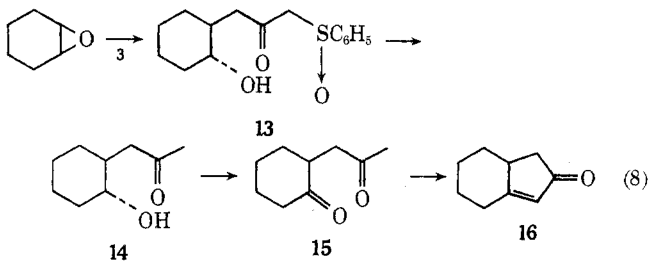
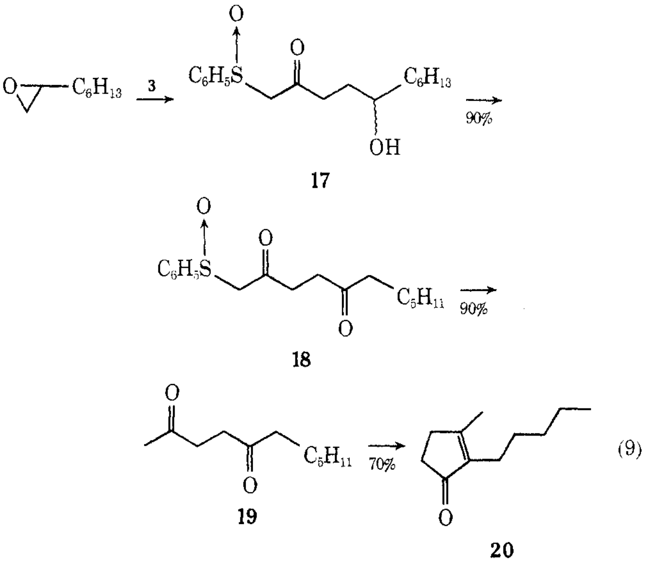


dianion **3** in THF at room temperature for 24 hr resulted in an 85% crude yield of ketol **13** (a 54% isolated yield of pure **13**, mp 104-105°, was obtained by direct crystallization of the crude product). Cleavage of the carbon-sulfur bond was achieved (Al/Hg) in aqueous THF as previously described in 85% yield. Jones oxidation of **14** followed by aldol condensation afforded hydrindenone **16** in 70% overall yield from **14**.

To further demonstrate the efficiency of this synthetic scheme, we have carried out the synthesis of dihydrojasmone[11] (**20**) as illustrated in eq 9. Reaction of the epoxide



derived from 1-octene with dianion **3** in THF provided an 80% yield of ketol **17** (**17** was in equilibrium with its cyclic hemiacetal). Oxidation followed by reductive cleavage and cyclization afforded dihydrojasmone (**20**) which exhibited spectral properties in agreement with published data.[11]

This novel and efficient method for the construction of 1,4 diketones makes dianions of β-keto sulfoxides useful intermediates in organic synthesis. In addition, dianion **3** should provide an attractive synthetic route to a wide variety of ketones and aldols.[8]

Acknowledgment. We thank the National Cancer Institute (Public Health Service Research Grant No. RO1 CA 13689-02), Eli Lilly and Co., and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for generous support of this research.

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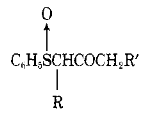
(5) We recently reported that dianions of β-keto phosphonates undergo specific alkylation on the γ carbon, providing a versatile synthesis of dimethyl (2-oxoalkyl) phosphonates [P. A. Grieco and C. S. Pogonowski, *J. Amer. Chem. Soc.*, **95**, 3071 (1973); P. A. Grieco and C. S. Pogonowski, *Synthesis*, 425 (1973)]. For a review on dianions of β-dicarbonyl compounds, see T. M. Harris and C. M. Harris, *Org. React.*, **17**, 155 (1969); L. Weiler, *J. Amer. Chem. Soc.*, **92**, 6702 (1970).
(6) Prepared by treatment of phenyl (2-oxopropyl) sulfide with sodium metaperiodate in aqueous methanol at 0° [C. R. Johnson and H. E. Keiser, *Org. Syn.*, **46**, 78 (1966)].
(7) The nmr spectrum of phenyl (2-oxopropyl) sulfoxide has the following signals: δ (CCl_4) 2.23 (s, 3 H, COMe), 3.80 (s, 2 H, $-CH_2-$), 7.55 (m, 5 H).
(8) One can prepare α- and γ-substituted β-keto sulfoxides (*e.g.*, i) which provides for a general route to ketones (unpublished results, P. A. Grieco and C. S. Pogonowski).



$C_6H_5S(\rightarrow O)CH(R)COCH_2R'$

i

(9) Kindly provided through the courtesy of Dr. Bernard J. Kane, Glidden-Durkee, Jacksonville, Fla.
(10) In addition to the epoxides cited, propylene oxide undergoes smooth reaction with dianion **3**. A report describing the opening of epoxides with the dianion of ethyl acetoacetate for the preparation of tetrahydrofurylidene acetates has recently appeared [T. A. Bryson, *J. Org. Chem.*, **38**, 3428 (1973)].
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Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260

Paul A. Grieco*
Chester S. Pogonowski

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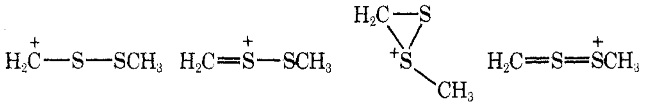
α-Disulfide Carbonium Ions

Summary: Evidence from solvolysis studies on chloromethyl methyl disulfide and spectroscopic studies with various disulfides is taken to indicate that acyclic α-disulfide carbonium ions are far less stable than α-sulfide carbonium ions.

Sir: While carbonium ion stabilization by adjacent thiyl groups is well-known,[1] the stability of α-disulfide carbonium ions has not been reported. In connection with studies involving α-heteroatom-substituted alkyl disulfides[2] we required information on the properties of the methyldithiomethyl cation (shown in various canonical or valence tautomeric representations **1a**-**1d**) and its alkyl-substituted derivatives. In this communication we present the preliminary results of our investigation.



1a **1b** **1c** **1d**

We have determined the rate of hydrolysis of CH_3SSCH_2Cl[3] under S_N1 conditions, following the general procedure used by Bordwell in his classical study of the hydrolysis of α-chloro sulfides.[1a] The hydrolysis of a $\sim$0.005 *M* solution of the α-chloro disulfide in 50% dioxane-water at 34.85° was followed using either an automatic titrator or a conductivity cell.[4] Least-squares analysis of data obtained from a duplicate run using a photometric titrator[5] automatically maintained at the pH 4.6 Bromphenol Blue end point gave a first-order rate constant of 1.82×10^{-4} sec^{-1} (correlation coefficient 0.995). A comparison of the rate constants for hydrolysis of CH_3SSCH_2Cl and CH_3SCH_2Cl (Table I) indicates a rate retardation for the former of over 6800, providing clear evidence for the decreased stability of $CH_3SSCH_2^+$ compared to $CH_3SCH_2^+$.

Table I
Rate Constants for the Hydrolysis of Chloromethyl Methyl Disulfide and Some Related Compounds at 34.85° in Aqueous Dioxane

Compd	$k \times 10^5$ sec^{-1}	Ref
p-$NO_2C_6H_4SCH_2Cl$	5.7	1a
CH_3SSCH_2Cl	18	This work
$(CH_3)_3CCl$	58	1a, this work
$C_6H_5SCH_2Cl$	560	1a
CH_3SCH_2Cl	123,000	8

Spectroscopic data on alkyl and vinyl disulfides and sulfides is also consistent with the lesser stability of α-disulfide carbonium ions compared to the corresponding α-thiyl carbonium ions. Thus, while the mass spectra of dialkyl sulfides show a prominent α-fission fragment (*i.e.*,

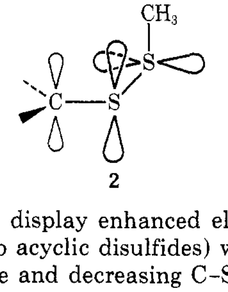
$$n\text{-Pr}\overset{\cdot+}{\text{S}}\text{Pr-}n \xrightarrow{-\text{Et}\cdot} n\text{-PrSCH}_2^{+} \qquad (1)$$

eq 1, 86% base),[6,7] this same process is insignificant in the mass spectra of dialkyl disulfides (*i.e.*, eq 2, 0.09% base).[6]

$$n\text{-PrS}\overset{\cdot+}{\text{S}}\text{Pr-}n \xrightarrow{-\text{Et}\cdot} n\text{-PrSSCH}_2^{+} \qquad (2)$$

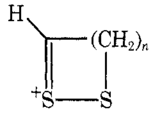
The extent of shielding of β-vinyl protons in the nmr spectra of vinyl compounds ($CH_2{=}CHX$, X = RS, R_2S^+, RO, R_2N, R_3Si) has been used as a measure of the importance of electron-donating resonance structures such as $^-CH_2{-}CH{=}X^+$ in competition with inductive and conjugative electron-withdrawing effects as in $^+CH_2{-}CH{=}X^-$.[9] The fact that β protons of vinyl disulfides are *less shielded* than β protons of vinyl sulfides supports the contention that the disulfide group is a poorer electron donor than the sulfide group (compare the chemical shifts of δ 4.84–4.97 and 5.08–5.11 for the β-vinyl protons, respectively, cis and trans to the alkylthio group in ethyl or methyl vinyl sulfide[9] with the corresponding *cis-* and *trans-β-*vinyl proton shifts of δ 5.40–5.45 and 5.25–5.30 in ethyl or methyl vinyl disulfide[10]) as indicated by a variety of chemical studies.[11]

To explain the low stability of **1** it can be argued that the near 90° C–S–S–C dihedral angle adopted by acyclic disulfides is also favored for ion **1**, thereby precluding any contributions from structure **1d** (since the requisite p orbitals are orthogonal as indicated in **2**). While **1c** could contribute to the overall stability of **1**, it could only do so at the expense of contributions from **1a** and **1b** (since the geometry favoring **1c** should differ from the ideal geometry for **1a** and **1b**).[12] The reduced stability of $CH_3SSCH_2^+$ compared to $CH_3SCH_2^+$ can be attributed to inductive and conjugative (*i.e.*, involving sulfur 3d orbitals) electron-withdrawal effects by the second sulfur atom.[13] From the data of Table I it is seen that, in electron-withdrawal ability, the CH_3S group is similar to the *p*-nitrophenyl group.

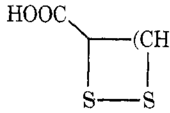


2

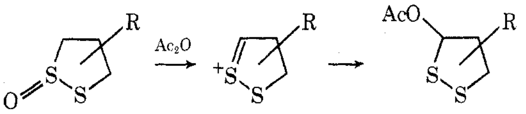
Cyclic disulfides display enhanced electron-donor properties (compared to acyclic disulfides) which increase with decreasing ring size and decreasing C–S–S–C dihedral angle.[11a,c] This phenomenon is explained in terms of the destabilization of the ground state of small ring disulfides due to lone pair–lone pair repulsion.[11] We suggest that the stability of cyclic α-disulfide carbonium ions (*i.e.*, **3**) should also increase with decreasing ring size since extended conjugation (as in **1b** and **1d**) should relieve lone pair repulsions. This postulate finds some support in the following observations: (1) the base peak in the mass spectrum of 1,2-dithiolane-3-carboxylic acid (**4a**) corresponds to ion **3a** while in the mass spectrum of 1,2-dithiane-3-carboxylic acid (**4b**) the peak corresponding to the M − CO_2H ion **3b** represents only 29% of the base intensity;[14] (2) 1,2-dithiolane *S*-oxide **5** undergoes a Pummerer rearrangement (presumably involving a carbonium ion such as **6** as a key intermediate) on treatment with acetic anhydride,[15] while, in our hands, *tert*-BuSS(O)Me[16] was unreactive under the same conditions.[17,18]



3a, $n = 2$
b, $n = 3$



4a, $n = 2$
b, $n = 3$



5 **6**

Finally, it should be noted that *α-alkylperoxy carbonium ions* (*i.e.*, $^+CH_2OOR$) should be less stable than α-alkoxy carbonium ions for essentially the same reasons advanced above to explain the relative instability of acyclic *α-disulfide carbonium ions.* Consistent with this argument is the observation that replacement of both alkoxy groups of an acetal with peroxy groups (*i.e.*, using *t*-BuOOH; see eq 3) requires more drastic conditions, such as acid catalysis, than replacement of a single alkoxy group (which occurs without catalyst).[20]

$$\text{RCH(OEt)}_2 + t\text{-BuOOH} \xrightarrow{\Delta} \text{RCH(OEt)(OO-}t\text{-Bu)} \xrightarrow[\text{HClO}_4]{t\text{-BuOOH}} \text{RCH(OO-}t\text{-Bu)}_2 \qquad (3)$$
$$\text{R} = \text{alkyl}$$

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(13) (a) A somewhat similar situation may prevail for $CH_3SSCH_2\cdot$ [*cf.* P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971)]; (b) for a dramatic demonstration of acceptive resonance by divalent sulfur, see C. B. Quinn and J. R. Wiseman, *ibid.*, **95**, 6120 (1973).

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(17) An extreme example of a stabilized cyclic α-disulfide carbonium ion is the aromatic 1,2-dithiolium ion [*cf.* A. Hordvik, *Quart. Rep. Sulfur Chem.*, **5**, 21 (1970)].

(18) The C–S–S–C dihedral angle in dimethyl disulfide is actually somewhat less than 90° (~85° in the gas phase[19]) and a similar situation may prevail for CH_3SSCH_2Cl and ion **1**. Preliminary kinetic measurements on the rate of hydrolysis of $(CH_3)_3CSSCH_2Cl$, a compound which on steric grounds[19] might be expected to have a dihedral angle closer to 90°, indicate a rate constant less than half as large as that for CH_3SSCH_2Cl. This result, which is in the opposite direction from that expected on the basis of inductive effects, is consistent with the dihedral angle arguments presented above.

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(21) Visiting Professor at Harvard University, 1974. Address correspondence to author at the Department of Chemistry, Harvard University, Cambridge, Mass. 02138.

Department of Chemistry
University of Missouri—St. Louis
St. Louis, Missouri 63121

Eric Block[21]

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The Chlorination of Cyclopentadiene

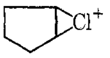
Summary: Chlorination of cyclopentadiene under ionic condition in several solvents produces (in varying amounts) the following dichlorides (yields ~60%): *cis*-3,4-dichlorocyclopentene (1), *trans*-3,4-dichlorocyclopentene (2), *cis*-3,5-dichlorocyclopentene (3), and *trans*-3,5-dichlorocyclopentene (4); 1 is formed by cis-1,2 addition of chlorine.

Sir: We wish to report the first example of extensive *cis*-1,2 addition of chlorine to a simple, aliphatic olefinic system.[1] The results in Table I show that chlorination of cyclopentadiene gives *cis*-3,4-dichlorocyclopentene (1) under all of the conditions that were examined.

Table I
Chlorination of Cyclopentadiene

Solvent	Percentage of dichlorides 1	2	3	4	Yield, %
CH_2Cl_2	38	35	18	9	52
CCl_4	27	23	39	11	60
C_5H_{12}	13	29	29	28	68

The stereochemistry of 1,2 addition of chlorine to cyclopentadiene stands in marked contrast to cyclopentene. We have established that chlorination of cyclopentene does not give a trace of the cis-1,2 isomer.[2] We account for the difference in the stereochemistry of 1,2 addition between these two olefins on the basis of the bonding between the chlorine and carbon atoms in intermediates **5** and **6**.



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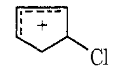

6

Intermediate **5** (from cyclopentene) gives only trans addition, apparently because bonding between the carbon atoms and chlorine atoms prevents cis attack of the chloride ion. By contrast, intermediate **6** (from cyclopentadiene) has no bonding (or weak, in the case of pentane) between the chlorine atom and adjacent allylic carbon atom, and the chloride ion can attack either cis or trans to the chlorine atom. The results in Table I also suggest that the charge density in intermediate **6** in the least polar solvent pentane is highly dispersed since considerable attack occurs at both ends of the allylic system (ratio of 1,2:1,4 addition equals 1:1.3). In polar dichloromethane the charge density is substantially localized at one allylic carbon atom (ratio of 1,2:1,4 addition equals 1:0.3).

Our results are in sharp disagreement with rather recent studies on the chlorination of cyclopentadiene. One study[3] states that the only product is **4**, and the other investigators claim[4] that 3,5-dichlorocyclopentene (85%) is the principal product (3,4-dichlorocyclopentene, 15%); the stereochemistry was not established.[5]

Reactions were carried out (−15°) at 0.02 mol fraction in diene in the selected solvent (reaction volume ~25 ml) in the presence of O_2. The chlorine was added both as a gas and dissolved in solvent, without any significant differences. Under these conditions cyclohexane was not chlorinated, which confirmed ionic conditions. (Under radical conditions cyclohexane was chlorinated.) Vpc and nmr analyses of reaction mixtures were in close agreement indicating that there was no rearrangement during vpc analysis. Although the yields are not quantitative, the product compositions in Table I seem to be valid since chlorinations at both very low and high completion gave essentially the same mixtures of dichlorides.

Vpc analysis (2.5% SE-30, 18 ft × 0.25 in., 55°, and 100 ml/min) of chlorination mixtures showed four principal peaks with retention times of 9.2, 11.0, 15.4, and 16.4 min. The peaks were assigned to **2**, **4**, **3**, and **1**, respectively. Pure samples of **2** and **4** were isolated from chlorination mixtures by distillation or vpc collection; **1** and **3** were obtained together as a mixture. Samples of **3** and **4** were obtained by independent synthesis from their corresponding dibromides as follows: *cis*- or *trans*-3,5-dibromocyclopentene was allowed to react with excess lithium chloride in DMSO at 15° for 15 min, after which the mixture was added to water and the product extracted into pentane. Structural assignments for **2**, **3**, and **4** are therefore based on independent synthesis (**3** and **4**) and their nmr spectra. The nmr spectra of **2**, **3**, and **4** are strikingly similar to the spectra of the corresponding cyclopentadiene dibromides.[6] The 60-MHz spectral data (CCl_4) for the four dichlorides is summarized as follows. **1**: δ 2.71 (br d, 2, CH_2, $J_{5(5')4}$ = 7.0 Hz), 4.45 (dt, 1, $CH_2C\mathbf{H}Cl$, $J_{45(5')}$ = 7.0, J_{43} = 5.7 Hz), 4.89 (d, 1, $CH{=}CHC\mathbf{H}Cl$, J_{34} = 5.7 Hz), 5.99 (br s, 2, $CH{=}CH$). **2**: 2.52 [br d, 1, *cis*-$C(Cl)C(\mathbf{H})H$, $J_{55'}$ = 18.2 Hz], 3.15 [dd, 1, *trans*-$C(Cl)C(\mathbf{H})H$, $J_{5'5}$ = 18.2, $J_{5'4}$ = 6.0 Hz], 4.48 [d, 1, $CH_2C(\mathbf{H})Cl$, $J_{45'}$ = 6.0 Hz], 4.91 [br s, 1, $CH{=}CHC(\mathbf{H})Cl$], 5.88 (br s, 2, $CH{=}CH$). **3**: 2.30 [dd, 1, *cis*-$C(Cl)C(\mathbf{H})H$, $J_{44'}$ = 15.7, $J_{43(5)}$ = 3.0 Hz], 3.06 [dd, 1, *trans*-$C(Cl)C(\mathbf{H})H$, $J_{4'4}$ = 15.7, $J_{4'3(5)}$ = 7.4 Hz], 4.89 (dd, 2, CHCl, J = 3.0, J = 7.4 Hz), 5.95 (d, 2, $CH{=}CH$, J = 1.0 Hz). **4**: 2.66 (t, 2, CH_2, J = 5.4 Hz), 5.17 (t, 2, CHCl, J = 5.4, J = 1.1 Hz), 6.06 (d, 2, $CH{=}CH$, J = 1.1 Hz).