

process k_x , k_c competes favorably. The oxidation of an amino acid may take a similar course, loss of CO_2 from a radical zwitterion, and differ from that of an amine, loss of α -proton from a radical cation. The importance of alkali in reduction by *N*-acetylmethionine indicates that alkali may remove the amide proton in the CTC-S, facilitating electron transfer from N to S, and then loss of CO_2 . The α -acetamido radicals may be ionized at pH 12,⁸ and disproportionate rather than reduce ground state ketone efficiently.

Acknowledgment. This work was supported by the National Science Foundation GP 32452. We are indebted to Dr. M. Toth for determination of the triplet lifetimes.

References and Notes

- (1) (a) S. G. Cohen and J. I. Cohen, *J. Phys. Chem.*, **72**, 3782 (1968); (b) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973).
- (2) J. B. Guttenplan and S. G. Cohen, *J. Org. Chem.*, **38**, 2001 (1973).
- (3) S. G. Cohen, G. C. Ramsay, N. M. Stein, and S. Y. Weinstein, *J. Am. Chem. Soc.*, **96**, 5124 (1974).
- (4) S. G. Cohen and N. M. Stein, *J. Am. Chem. Soc.*, **93**, 6542 (1971).
- (5) S. Ojanpera and S. G. Cohen, *J. Am. Chem. Soc.*, **96**, 7379 (1974).
- (6) (a) R. S. Davidson and P. R. Steiner, *J. Chem. Soc. C*, 1682 (1971); (b) *Chem. Commun.*, 1115 (1971); (c) R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc. C*, 3480 (1971).
- (7) (a) S. F. Yang, H. S. Ku, and H. K. Pratt, *J. Biol. Chem.*, **242**, 5274 (1967); (b) J. R. Bowen and S. F. Yang, *Photochem. Photobiol.*, **21**, 201 (1975).
- (8) M. Simic, P. Neta, and E. Hayon, *Int. J. Radiat. Phys. Chem.*, **3**, 309 (1971).

Saul G. Cohen,* Salme Ojanpera

Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154

Received June 16, 1975

Stereochemical Course of an Associative Nucleophilic Displacement at Tetracoordinate Sulfur(IV). An Optically Active Trigonal Bipyramidal Molecule, a Chlorosulfurane¹

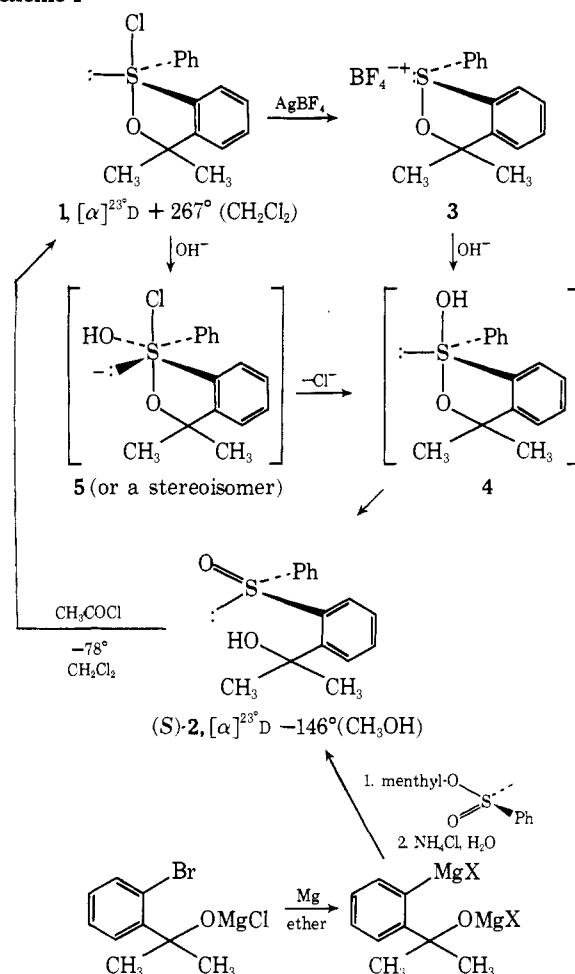
Sir:

We report the synthesis of optically active chlorosulfurane **1** in 95% enantiomeric purity by the route indicated in Scheme I, the first example of an optically active tetracoordinate sulfur(IV) species. It is hydrolyzed in base by an associative mechanism to give sulfoxide **2** with retention of configuration about sulfur.

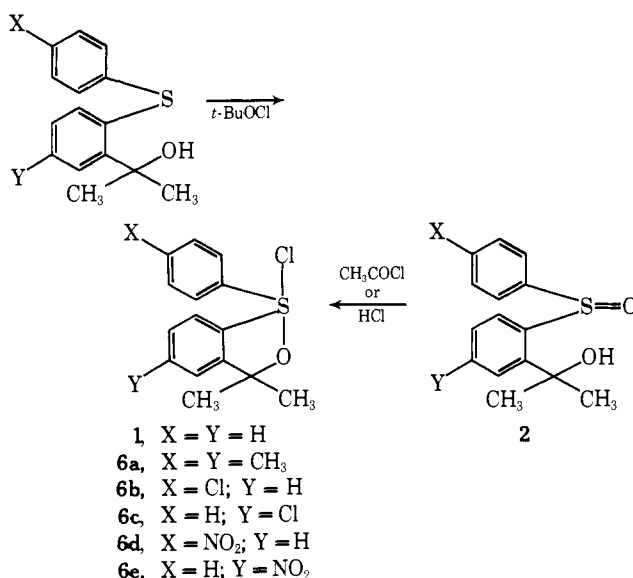
The stability of fluorosulfuranes is sufficiently high that many examples of this class of compound have been isolated and studied.² The chlorosulfuranes, in contrast, are much less stable. Several have been observed, without isolation, as reaction intermediates.³ Those which have been isolated^{4a-d} have usually been thermally unstable^{4e} and easily hydrolyzed. Chlorosulfurane **1**, which includes one oxygen ligand and one carbon ligand to sulfur in a five-membered ring,^{4a} is stable in crystalline form indefinitely at room temperature. Racemic **1** (mp 125–126°) is only slightly decomposed after two melting-cooling cycles (ca. 1° lowering in melting point). Less than 15% hydrolysis was noted by NMR after overnight exposure of crystalline **1** to air.

Racemic **1** and its substituted analogs, **6a–e**, are easily formed from the corresponding sulfoxides in chloroform by treatment with acetyl chloride or anhydrous HCl or from the corresponding sulfides by treatment with *tert*-butyl hypochlorite. Removal of the solvent from a chloroform solution of acetyl chloride and **2** gave **1** in 100% isolated yield: NMR (CDCl_3) δ 1.26 (s, 3), 1.68 (s, 3), 7.44 (s, 7), 7.70 (m, 2), 9.33 (m, 1); ir (CHCl_3) 2980 (s), 1448 (m), 1240 (m), 1150 (m), 997 (s) cm^{-1} . This compound, and all oth-

Scheme I



ers isolated in this study, gave satisfactory elemental analyses. Addition of 1 equiv of H_2O to a chloroform solution of **1** gives no hydrolysis detectable by NMR. Further addition of 1 equiv of diisopropylethylamine or *N,N*-dimethylaniline results in complete hydrolysis. Competitive rates of hydrolyses of binary mixtures of the above chlorosulfuranes (**1** and **6a–e**) were followed using limited H_2O in the presence of an equivalent amount of one of the named amines, analyzing for products and unreacted starting material by ^1H NMR.



The covalent nature of the S-Cl bond in chlorosulfuranes **1** and **6a-e** is indicated by the presence of a molecular ion at m/e 278 in the field desorption mass spectrum of **1** and by several NMR comparisons. The ^1H NMR peaks for the proton ortho to sulfur in the disubstituted ring of **1** and the analogous protons in **6a-e** occur at lower field than δ 9.10. The analogous protons occur at higher field than δ 8.35 for the ionic fluoroborates or trifluoromethanesulfonates. The separation between the two *gem*-dimethyl signals is consistently more than 25 Hz for covalent derivatives, including alkoxysulfurane analogs of the chlorosulfuranes, and less than 15 Hz for the ionic species. The NMR of **1** in CDCl_3 is independent of the concentration of added tetraethylammonium chloride from 0 to 2.25 *M*. This evidence for the covalent character of the S-Cl bond parallels that from earlier studies^{3a} of unisolated chlorosulfuranes studied in solution by ^1H NMR.

The relative rate constants for hydrolysis of **1** (1), **6a** (0.3), **6b** (1.15), **6c** (2.8), **6d** (1.54), and **6e** (26.0) show that substituents, Y, in the fused-ring system are much more effective than those, X, in the freely rotating aromatic ring ($\rho_Y = 2.0$, $\rho_X = 0.3$). Both are positive, consistent with the operation of an associative mechanism involving the development of negative charge on sulfur in a transition state resembling **5**. There are 24 stereoisomers (12 pairs of enantiomers) of the general octahedral structure **5**, and the somewhat arbitrary choice of **5** for illustration in Scheme I will be discussed in a later paper. Known analogs of **5** include the SF_5^- species reported by Christie^{5a} and Muetterties.^{5b}

The silver assisted ionization of Scheme I initiates a dissociative route for displacement via sulfonium salt **4**. If this ionization can be considered to proceed with retention of configuration at sulfur and the further reaction with hydroxyl ion is considered to proceed to give **4** and **2** by the stereochemical route demonstrated for the basic hydrolysis of acyclic alkoxy sulfonium salts,⁶ the relationship between **1** and **2** is established as that shown in Scheme I. Associative displacement of the chloride of **1** by hydroxide, under the same conditions used for the competitive rate studies, proceeds to give **2** of the same configuration with less than 9% racemization. This direct displacement must therefore also proceed with retention of geometry.

The synthesis of **2** by a Grignard displacement^{7a} on methyl (*S*)-benzenesulfinate ($[\alpha]_D -202^\circ$, acetone; lit.⁸ $[\alpha]_D -206^\circ$, acetone), a reaction known to proceed with inversion,^{7b} completes the definition of stereochemistry as that shown in Scheme I. Enantiomeric purities⁹ of **1** and **2** were determined by the method of Pirkle¹⁰ using (*S*)-(+)-1-(10-methyl-9-anthryl)-2,2,2-trifluoroethanol¹¹ (**7**) in CDCl_3 to provide the chiral medium in which the methyl signals for enantiomers of **1** and **2** were clearly resolved.^{12,13}

Acknowledgment. This research was supported in part by a grant from the National Science Foundation, MPS71-03222, and in part by a grant from the National Institutes of Health (CA-13963).

References and Notes

- (1) Paper XVIII in a series of papers on sulfuranes. For paper XVII see J. C. Martin and J. A. Franz, *J. Am. Chem. Soc.*, in press.
- (2) See W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, for numerous references. See also W. J. Middleton, *J. Org. Chem.*, **40**, 574 (1975); D. B. Denney, D. Z. Denney, and Y. F. Hsu, *J. Am. Chem. Soc.*, **95**, 4064 (1973); P. Meakin, D. W. Ovenall, W. A. Sheppard, and J. P. Jesson, *ibid.*, **97**, 522 (1975); D. T. Sauer and J. M. Shreeve, *J. Fluorine Chem.*, **1**, 1 (1971).
- (3) (a) C. R. Johnson and J. J. Rigau, *J. Am. Chem. Soc.*, **91**, 5398 (1969); D. C. Owsley, G. K. Helmkamp, and M. F. Rettig, *ibid.*, **91**, 5239 (1969); (c) see also G. H. Schmidt and V. J. Nowlan, *J. Org. Chem.*, **37**, 3086 (1972).
- (4) (a) J. C. Martin and E. F. Perozzi, *J. Am. Chem. Soc.*, **96**, 3155 (1974); (b) N. C. Baenziger, R. E. Buckles, R. J. Maner, and T. D. Simpson, *ibid.*, **91**, 5749 (1969); (c) O. Ruff, *Chem. Ber.*, **37**, 4513 (1904); (d) I. B.

- Douglass, K. R. Brower, and F. T. Martin, *J. Am. Chem. Soc.*, **74**, 5770 (1952); (e) G. E. Wilson, Jr., and M. M. Y. Chang, *ibid.*, **98**, 7533 (1974).
- (5) (a) K. O. Christie, E. C. Curtis, C. J. Schack, and D. Pllipovch, *Inorg. Chem.*, **11**, 1679 (1972); (b) C. W. Tullock, D. D. Coffman, and E. L. Muetterties, *J. Am. Chem. Soc.*, **86**, 357 (1964).
 - (6) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 5404 (1965); R. Tang and K. Mislow, *ibid.*, **91**, 5644 (1969).
 - (7) (a) K. K. Andersen, *Tetrahedron Lett.*, 93 (1962); (b) P. Bickart, M. Axelrod, J. Jacobus, and K. Mislow, *J. Am. Chem. Soc.*, **89**, 697 (1967).
 - (8) J. Jacobus and K. Mislow, *J. Am. Chem. Soc.*, **89**, 5228 (1967).
 - (9) We have assumed optical and enantiomeric purity to be identical.
 - (10) W. H. Pirkle and S. D. Beare, *J. Am. Chem. Soc.*, **90**, 6250 (1968).
 - (11) We are indebted to W. H. Pirkle and D. Sikkenga for a sample of this material.
 - (12) The methyl signals for **1** (Scheme I) were at lower field than those for its enantiomer by about 9 Hz while those for (*R*)-**2** were at higher field than those of (*S*)-**2** by about 7 Hz in the presence of 0.18 *M* 7 .
 - (13) We propose extension of the *R-S* nomenclature system^{14,15} to trigonal bipyramidal molecules using the usual sequence rules,¹⁴ by viewing the molecule along the apical axis with the higher ranking of the two apical ligands at the nearer end of that axis. (For a distorted trigonal bipyramid the most nearly collinear pair of bonds joining ligands to the central atom is designated the apical axis.) The chirality of the molecule is then defined in terms of the sequence of equatorial ligands in the usual way.¹⁴ By this convention the chlorosulfurane pictured in Scheme I is (*S*)-(+)-**1**. The validity of this assignment rests, of course, on the arguments outlined in the text.
 - (14) R. S. Cahn, C. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966), proposed a nomenclature system for the specification of molecular chirality which has been generally accepted. They explicitly refrained (p 410) from considering trigonal bipyramidal molecules since no compounds were known at that time whose chirality depended on the configurational stability of the central atom of such a structure. Since 1966 reports have appeared of a spiro derivative of hypervalent selenium by B. Lindgren, *Acta Chem. Scand.*, **26**, 2560 (1970); a spirophosphorane by D. Hellwinkel, *Chem. Ber.*, **99**, 3628 (1966); and phosphoranes bearing chiral ligands by J. F. Brazier, J. Ferekh, A. Munoz, and R. Wolf, *C. R. Acad. Sci.*, **272**, 1521 (1971), and J. Ferekh, J. F. Brazier, A. Munoz, and R. Wolf, *ibid.*, **270**, 865 (1970).
 - (15) Professor Prelog, private communication, has suggested an alternative set of conventions which could be used to factor the trigonal bipyramid into two distorted tetrahedra which might be used to designate the sense of chirality. We will further discuss this problem in a later publication. P. C. Lauterbur and F. Ramirez, *J. Am. Chem. Soc.*, **90**, 6722 (1968), and K. E. DeBruin, K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 7031 (1969), have also discussed the problems of designating chirality in phosphoranes in a discussion of the pseudorotation processes interconverting isomers.

T. M. Balthazor, J. C. Martin*

Department of Chemistry, Roger Adams Laboratory
University of Illinois,
Urbana, Illinois 61801
Received May 23, 1975

Generation of Photochemical Species on Ground, Excited Singlet, and Triplet Hypersurfaces in Barrelene Photochemistry^{1,2}

Sir:

The di- π -methane rearrangement³ has developed into one of the most general of photochemical reactions and its mechanism has been the subject of considerable study.⁴ The cyclopropyldicarbonyl diradical species **1** has been postu-



lated⁴ to be involved in both cyclic and acyclic examples of the rearrangement. In the specific examples of the di- π -methane rearrangements of barrelene (**2**), benzobarrelene (**3**), and 2,3-naphthobarrelene (**4**) the mechanism⁵ in Chart I is seen to involve the triplet cyclopropyldicarbonyl diradicals **5**, **6**, and **7**.

That such cyclopropyldicarbonyl diradical species should lead onward to di- π -methane products poses a dilemma, since ground^{6a-d} and excited^{6e,f} state precedent give no evidence of such rearrangements but rather suggest that dirad-