hydroxy-2-methyl-2-pentanesulfonic acid and that at 8.5–8.6 μ for the δ-sultones of 4-hydroxy-2-methyl-1-butane- and -pentanesulfonic acids are not attributable to ring size. Thus, the γ-sultones of 3-hydroxy-1-propanesulfonic acid,[8] 3-hydroxy-2-methyl-1-propanesulfonic acid,[8,9] and 3-hydroxy-2,2-dimethyl-1-propanesulfonic acid[10] do not absorb strongly in the 8.8-μ region. Instead of ring size, the significant attribute is whether the sulfonate grouping is that of a primary or tertiary sulfonic acid. In Table I are compared these and other sultones, several acyclic sulfonates, and some other tertiary sulfonyl compounds.[11]

The mass spectrum of the γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid indicates considerable methyl group fragmentation consistent with the extensive substitution at the tertiary carbon atom to which the sulfur atom is bonded. On the other hand, the sultone from chlorosulfonylated 3-methyl-1-butyl chloride shows relatively little methyl group fragmentation, thus indicating less extensive methyl substitution, consistent with a primary sulfonate grouping. The relative degree of shattering of the two compounds is shown in Table II.

TABLE II

RELATIVE DEGREE OF METHYL GROUP SHATTERING[a] IN THE MASS SPECTROMETER

Compd	P–Me[a] / P
Sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid	24.
Sultone of 4-hydroxy-2-methyl-1-butanesulfonic acid	0.4

[a] Determined by calculating the ratio of material with mass showing loss of one methyl group to that of unshattered material; P = parent mass, Me = methyl mass.

Experimental Section

The γ-sultone from chlorosulfonylated 1-propyl chloride was prepared according to Asinger[8] and the sultones from chlorosulfonylated 3-methyl-1-butyl and 4-methyl-2-pentyl chlorides were prepared as described by Helberger.[4]

The γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid was prepared according to Willems[6] and characterized as the hemihydrate of the pyridine adduct, mp 232–232.5°.

Anal. Calcd for $C_{11}H_{17}NO_3S \cdot 0.5H_2O$: C, 52.36; H, 7.19. Found: C, 52.18; H, 7.23.

The δ-Sultone of 4-Hydroxy-2-methyl-1-pentanesulfonic Acid.—The δ-sultone of 4-hydroxy-2-methyl-1,3-pentadiene-1-sulfonic acid, prepared by sulfonation of mesityl oxide with chlorosulfonic acid in acetic anhydride according to Eastman[7a] and Morel,[7b] melted at 70–70.5°. A solution of 34.4 g (0.21 mole) of this and 4.6 g (0.11 mole) of sodium hydroxide in 70 ml of water was heated to 70° and a warm solution of 4.0 g (0.11 mole) of sodium borohydride in 80 ml of water was added with stirring during 0.5 hr. The mixture was allowed to cool for 1.5 hr, then was neutralized with dilute hydrochloric acid, and dried *in vacuo*. Upon evaporation of a hot ethanol extract of the residue, 15.0 g (0.07 mole) of hygroscopic sodium 4-hydroxy-2-methyl-1-pentene-1-sulfonate was obtaned. A solution of 6.5 g (0.03 mole) of this salt was hydrogenated in 80 ml of water in the presence of 0.1 g of platinum oxide with an initial pressure of 515-psi gauge at 75° for 3 hr and then cooled to room temperature overnight. The dry sodium 4-hydroxy-2-methyl-1-pentanesulfonate resulting on evaporation of the aqueous filtrate from the hydrogenated product was slurried in 75 ml of ether and treated with gaseous hydrogen chloride over a period of 4 hr. The ether solution then was filtered and evaporated to give 4.6 g (0.02 mole) of dark brown 4-hydroxy-2-methyl-1-pentanesulfonic acid, which then was heated at 180°–195° *in vacuo* to distil over 1.2 g (0.007 mole) of crude sultone, bp 135–142° (4 mm), which solidified after standing. Recrystallization from 2,2,4-trimethylpentane containing some carbon tetrachloride produced needles of the pure δ-sultone, mp 46.5–47°. A mixture of this sultone and that derived from chlorosulfonylated 4-chloro-2-methylpentane showed no depression in melting point, whereas a mixture with the γ-sultone of 4-hydroxy-2-methyl-2-pentanesulfonic acid was a liquid at room temperature.

Ethyl 2-Methyl-2-propanesulfonate.—The ethyl ester of 2-methyl-2-propanesulfonic acid was prepared by treating an ether solution of the sulfonic acid with diazoethane[12] and also by ethylating the silver salt of the acid.[13] The ester is a liquid,[14] bp 51° (1 mm), $n^{25}D$ 1.4241, d^{25}_4 1.0670, MD 39.3.

Anal. Calcd for $C_6H_{14}O_3S$: C, 43.37; H, 8.43; sapon equiv, 164. Found: C, 43.28; H, 8.46; sapon equiv, 164.

Other Sulfonyl Compounds in the Infrared Comparison.—The γ-sultone[10] of 3-hydroxy-2,2-dimethyl-1-propanesulfonic acid, ethyl 2,2-dimethyl-1-propanesulfonate,[10] and ethyl 2,3-dimethyl-1-butanesulfonate[15] were prepared in earlier work already reported.

2-Methyl-2-propanesulfonyl chloride[16] was prepared by a modification of the Cherbuliez process,[17] N-cyclohexyl-2-methyl-2-propanesulfonamide[16] by oxidation of the corresponding sulfenamide, and methyl 2-methyl-2-propyl sulfone[16] by oxidation of the corresponding sulfide.

Infrared absorption data for the sultone[9a] of 3-hydroxy-2-methyl-1-propanesulfonic acid was obtained from a private source.[9b]

(8) F. Asinger, H. Eckoldt, and F. Ebeneder, *U. S. Dept. Comm., Office Tech. Serv., PB Rept.*, **70**, **183**, 892 (1943).

(9) (a) C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **75**, 748 (1953); (b) C. W. Smith, private communication, 1957.

(10) R. B. Scott, Jr., and H. L. McLeod, *J. Org. Chem.*, **21**, 388 (1956).

(11) Much of the previously published information concerning derivatives of 2-methyl-2-propanesulfonic acid is in error. One part of that is corrected in this paper, the rest is part of the subject of a paper in preparation.

(12) M. K. Frye, unpublished post-masters research, University of Alabama, 1951.

(13) H. L. McLeod, Ph.D. Dissertation, University of Alabama, 1956.

(14) H. Rheinboldt, F. Mott, and E. Motzkus, *J. Prakt. Chem.*, **134**, 257 (1932), obtained a solid, mp 114.5°, having the proper sulfur content for the ethyl ester. They also reported a similar preparation of the methyl ester, mp 116°. Each ester was reported to have been recrystallized from chloroform, in which we find the ethyl ester is freely soluble. According to H. J. Backer and P. L. Stedhouder [*Rec. Trav. Chim.*, **52**, 437 (1933)], 2-methyl-2-propanesulfonic acid is a solid which forms a monohydrate melting at 114–116°. Consideration of the symmetry of the acid and of the esters suggests that the acid should be a solid and the simple esters liquids. It seems likely that Rheinboldt may have obtained alcoholates of the acid, particularly if moisture was not meticulously excluded from the reactants and the solvent. However, this does not seem compatible with his statement that the solid methyl ester is soluble in the usual organic solvents and insoluble in water.

(15) R. B. Scott, Jr., and M. S. Heller, *J. Org. Chem.*, **20**, 1159 (1955).

(16) R. B. Scott, Jr., and co-workers, paper in preparation.

(17) R. B. Scott, Jr., J. B. Gayle, M. S. Heller, and R. E. Lutz, *J. Org. Chem.*, **20**, 1165 (1955).

Cyclopropylcarbinyl *p*-Toluenesulfonate Solvolysis. II.[1] 1-Methyl-Substituent Effect

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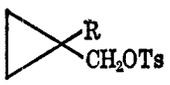
In previous studies[1,2] it was shown that the SN1 solvolytic reactivity of cyclopropylcarbinyl arenesulfonate derivatives was markedly insensitive to 1-ring substitution. On the basis of the experimental evidence, it was proposed[1] that resonance interaction between the delocalized carbonium ion and the phenyl group was hindered owing to the geometrical requirements of the involved orbitals.

(1) Paper I: D. D. Roberts, *J. Org. Chem.*, **30**, 23 (1965).

(2) D. D. Roberts, *ibid.*, **29**, 294 (1964).



Ia, R = H
b, R = C_6H_5
c, R = CH_3

The present paper deals with a related investigation of the influence of the 1-methyl group upon the solvolysis products and solvolytic reactivity of cyclopropylcarbinyl *p*-toluenesulfonate (Ia) in three solvents. The purpose of the study was to obtain product data as well as kinetic data with which the behavior of the unsubstituted cyclopropylcarbinyl tosylate could be compared.

Results

The rate constants for the solvolysis of 1-methylcyclopropylcarbinyl *p*-toluenesulfonate (Ic) in methanol and ethanol are listed in Table I. The course of the

TABLE I
SOLVOLYSIS RATE CONSTANTS FOR 1-METHYLCYCLOPROPYLCARBINYL TOSYLATE

Solvent	Concn, 10^2 *M*	Temp, °C	$k_1 \times 10^5$ sec^{-1}
CH_3OH	4.2	20.0	71.0
	4.2	30.0	185.0
	4.2	40.0	400.0
EtOH	4.3	25.0	29.0[a]
	4.2–5.1	30.0	47.0[b]
	3.1	35.0	68.0
	4.7	40.0	102.0
	3.1	50.0	225.0[a]

[a] Average of two runs. [b] Average of five runs.

reaction was followed by titrating the liberated *p*-toluenesulfonic acid and obeyed first-order kinetic law up to 75% conversion.

The experiments summarized in Table II were undertaken to observe the influence of an inert

TABLE II
ETHANOLYSIS RATE CONSTANTS FOR 1-METHYLCYCLOPROPYLCARBINYL TOSYLATE IN THE PRESENCE OF SALTS AT 30°

[Ester] + 10^2 *M*	Salt	[Salt] × 10^2 *M*	$k_1 \times 10^5$ sec^{-1}
4.2–5.1	...	0.0	47.0[a]
4.8	LiOTs	6.0	48.0
5.3	$LiOCl_4$	3.0	57.0[b]
5.4	$LiOCl_4$	6.0	74.0[b]
5.8	$LiOCl_4$	12.0	105.0
5.8	$LiOCl_4$	18.0	134.0

[a] Average of five runs. [b] Average of two runs.

salt upon the reaction rate. Analysis of the data by use of eq 1 revealed the presence of a linear salt effect. The magnitude of the *b* value, 12.0, is of

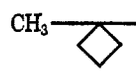
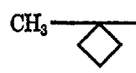
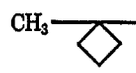
$$k_t = k_t^0[1 + b(MY)] \quad (1)$$

the expected order for a normal salt effect upon an SN1-type reaction.[3]

The products of acetolysis, methanolysis, and ethanolysis of 1-methylcyclopropylcarbinyl tosylate

(3) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

TABLE III
SOLVOLYSIS PRODUCTS OF 1-METHYLCYCLOPROPYLCARBINYL TOSYLATE

Solvent	Time, hr	Products	
AcOH	15		(II)
MeOH	15		(III)
EtOH[a]	15		(IV)

[a] In the presence of ammonium acetate.

were determined by the gas chromatographic method and are presented in Table III. The influence of the 1-methyl group on the reaction products is predominant in all three reaction media which vary from an ionizing solvent (acetic acid) to a nucleophilic solvent (ethanol). In order to establish that the initial products of solvolysis are rearranged cyclobutyl compounds, the stability of ethyl 1-methylcyclopropylcarbinyl ether (V) was determined in ethanol containing *p*-toluenesulfonic acid. The ether V was found to rearrange to IV; however, in the presence of ammonium acetate the rearrangement was completely suppressed.

Discussion

Previous findings[1,2] have established the general applicability of activation parameter analysis for diagnosing transition-state geometry of the structures involved. With the unsubstituted cyclopropylcarbinyl tosylate (Ia), in ionizing solvents (acetic acid, sulfolane and aqueous acetone), the solvolyses tend to display a ΔS^* of -20 to -30 eu while, in nucleophilic solvents (methanol and ethanol), the solvolyses tend to be associated with a ΔS^* of -7 to -8 eu. These results can be interpreted by associating a bicyclobutonium ion[4] type transition state with the former entropy values while the latter are characteristic of a homoallylic ion[5] type transition state.

With the 1-methylcyclopropylcarbinyl tosylate (Ic), the solvolyses are characterized by an opposite trend in ΔS^*, suggesting a more extensive reorganization of the substrate structure in nucleophilic solvents than in ionizing solvents *via* a common intermediate. In addition, the apparent lack of 1-methylsubstituent influence upon the rate constants which are compiled in Table IV is nearly constant with several solvents and three leaving groups.[6a] Thus, it appears that $\Delta\Delta F^*$ for the solvolysis of 1-methyl cyclopropylcarbinyl derivatives relative to the corresponding cyclopropylcarbinyl derivatives is independent of both solvent ionizing strength and leaving group.

The close parallel in free energy of activation for solvolysis of Ia and Ic indicates a similar change in

(4) For a review of cyclopropylcarbinyl carbonium ion chemistry, see R. Breslow in "Molecular Rearrangements," Vol. 1, Paul de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 259 ff.

(5) S. Winstein and E. M. Kosower, *J. Am. Chem. Soc.*, **81**, 4399 (1959).

(6) (a) M. Nikoletic, S. Borcic, and D. E. Sunko [*J. Pure Appl. Chem.*, **8**, 441 (1964)] reported relative rates of 4.7 for the methanesulfonates of 1-methylcyclopropylcarbinol and cyclopropylcarbinol in 96% aqueous ethanol at 20° and 7.0 for the corresponding chlorides in 50% aqueous ethanol at 30°. (b) Ia gives rearranged products in acetic acid and unrearranged products in ethanol; Ic gives rearranged products in both solvents.

TABLE IV

COMPARISON OF RELATIVE RATES, ACTIVATION ENTHALPIES, AND ACTIVATION ENTROPIES FOR CYCLOPROPYLCARBINYL AND 1-METHYLCYCLOPROPYLCARBINYL TOSYLATE IN VARIOUS SOLVENTS

p-Toluenesulfonate	Solvent	Rel rate, 30°	ΔH^*, kcal/mole	ΔS^*, eu
Cyclopropylcarbinyl	AcOH	1.0[a]	16.7	−19.0
1-Methylcyclopropylcarbinyl	AcOH	4.9[a]	20.1	−5.2
Neopentyl	AcOH	2.0×10^{-7} [b]	31.5	−1.0
Cyclopropylcarbinyl	EtOH	1.0[a]	21.0	−7.7
1-Methylcyclopropylcarbinyl	EtOH	4.0	16.2	−16
Cyclopropylcarbinyl	MeOH	1.0[c]	20.1	−7.3
1-Methylcyclopropyl-	MeOH	4.3	15.6	−18

[a] From data of Roberts.[1] [b] Extrapolated from data of S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952). [c] From data of Roberts.[2]

carbonium ion stability with changing solvent type. This observation coupled with the dissimilar influence of solvent upon product composition[6b] lends considerable support to the hypothesis that electron delocalization in the cyclopropylcarbinyl system is sufficiently extensive to minimize specific bonding to solvent in the transition state.

The fact, however, that the entropic behavior of Ia and Ic in solvolyses is dissimilar, coupled with the rearranged products obtained for Ic in all solvents investigated, reflects the significant influence of the methyl group upon localization of the charge at the methinyl carbon.

Experimental Section

All boiling points are uncorrected for stem exposure. Infrared spectra were recorded on a Perkin-Elmer Model 21 instrument using sodium chloride optics. An F & M Model 700 gas chromatographic instrument was used for this work, and the following three columns (6 ft × 1/4 in.) were employed: (A) packed with 20% ethylene glycol succinate on 30–60 mesh Chromosorb; (B) packed with 20% polyethylene glycol (containing 1% silver nitrate) on 30–60 mesh Chromosorb; and (C) packed with 40–60 mesh Tide.[7] Nmr spectra were obtained with a Varian HA-60 spectrometer as approximately 10% by weight solutions in carbon tetrachloride. All microanalyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

1-Methylcyclopropylcarbinol was prepared in 70% yield by lithium aluminum hydride reduction of methyl 1-methylcyclopropanecarboxylate, bp 126–127° (760 mm), lit.[8] bp 126° (760 mm). The infrared spectrum (characteristic frequencies for cyclopropane ring[9] at 3100 and 1025 cm^{-1}), the nmr spectrum (cyclopropane peaks[10] at τ 9.77), and vpc (columns A and C) revealed the absence of impurities.

1-Methylcyclopropylcarbinyl p-toluenesulfonate (Ic) was prepared several times. In a typical run, 6.8 g (36 mmoles) of freshly recrystallized *p*-toluenesulfonyl chloride was rapidly added to 2.0 g (24 mmoles) of 1-methylcyclopropylcarbinol dissolved in 25 ml of purified *s*-collidine and maintained at −10° by means of an ice–salt bath. The reaction was held at −10° for 60 min, then the red-brown, semisolid material was dissolved in 50 ml of cold methylene chloride. The mixture was washed three times with cold, 50-ml portions of 10% aqueous sulfuric acid and twice with 50-ml portions of cold water and dried over anhydrous sodium sulfate; the volatile components were removed by flash distillation under reduced pressure (*ca.* 0.1 mm) to yield 4.0 g of an oil. The crude ester was immediately stored in a Dry Ice–acetone bath.[11] The purities, calculated from "infinity" titers of the ethanolysis, ranged from 85–98%. Infrared analysis and treatment with ethanolic silver nitrate revealed that *p*-toluenesulfonyl chloride accounted for most of the impurity. The material had the infrared absorption bands at 3100 and 1020 cm^{-1} characteristic of the cyclopropane ring and lacked the absorption bands characteristic of the carbon–carbon double bond or the hydroxyl group. Attempts to crystallize the crude ester from petroleum ether (bp 30–60°) at −78° were unsuccessful[12] and did little to improve the purity.

1-Methylcyclobutanol was prepared in 90% yield by hydrochloric acid catalyzed ring expansion of 1-methylcyclopropylcarbinol,[6] bp 117–118° (758 mm), lit.[8] bp 118.3° (765 mm). The infrared spectrum was transparent in the 3100- and 1025-cm^{-1} region. The nmr spectrum and vpc (columns A and C) revealed the absence of impurities.

Ethyl 1-methylcyclopropylcarbinyl ether (V) resulted when the sodium salt of 1-methylcyclopropylcarbinol (prepared from 2.0 g, 24 mmoles, of alcohol and 1.4 g, 25 mmoles, of sodium hydride in mineral oil) in dry petroleum ether (bp 30–60°, 50 ml) and ethyl *p*-toluenesulfonate (4.65 g, 24 mmoles) were stirred together at reflux temperature for 24 hr. After cooling and the usual work-up, distillation yielded the ether, 1.8 g, bp 110–112° (760 mm), $n^{25}D$ 1.4140. The infrared and nmr spectra of the compound were consistent with the assigned structure.

Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 74.02; H, 12.50.

Ethyl 1-Methylcyclobutyl Ether (IV).—To the sodium salt of 1-methylcyclobutanol (prepared from 4.0 g, 46 mmoles, of alcohol and 2.26 g, 47 mmoles, of sodium hydride in mineral oil) in dry *n*-pentane (100 ml) was added 8.6 g (46 mmoles) of ethyl *p*-toluenesulfonate. After stirring at reflux temperature for 24 hr, the mixture was poured into 200 ml of ice–water, and the pentane layer separated. The aqueous layer was extracted twice with 50-ml portions of *n*-pentane. The combined organic phases were washed with 50 ml of cold water and dried over anhydrous sodium sulfate. Distillation yielded the ether, 2.0 g, bp 102–104° (760 mm), $n^{25}D$ 1.4156. The infrared and nmr spectra of the compound were consistent with the assigned structure.

Anal. Calcd for $C_7H_{14}O$: C, 73.63; H, 12.36. Found: C, 73.64; H, 12.43.

Methyl 1-methylcyclobutyl ether (III) resulted when the sodium salt of 1-methylcyclobutanol (prepared from 1.5 g, 18 mmoles, of alcohol and 1.0 g, 19 mmoles, of sodium hydride in mineral oil) in dry *o*-xylene (30 ml) and dimethyl sulfate (1.15 g, 9 mmoles) were stirred together at room temperature for 24 hr. After cooling and the usual work-up, distillation yielded the ether, 0.8 g, bp 100–101° (760 mm), $n^{25}D$ 1.4072. The infrared and nmr spectra of the compound were consistent with the assigned structure.

Anal. Calcd for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: C, 72.02; H, 12.20.

Rate measurements were accomplished by titration of the liberated *p*-toluenesulfonic acid with approximately 0.05 *N* methanolic sodium methoxide to a bromothymol blue end point. The aliquot technique was employed and the base was frequently restandardized during the course of the work with little change in normality.

Solvents.—Absolute methanol was prepared by distillation from magnesium turnings and absolute ethanol was prepared according to the method of Fieser.[13]

Product Studies. A. In Ethanol.—1-Methylcyclopropylcarbinyl *p*-toluenesulfonate (Ic, 2.0 g) was solvolyzed in 25 ml of absolute ethanol (containing 20 mmoles of ammonium acetate in one of three runs) at 25° for 15 hr (30 half-lives). The material was added to 50 ml of ice–water and extracted with five 20-ml portions of methylene chloride. The combined extracts were dried over anhydrous sodium sulfate and most of the solvent was removed by distillation. Analysis by glpc (columns A, B, and C) revealed a single product peak with a retention time identical with that of authentic ethyl 1-methylcyclobutyl ether (IV).

(7) Commercial detergent made by Procter and Gamble.

(8) E. F. Cox, M. C. Casserio, M. S. Silver, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 2719 (1961).

(9) G. E. Cartier and S. C. Bunce, *ibid.*, **85**, 932 (1963).

(10) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *ibid.*, **85**, 3218 (1963).

(11) The tosylate readily decomposed to a purple mass on standing for 60 min at 25°; therefore, the work-up was carried out as rapidly as possible, usually within 20 min.

(12) At −78°, the crude ester separates as a pink solid.

(13) L. F. Fieser, "Experiments in Organic Chemistry," 3rd rev ed, D. C. Heath and Co., Boston, Mass., 1957, p 285.

B. In Methanol.—1-Methylcyclopropylcarbinyl *p*-toluenesulfonate (Ic, 2.0 g) was solvolyzed in 25 ml of absolute methanol at 25° for 15 hr. The material was worked up as before and analysis by glpc (columns A, B, and C) revealed a single product peak with a retention time identical with that of authentic methyl 1-methylcyclobutyl ether (III).

C. In Acetic Acid.—1-Methylcyclopropylcarbinyl *p*-toluenesulfonate (Ic, 5.1 g) was solvolyzed in 50 ml of acetic acid solvent (prepared as before[2] and containing 26 mmoles of sodium acetate) at 25° for 15 hr. The material was diluted with 200 ml of ice–water and extracted with three 75-ml portions of ether. Neutralization of the combined extracts with saturated aqueous sodium carbonate and concentration by flash distillation was followed by treatment with 25 ml of 5% aqueous sodium hydroxide for 4 hr at room temperature. The mixture was extracted with three 30-ml portions of ether and dried over anhydrous sodium sulfate; most of the solvent was removed by distillation. Analysis by glpc (columns A and C) revealed a single product peak with a retention time identical with that of authentic 1-methylcyclobutanol.

The Rearrangement of Chloroalkyl Thionocarbonates

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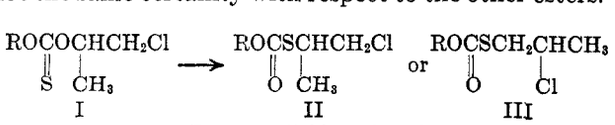
The observation that 2-chloroethyl 3,4-dichlorophenyl thionocarbonate rearranges spontaneously to the S-(2-chloroethyl) thiolcarbonate ester[1] led to an investigation of the behavior of some related chloroalkyl thionocarbonates. The thionocarbonates were prepared by the reaction of 3,4-dichlorophenyl chlorothionoformate with chloro alcohols and pyridine in chloroform at 0°. The rearrangement of the thionocarbonate to the S-chloroalkyl thiolcarbonate was indicated by the appearance of a carbonyl band at 1725–1727 cm^{-1}, and in the nmr spectrum, by replacement of the OCH_2 peak at τ 5.34–5.42 by the SCH_2 peak at τ 6.78–6.89 or by the SCH peak at about τ 6.30.

All of the 2- and 3-chloroalkyl esters that were investigated could be converted to the thiolcarbonate, the relative ease of rearrangement being in the order CH_2CH_2Cl> $CH(CH_3)CH_2Cl$ > $CH_2CHClCH_3$ > $CH_2CH_2CH_2Cl$ > $CH_2CH_2CHClCH_3$. The 4-chlorobutyl thionocarbonate was resistant to rearrangement, showing very slight conversion to the thiolcarbonate after being heated at 200° for 2 hr.

Although it was apparent that the rearrangement product from the 3-chloropropyl thionocarbonate must be the S-(3-chloropropyl) thiolcarbonate, there was not the same certainty with respect to the other esters.



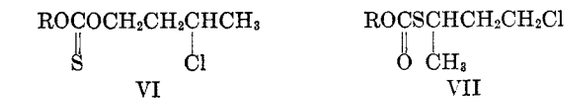
R = 3,4-dichlorophenyl

Thus the rearrangement of the 1-chloro-2-propyl ester I could conceivably lead to either II or III, depending on whether the reaction proceeded *via* a four-membered cyclic intermediate as in the Schönberg rearrangement of diaryl thionocarbonates,[2] or by displacement of chlorine by sulfur with consequent migration of the chlorine atom. The nmr spectrum was found to be in accord with structure III (Table I).

Examination of the spectra of compounds VIII, IX, and X, which are of unequivocal structure, permitted the identification of the chemical shifts. Assignment of τ 6.30–6.36 to the CH_2Cl group was indicated because it is the only methylene group which all these compounds have in common. It then follows that the signal at τ 5.34–5.42 is due to the OCH_2 group, and the one at τ 6.89 is due to the SCH_2 group. The rearrangement product obtained from I must correspond to the structure III, because it has a signal at τ 6.78 corresponding to two hydrogens (SCH_2) and a single hydrogen peak at τ 5.82, which must be due to CHCl. Structure II is excluded because it would be expected to give a peak at τ 6.30–6.36 for the CH_2Cl group.

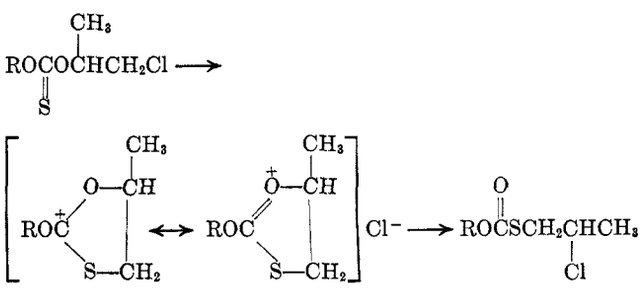
The 1-chloro-2-propyl ester was completely rearranged by heating at 140° for 30 min, but similar treatment of the 2-chloro-1-propyl ester (IV) gave an approximately equal mixture of unchanged thiono ester and the S-(1-chloro-2-propyl) thiol ester (V).

The rearrangement of the 3-chloro-1-butyl ester VI, brought to completion by heating at 200° for 2 hr, gave the S-(4-chloro-2-butyl) thiol ester VII. The

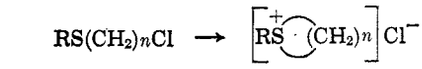


product gave a multiplet at τ 6.30 corresponding to three hydrogens which include the CH_2Cl and the SCH groups. The possible alternative structure, $ROC(O)SCH_2CH_2CHClCH_3$, is excluded because it would be expected to give a SCH_2 signal at τ 6.78–6.89 and a CHCl signal at τ 5.82.

These results indicate that the rearrangement occurs *via* a cyclic intermediate arising from nucleophilic displacement of chlorine by sulfur.



It has been shown that 2-chloroalkyl groups react more or less readily, 3-chloroalkyl groups relatively slowly, and the 4-chlorobutyl group very slowly. This order of reactivity, which corresponds to the relative ease of ring formation, is similar to that observed for the formation of cyclic sulfonium salts from ω-chloro sulfides.[3]



The five-membered ring was found to be formed bout 75 times as fast as the six-membered ring, with a

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(3) G. M. Bennett and E. G. Turner, *J. Chem. Soc.*, 813 (1938).