyl acetates and samples of trimethylene oxide prepared from each were taken on a Consolidated model 21-101 (modified) mass spectrometer at an ionizing current of 10 amperes and an ionizing voltage of 70. Table I gives the abridged mass spectra of the labeled and unlabeled acetates and Table II of the trimethylene oxide from the respective acetates.

TABLE I

MASS SPECTRA OF CARBONYL-O^{18}-LABELED 3-CHLOROPROPYL ACETATE AND UNLABELED 3-CHLOROPROPYL ACETATE

	Relative intensity[a]		
Mass	Unlabeled	Labeled	Probable fragment
61	100.0	100.0	$CH_3C(OH)_2^+$
63	3.0	4.3	$CH_3C(O^{18}H)OH^+$
73	48.8	48.0	$CH_3COOCH_2^+$
75	1.6	2.2	$CH_3CO^{18}OCH_2^+$
87	6.0	5.8	$CH_3COOCH_2CH_2^+$
89	0.07	0.14	$CH_3CO^{18}OCH_2CH_2^+$
93	12.2	12.2	$Cl^{35}CH_2CH_2CH_2O^+$
95	3.8	3.8	$Cl^{37}CH_2CH_2CH_2O^+$
Normalized on Basis of Mass 93			
87	49.4	49.1	
88	2.3	2.3	
89	0.74	0.97	
90	0.08	0.11	
93	100.0	100.0	
95	32.5	32.7	
101	29.6	29.1	$CH_3COOCH_2CH_2CH_2^+$
103	0.26	0.45	$CH_3CO^{18}OCH_2CH_2CH_2^+$

[a] Normalized to intensity 100 for abundant peaks (61 and 93).

Estimation of Enrichment of Labeled 3-Chloropropyl Acetate.—The method is similar to that used by Long and Pritchard for propylene and isobutylene glycols.[22] They

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[17] J. S. Harding, L. W. C. Miles and L. N. Owen, *Chemistry & Industry*, 887 (1951); L. W. C. Miles and L. N. Owen, *J. Chem. Soc.*, 817 (1952); J. S. Harding and L. N. Owen, *ibid.*, 1528 (1954).

[18] E. L. Eliel and D. W. Delmonte, *J. Org. Chem.*, **21**, 596 (1956).

[19] D. D. Reynolds and W. O. Kenyon, THIS JOURNAL, **72**, 1593 (1950).

[20] C. S. Marvel and H. O. Calvery, "Organic Syntheses," Coll. Vol. I, 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 533.

[21] S. M. McElvain and J. P. Schroeder, THIS JOURNAL, **71**, 40 (1949).

[22] F. A. Long and J. G. Pritchard, *ibid.*, **78**, 2663 (1956).

TABLE II

MASS SPECTRA OF TRIMETHYLENE OXIDE PREPARED FROM LABELED AND UNLABELED 3-CHLOROPROPYL ACETATES

Mass	Relative intensity[a] From unlabeled ester	Relative intensity[a] From labeled ester	Probable fragment
42	2.4	2.4	$CH_2CH_2CH_2^+$
43	1.3	1.3	
52	0.25	0.24	
53	0.97	0.95	
55	1.3	1.3	
56	1.7	1.7	
57	17.6	17.6	$CH_2{=}CHCH_2O^+$
58	100.0	100.0	$CH_2CH_2CH_2O^+$
59	3.5	3.4	
60	0.26	0.26	$CH_2CH_2CH_2O^{18+}$

[a] Reference *a*, Table I.

TABLE III

MASS RATIOS AND CALCULATED PERCENTAGE ENRICHMENT OF O^{18} IN 3-CHLOROPROPYL ACETATE

Mass ratios	O^{16} Acetate	O^{18} Acetate	Difference in ratios	Atom % O^{18}
63/61	0.030	0.043	0.013	1.7
75/73	.033	.046	.013	1.7
89/87	.012	.025	.013	1.7
	.014	.026	.012	1.6
	.015	.020	.005	0.9
103/101	.009	.015	.006	1.0
	.006	.018	.012	1.6
	.007	.014	.007	1.1

were careful to use in their calculations only those peaks for which only one fragment could be written for the O^{16}-containing isotope and for which only the enriched species of the same fragment was possible for a mass number two units higher. Since the natural O^{18}/O^{16} ratio is 0.002 (0.2%) for a fragment containing only one oxygen, the ratio of the relative intensity of the mass number two units higher to the relative intensity of the mass number for this fragment should be 0.002. For a fragment containing two oxygen atoms the ratio would be 0.004, and for a fragment containing two oxygen atoms one of which is enriched to 1.4% in O^{18}, the ratio would be 0.016.

Since none of the presumed oxygen-containing fragments gave a ratio of 0.002 or 0.004 (with the exception of mass 103) but gave higher values, it is likely that these peaks are contaminated with other unknown fragments. If a constant amount of contamination by an unknown fragment or fragments is assumed in the peaks of mass $M + 2$, a rough estimate of the enrichment can be made as follows: Let

h = peak height of mass M for unenriched cmpd. due to single fragment
h' = peak height of mass M for enriched cmpd. due to a single fragment
h_2 = peak height of mass $M + 2$ for unenriched compound
h_2' = peak height of mass $M + 2$ for enriched compound
x = height of peak due to O^{18} fragment in h_2
x' = height of peak due to O^{18} fragment in h_2'
y = peak height due to unknown fragment (or combn. of fragments) in h_2
y' = peak height due to unknown fragment (or combn. of fragments) in h_2'

Consider a peak for which a fragment containing two oxygens can be written. Then

$$x + y = h_2$$
$$x' + y' = h_2'$$
$$y'/y = h'/h$$

Assume $x/h = 0.004$ and $x = 0.004h$

$$y = h_2 - 0.004h$$
$$y' = (h'/h)(h_2 - 0.004h)$$
$$x' = h_2' - ((h'/h)(h_2 - 0.004h))$$

Therefore, the O^{18}/O^{16} ratio is $x'/h' = h_2'/h' - h_2/h + 0.004$

This derivation is not completely satisfactory because it assumes that the mass peak heights of the fragments which contain O^{16} (unenriched) are uncontaminated by any other fragment. However, it seems likely that most of the height of the peak may be accounted for by the O^{16}-containing fragment. The results are given in Table III.

It seems likely that the enriched 3-chloropropyl acetate actually contains about 1.6 to 1.7% O^{18} which is the value to be expected from acetate prepared from water containing in excess of 1.4 atom per cent. O^{18}. The method of preparation of the enriched acetate is such that acetate should have the same enrichment in its carbonyl oxygen as the water used.

It is interesting to observe that the 93/95 ratio for 3-chloropropyl acetate is close to the natural ratio of 3 for Cl^{35}/Cl^{37}.

3-Chloropropyl Chloroacetate.—Chloroacetic acid (118.1 g., 1.25 moles), 3-chloropropanol (94.5 g., 1.0 mole), *p*-toluenesulfonic acid (1 g.) and 150 ml. of benzene were refluxed in a 500-ml. flask equipped with a 25-cm. column packed with glass helices to which was attached a Dean and Stark water-separator with a reflux condenser. When no further separation of water occurred, the reaction was stopped, and the benzene solution was washed with 120 ml. of 10% aqueous sodium carbonate and 25 ml. of saturated sodium chloride solution. The benzene solution was dried over anhydrous magnesium sulfate and the benzene distilled. Distillation yielded 117.8 g. (69%) of 3-chloropropyl chloroacetate, b.p. 166–169° (142–147 mm.). After a further drying over magnesium sulfate, the sample was redistilled at atmospheric pressure, b.p. 222–223°, $n^{25.4}D$ 1.4595.

Anal. Calcd. for $C_5H_8O_2Cl_2$: C, 35.10; Cl, 41.17; H, 4.71. Found: C, 35.22; Cl, 41.36; H, 4.74.

3-Chloropropyl trichloroacetate was prepared by the procedure used for 3-chloropropyl chloroacetate. The 3-chloropropyl trichloroacetate distilled at 69–70° (0.9 mm.), $n^{22.5}D$ 1.4773, $n^{20}D$ 1.4784 (lit.[23] b.p. 107° (8 mm.), 97.0–97.7 (3 mm.); $n^{15}D$ 1.4830, $n^{20}D$ 1.47985).

3-Chloropropyl Trifluoroacetate.—A variation of a general method of Burgoyne and Condon was used.[24] Trifluoroacetic acid (40 g., 0.36 mole), 3-chloropropanol (25.6 g., 0.27 mole) and chloroform (50 ml.) were distilled from a 250-ml. flask fitted with an addition funnel and a 25-cm. column packed with glass helices. The distillate was placed in an addition funnel where the aqueous layer was separated from the chloroform layer. The chloroform was allowed to run back into the distilling flask. In this way 30 g. (62%) of 3-chloropropyl trifluoroacetate was obtained, b.p. 143–144°, $n^{24}D$ 1.3700, $n^{25}D$ 1.3698. The ester was insoluble in water but soluble in chloroform, carbon tetrachloride and carbon disulfide. A further distillation gave a sample, b.p. 143.5–144.2°, $n^{25}D$ 1.3694, d^{20}_4 1.349. Infrared absorption spectra showed bands at 1786, 1400, 1347, 1225 and 1146–1170 cm.$^{-1}$. A yield of 82% was obtained by using doubled amounts of starting materials.

Anal. Calcd. for $C_5H_6O_2ClF_3$: C, 31.49; H, 3.15. Found: C, 31.60; H, 3.31.

Preparation of Trimethylene Oxide from 3-Chloropropyl Esters.—The procedure used for the preparation of trimethylene oxide from 3-chloropropyl acetate was followed.[1b]

Potassium hydroxide (90.6 g.), 3-chloropropyl chloroacetate (92.2 g., 0.54 mole) and water (8 ml.) were allowed to react. Trimethylene oxide (7.6 g., 24.3%) was obtained, b.p. 46–48°, $n^{26}D$ 1.3885. A higher boiling fraction (99°) gave a positive test with ceric nitrate reagent.[25] It may have been allyl alcohol.

When 3-chloropropyl trifluoroacetate was used, the temperature of the reaction mixture rose rapidly to 200°. No trimethylene oxide was isolated. The residue gave a positive ceric nitrate test.[25]

The reaction of 3-chloropropyl trichloroacetate with potassium hydroxide gave chloroform but no trimethylene oxide. The residue gave a positive ceric nitrate test.[25]

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[23] C. W. Gayler and H. M. Waddle, THIS JOURNAL, **63**, 3358 (1941); M. H. Palomaa, E. J. Salmi and R. Korte, *Ber.*, **72**, 790 (1939).

[24] E. E. Burgoyne and F. E. Condon, THIS JOURNAL, **72**, 3276 (1950).

[25] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 96.

3-Chloropropyl Trimethylsilyl Ether.—The procedure of Sprung and Nelson was followed.[26] Commercial grade trimethylchlorosilane (kindly donated by the General Electric Company) was purified by precipitation of excess hydrogen chloride with pyridine and distillation of the chlorosilane through a 25-cm. column packed with glass helices. This procedure was repeated, and the chlorosilane was stored with a small amount of pyridine.

Dry pyridine (55.0 g., 0.7 mole, Mallinckrodt reagent grade), 3-chloropropanol (57.5 g., 0.6 mole, dried over Drierite) were placed in a dry, 3-necked 500-ml. flask provided with a mechanical stirrer, thermometer and condenser. The flask was cooled to 10° in an ice-bath. Purified trimethylchlorosilane (74.5 g., 0.68 mole) was added slowly from a dropping funnel on top of the condenser while the reaction mixture was being stirred. The funnel was provided with a calcium chloride drying tube. After the addition, the stirrer was removed, and the reaction mixture was refluxed 15 minutes. Dilute hydrochloric acid was added to neutralize the excess pyridine, and the solution was extracted three times with one-half its volume of ether. The ether extracts were combined, washed twice with 0.1 *N* hydrochloric acid, twice with water and dried over anhydrous magnesium sulfate. After the ether was removed, distillation gave 56 g. (56%) of 3-chloropropyl trimethylsilyl ether, b.p. 141–146.5°, $n^{23.5}\mathrm{D}$ 1.4170. A further distillation gave a purer product, b.p. 53° (17–20 mm.), $n^{28.1}\mathrm{D}$ 1.4148, $d^{28.7}{}_4$ 0.931. Infrared analysis showed characteristic bands at 1253, 1176, 1105 and 846 cm.$^{-1}$.

Anal. Calcd. for $C_6H_{15}OClSi$: C, 43.17; H, 9.07; Cl, 21.27. Found: C, 43.32; H, 9.21; Cl, 21.47.

Trimethylene Oxide from 3-Chloropropyl Trimethylsilyl Ether.—The procedure used in the preparation of trimethylene oxide from 3-chloropropyl acetate was followed.[1b] The distillate from the reaction mixture containing trimethylene oxide and probably water, trimethylsilanol and hexamethyl disiloxane was dried over potassium hydroxide and distilled through a Vigreux column. The first fraction (to 61°) gave 9.5 g. of impure trimethylene oxide. This fraction was dried over sodium and distilled, after removal of the sodium, to give 7 g. (41%) of trimethylene oxide. A third fractionation gave 6 g. (35%) of the oxide which was distilled directly from sodium, b.p. 47–49°, $n^{23}\mathrm{D}$ 1.3910.

3-Hydroxypropyl acetate was prepared at first by the method of Bogert and Slocum from acetyl chloride and trimethylene glycol.[27] Distillation gave a fraction, b.p. 206–209°, $n^{25}\mathrm{D}$ 1.4191 (lit.[27] b.p. 202–203°).

Another preparation was from 95 g. (1.58 moles) of glacial acetic acid, 114 g. (1.5 moles) of trimethylene glycol (redistilled), 115 ml. of chloroform and 1 ml. of concentrated sulfuric acid which was refluxed, and the water was removed by a Dean and Stark separator. When 30 ml. of water and acetic acid had been separated, a third of the chloroform was distilled and the reaction mixture washed with a small amount of sodium bicarbonate solution. The mixture was distilled through a 25-cm. column packed with glass helices, and two fractions were collected: 24.2 g., b.p. 136–140° (95 mm.), and 72.8 g., b.p. 110–115° (25 mm.), $n^{25}\mathrm{D}$ 1.4175, $d^{25}{}_4$ 1.026.

A third preparation of 3-hydroxypropyl acetate was tried using an adaptation of the method of Meerwein and Sönke for preparing glycol monoesters.[10] Trimethylene glycol (76.1 g., 1 mole) was dissolved in 100 ml. of dioxane in a 500-ml. flask cooled in an ice-bath. Acetyl chloride (78.5 g., 1 mole) was added dropwise with stirring, and the mixture was refluxed for 2 hr. The dioxane was distilled at atmospheric pressure, and the residue was distilled under reduced pressure to give 63.8 g. (54%) of product, b.p. 105–115° (31 mm.), $n^{24}\mathrm{D}$ 1.4210.

3-Hydroxypropyl Chloroacetate.—Chloroacetyl chloride (103.7 g., 0.92 mole) in 20 ml. of dioxane was added to trimethylene glycol (68.5 g., 0.9 mole) in 80 ml. of dioxane in a 500-ml. flask immersed in an ice-bath. The mixture was refluxed for 3 hr., and, after removal of the dioxane and distillation through a 25-cm. column packed with glass helices, gave 46.8 g. (33.5%) of product, b.p. 95–112° (1.3–1.7 mm.), $n^{23}\mathrm{D}$ 1.4591.

3-Hydroxypropyl trichloroacetate was prepared by the method of Meerwein and Sönke[10] from trichloroacetyl chloride and trimethylene glycol. The trichloroacetyl chloride was prepared from trichloroacetic acid and phosphorus trichloride. The hydroxyester distilled at 98–115° (0.9–1.5 mm.), $n^{25.5}\mathrm{D}$ 1.4680.

3-Hydroxypropyl *p*-Toluenesulfonate.—Trimethylene glycol (128.2 g., 1.69 moles) was added to a stirred mixture of *p*-toluenesulfonyl chloride (160.5 g., 0.84 mole) in pyridine (133 g., 1.69 moles) in a 500-ml. flask immersed in a Dry Ice–acetone-bath. The addition was as fast as possible without causing a great rise in temperature. The reaction mixture was allowed to reach room temperature, and stirring was continued for 0.5 hr. The pyridine hydrochloride was removed by filtration, and the filtrate was poured into water to give an oil which was separated, washed with water, dilute hydrochloric acid and water again. The oil was dried over anhydrous magnesium sulfate. Distillation of the ester (74.2 g., 32%) at 1 mm. resulted in decomposition. Crystals of trimethylene glycol di-*p*-toluenesulfonate separated from the oil after standing, m.p. 92–93° (lit.[28] m.p. 93–94°).

Attempted Preparation of Trimethylene Oxide from Monoesters of Trimethylene Glycol.—No trimethylene oxide was obtained from 3-hydroxypropyl *p*-toluenesulfonate or 3-hydroxypropyl acetate on treatment with potassium hydroxide in the usual way[1b] or from 3-hydroxypropyl acetate, 3-hydroxypropyl chloroacetate, 3-hydroxypropyl trichloroacetate and 3-hydroxypropyl *p*-toluenesulfonate on treatment with sodium metal which was used in order to produce the alkoxide.

3-Chloropropyl thiolacetate was prepared by the method of Sjöberg[29] from allyl chloride and thiolacetic acid. The thiolester was obtained in 71% yield, b.p. 93–96° (20 mm.), $n^{27}\mathrm{D}$ 1.4910 (lit.[29] b.p. 83–84° (10 mm.), $n^{20}\mathrm{D}$ 1.4954).

Trimethylene Sulfide.—3-Chloropropyl thiolacetate (119 g., 0.78 mole) was added gradually to potassium hydroxide (131 g., 2.34 moles) and water (12 ml.) in the apparatus used for the preparation of trimethylene oxide.[1b] The temperature of the reaction mixture varied from 150 to 170°. The product which distilled from the reaction mixture at 77° was dried over Drierite and redistilled through a 25-cm. column packed with glass helices to give trimethylene sulfide (13.8 g., 23.8%), b.p. 94–94.5°, $n^{25}\mathrm{D}$ 1.5027. It was characterized as the dimethyl sulfonium iodide, m.p. 97–98°.[30] The infrared spectrum of the sample was identical with that obtained by other workers.[31] No trimethylene oxide could be isolated from the reaction.

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