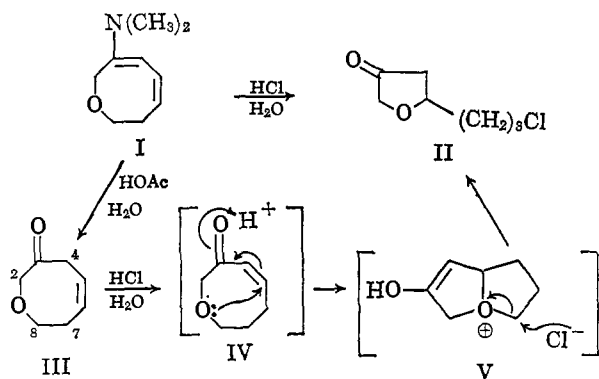


Thus, hydrochloric acid hydrolysis of the dienamine I⁵ gave rise in good yield to 5-(3-chloropropyl)dihydro-3(2H)-furanone (II), b.p. 100–101° (2.2 mm.); 2,4-dinitrophenylhydrazone, m.p. 94–95°. *Anal.* Found: C, 45.55; H, 4.41; Cl, 10.41; N, 16.35. Structure II follows from the elemental analysis, from the presence of an infrared carbonyl band at 1760 cm.⁻¹, which is typical of dihydro-3(2H)-furanones,⁶ and from the n.m.r. spectrum, which, except for the resonance lines of the substituent at position 5, was superimposable upon that of 5-methyldihydro-3(2H)-furanone.⁷ It should be noted that no vinyl proton was present in this spectrum and that the ultraviolet absorption of the 2,4-DNP derivative was that of a typical saturated ketone derivative.⁸

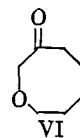
Further insight into the mechanism of the above transformation was obtained in the following manner. Hydrolysis of I in 10% aqueous acetic acid afforded the β,γ -unsaturated ketone III,⁵ b.p. 84–85° (15 mm.); 2,4-dinitrophenylhydrazone, m.p. 114–116°. The structure of III was readily established on the basis of spec-



tral evidence. The infrared absorptions for the carbonyl group and the *cis* double bond were located at 1720 and 1645 cm.⁻¹, respectively. The ultraviolet spectrum of III in isoctane displayed peaks at 290 m μ (ϵ 146), 298 (185), 308 (161), and 318 (89), which can only be reconciled with the strengthened $n \rightarrow \pi^*$ transition characteristic of β,γ -unsaturated ketones⁹ (the ultraviolet spectrum of the 2,4-DNP derivative was also typical of a nonconjugated ketone¹⁰). The presence of the various protons in III was obvious from the following chemical shifts and multiplicities: δ ca. 5.73 (complex multiplet, vinyl protons), 3.92 (singlet, H-2), ca. 3.75 (multiplet, H-8), 3.28 (doublet, H-4), and ca. 2.3 (multiplet, H-7).

The stability of α -alkoxyketones to acidic conditions in the absence of oxidizing agents has previously been demonstrated in a limited number of instances.¹¹ The point was further established in the present study by the observation that 5,6,7,8-tetrahydro-2H-oxocin-

3(4H)-one (VI),⁵ prepared by catalytic hydrogenation of III, proved to be totally inert to the acidic reaction



conditions utilized above. In view of these results, it would appear that the observed rearrangement can only be explained in terms of the ensuing mechanism. In the presence of hydrochloric acid, isomerization of III to the α,β -unsaturated isomer IV would be quite rapid; transannular nucleophilic attack by the remotely located divalent oxygen atom in a manner reminiscent of acid-catalyzed Michael additions leads to intermediate V. This oxonium salt (V) is expected to be extremely sensitive to nucleophilic attack by chloride ion¹²; ring cleavage (as shown) and ketonization eventuate in the formation of II.¹³

The facility with which divalent oxygen participates in this unusual transannular process is remarkable and suggests that the effect of substituting sulfur and nitrogen for this heteroatom can only be favorable. Furthermore, the replacement of nitrogen for oxygen should permit the isolation of the corresponding bicyclic intermediate V. Work to elucidate these points is presently in progress.

Acknowledgment. This work was supported in part by the Petroleum Research Fund, administered by the American Chemical Society. The authors are indebted to the donors of this fund. We also wish to thank the Elanco Products Co. for a generous gift of chloroacetaldehyde dimethyl acetal which was used in the preparation of I.

(12) H. Meerwein, *Angew. Chem.*, **70**, 630 (1958).

(13) These data lend strong support to the proposal that the hydrolysis of 1-oxacyclooctan-5-one to 1,7-dichloro-4-heptanone in aqueous hydrochloric acid proceeds through an intermediate bicyclic oxonium salt.⁵

(14) Alfred P. Sloan Foundation Research Fellow.

Leo A. Paquette,¹⁴ Robert W. Begland

Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

Received May 10, 1965

Sulfonium Salts. I. Fragmentations of Chlorosulfonium Chlorides. A Route to 1,4-Oxathienes¹

Sir:

Scission of the sulfur heteroatom bond is a common step in the reactions of acyloxy-,² halo-,³ and hydroxy-

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(2) For examples, see (a) R. Pummerer, *Chem. Ber.*, **43**, 1401 (1910); (b) W. E. Parham and M. D. Bhavsar, *J. Org. Chem.*, **28**, 2686 (1963); (c) L. Horner and P. Kaiser, *Ann.*, **626**, 19 (1959); (d) L. Horner and E. Jürgens, *ibid.*, **602**, 135 (1957).

(3) For lead references, see (a) W. E. Lawson and T. P. Dawson, *J. Am. Chem. Soc.*, **49**, 3119 (1927); (b) H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949); (c) F. G. Bordwell and B. M. Pitt, *J. Am. Chem. Soc.*, **77**, 572 (1955); (d) H. Böhme and H. Gran, *Ann.*, **581**, 133 (1953); (e) H. Richtzenhain and B. Alfredsson, *Chem. Ber.*, **86**, 142 (1953).

(5) Satisfactory elemental analyses were obtained for all new compounds reported herein.

(6) J. H. S. Wieland, H. Dijkstra, and A. B. Pik, *Rec. trav. chim.*, **82**, 651 (1963), and references cited therein.

(7) N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, "NMR Spectra Catalog," Vol. 2, Varian Associates, Palo Alto, Calif., 1963, Spectrum No. 439.

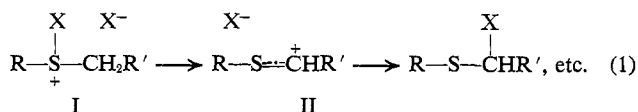
(8) $\lambda_{\text{max}}^{\text{EtOH}}$ 228 m μ (ϵ 15,200), 255 sh (11,000), and 356 (20,800).

(9) A. Moscovitz, K. Mislow, M. A. W. Glass, and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1945 (1962).

(10) $\lambda_{\text{max}}^{\text{EtOH}}$ 228 m μ (ϵ 14,600), 255 sh (11,400), and 356 (21,600).

(11) See ref. 6 and R. P. Mariella and J. L. Leech, *J. Am. Chem. Soc.*, **71**, 3558 (1949); note also that the ultimate product (II) is a member of this class of compounds.

sulfonium salts (I).⁴ Such reactions proceed in non-aqueous media often with neither alteration of the carbon skeleton nor disruption of the carbon-sulfur linkages. While the details of the mechanisms by which such sulfonium salts are transformed remain obscure, it is clear that the spectrum of products from these reactions can be explained by the intermediacy of sulfocarbonium ion II or its related α -substituted sulfide.²⁻⁴

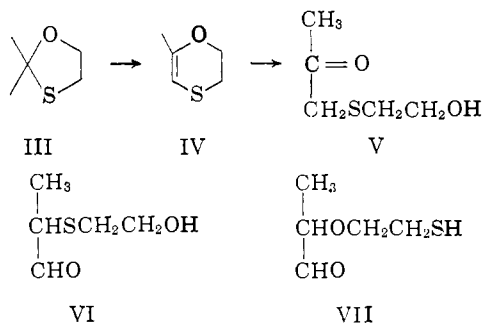


It seemed possible that substitution of the α -carbon atom of sulfonium salts such as I with groups which stabilize carbonium ions might favor rupture of that carbon-sulfur bond over the α -transfer reaction (eq. 1) in systems where both routes were possible. Intramolecular reaction of the sulfenyl chloride generated in this step with the incipient double bond could lend itself to application as a method of ring expansion of cyclic sulfides. An effective system on which to test this hypothesis was found in the cyclic sulfides, the 2,2-disubstituted 1,3-oxathiolanes.

Chlorination of the 1,3-oxathiolanes in a mixed solvent of methylene chloride-carbon tetrachloride led to chlorosulfonium chlorides⁵ which were not isolated but which were heated under reflux to promote fragmentation of the salts. The hydrogen chloride formed was swept from the refluxing mixture by a current of nitrogen. No chlorine could be detected in the effluent gases. The products, 1,4-oxathiene derivatives, were isolated either by distillation or preparative gas chromatography.

Treatment of 2,2-dimethyl-1,3-oxathiolane (III) with chlorine under the conditions described afforded 2-methyl-1,4-oxathiene (IV) in 54% yield. *Anal.* Calcd. for $\text{C}_5\text{H}_8\text{OS}$: C, 51.68; H, 6.94. Found: C, 51.59; H, 6.63. The n.m.r. spectrum (CDCl_3) of this material showed singlet resonances for methyl and vinyl protons 1.47 and 3.90 p.p.m., respectively, downfield from tetramethylsilane. Two deformed triplets ($J = 3.7$ c.p.s.) at 2.35 and 3.56 p.p.m. were assigned to the methylene protons contiguous to the sulfur and oxygen atoms, respectively.

Hydrolysis of the 2-methyl-1,4-oxathiene (IV) afforded in 80% yield 1-(2-hydroxyethylthio)acetone (V), isolated as its brilliant red 2,4-dinitrophenylhydrazone derivative, m.p. 82.2-82.9°. *Anal.* Calcd. for C_{11} -



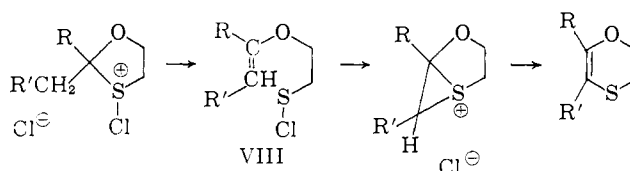
(4) (a) D. Walker and J. Leib, *Can. J. Chem.*, **40**, 1242 (1962); (b) H. Becker, G. J. Mikol, and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3410 (1963); (c) W. J. Kenney, J. A. Walsh, and D. A. Davenport, *ibid.*, **83**, 4019 (1961).

$\text{H}_{14}\text{N}_4\text{O}_5\text{S}$: C, 42.03; H, 4.49; N, 17.82. Found: C, 42.16; H, 4.66; N, 17.66.

The structural assignment of V as opposed to the isomeric structure VI followed directly from an analysis of the n.m.r. spectra of the 2,4-dinitrophenylhydrazone. The presence of a singlet methyl resonance, 2.17 p.p.m., confirmed that the 2,4-dinitrophenylhydrazone was an acetone derivative. Singlet and triplet ($J = 5.9$ c.p.s.) signals at 3.43 and 2.70 p.p.m. were assigned to methylene protons adjacent to the sulfur atom. The remaining methylene group was assigned as an unsymmetrical triplet at 3.78 p.p.m.

In deuteriochloroform the hydroxyl proton gave rise to a singlet, 2.40 p.p.m., which disappeared upon addition of deuterium oxide, but in dimethyl sulfoxide solution⁵ a triplet ($J = 5$ c.p.s.) at 4.73 p.p.m. was observed. The expected resonances for aromatic and amino protons were also found. No material identifiable as the 2,4-dinitrophenylhydrazone of 2-(2-mercaptoethoxy)propionaldehyde (VII) could be detected by thin-layer chromatography.^{6,7}

In analogy with ionic cleavage reactions of trityl aryl sulfides⁸ and thioglucosides⁹ under oxidative conditions, we consider at present that the ring expansion proceeds by an ionic cleavage-recombination sequence with a sulfenyl chloride intermediate (VIII). A similar situation obtains in the formation of isothiazolo-



derivatives from a thiazepine.¹⁰ Neither the molecularity nor any stereochemical requirements of the elimination to form our proposed intermediate XI can be given at this time. The subsequent combination of the sulfenyl chloride with the double bond and the opening of the episulfonium ion in the proposed sequence are completely analogous to known sequences.¹¹

The generality of this ring expansion is shown by the formation of $\Delta^{1,6}$ -2,5-oxathiabicyclo[4.4.0]decane and $\Delta^{1,6}$ -2,5-oxathiabicyclo[4.3.0]nonane in 53 and 61% yields from the ethylene hemithioacetals of cyclohexanone and cyclopentanone, respectively.

(5) O. L. Chapman and R. W. King, *ibid.*, **86**, 1256 (1964).

(6) A silica gel plate and ethyl acetate-chloroform (1:1) eluent were used for this chromatography.

(7) W. E. Parham, I. Gordon, and J. D. Swalen, *J. Am. Chem. Soc.*, **74**, 1824 (1952), obtained only the 2,4-dinitrophenylhydrazone of 2-(2-hydroxyethylthio)acetaldehyde in 30% yield from the hydrolysis of 1,4-oxathiene in the presence of less than 1 equiv. of 2,4-dinitrophenylhydrazine.

(8) (a) D. S. Tarbell and D. P. Harnish, *J. Am. Chem. Soc.*, **74**, 1862 (1952); (b) D. C. Gregg, K. Hazelton, and T. F. McKeon, Jr., *J. Org. Chem.*, **18**, 36 (1953); (c) K. C. Schreiber and V. P. Fernandez, *ibid.*, **26**, 2478 (1961).

(9) M. L. Wolfrom, H. G. Garg, and D. Horton, *ibid.*, **29**, 3280 (1964), and references therein.

(10) N. J. Leonard and G. E. Wilson, Jr., *Tetrahedron Letters*, No. 23, 1471 (1964); *J. Am. Chem. Soc.*, **86**, 5307 (1964).

(11) N. Kharasch in "Organic Sulfur Compounds," Vol. 1, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, pp. 382-384.

G. Edwin Wilson, Jr.

Department of Chemistry, Polytechnic Institute of Brooklyn
Brooklyn, New York 11201

Received July 6, 1965