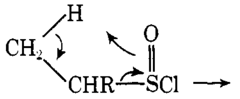
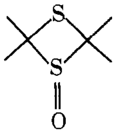
chloride affords HCl, ethylene or propene (respectively) and SO_2 and S_2O (presumably derived from decomposition of SO[13]), perhaps via a Cope-elimination (eq 8).



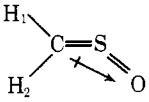
$$RCH{=}CH_2 + [HOSCl] \longrightarrow HCl + SO \quad (8)$$

We have, however, succeeded in generating a sulfine homologue, thioacetone *S*-oxide,[2] by a cycloreversion route, namely, FVP of 2,2,4,4-tetramethyl-1,3-dithietane 1-oxide[14] (eq 9).



$$\xrightarrow[400^\circ]{FVP} (CH_3)_2C{=}S + (CH_3)_2C{=}S{=}O \quad (9)$$

Microwave study of the pyrolysis products of 1,3-dithietane-d_2 1-oxide, -d_4 1-oxide, and -d_4 1-oxide-^{18}O,[6] Me_2SO-d_6 and -^{18}O[16] as well as the normal species led to the assignment of seven isotopic modifications of sulfine (d_1-syn, d_1-anti, d_2,^{18}O, ^{34}S, ^{13}C, and d_2 ^{34}S; ^{34}S and ^{13}C determined in natural abundance). These and the normal species assignment result in the following "substitution structure" for sulfine (labeled as in **5**):[17] $C\text{-}H_2 = 1.085\ (0.002)$ Å, $C\text{-}H_1 = 1.077\ (0.002)$ Å, $C\text{-}S = 1.610\ (0.004)$ Å, $S\text{-}O = 1.469\ (0.004)$ Å, $\angle H_1CH_2 = 121.86\ (0.04)^\circ$, $\angle H_2CS = 122.51\ (0.08)^\circ$, $\angle H_1CS = 115.63\ (0.10)^\circ$, and $\angle CSO = 114.72\ (0.04)^\circ$ (the uncertainty, estimated as twice the standard deviation, is given in parentheses).[18] By way of comparison the geometry of thioformaldehyde is $C\text{-}H = 1.093$ Å, $C\text{-}S = 1.611$ Å, and $\angle HCH = 116.87^\circ$.[8] Sulfine is planar with a dipole moment of 2.994 D oriented 25.50° relative to the S-O bond as shown in **5** (the indicated polarity is assumed).[20] The gas-phase infrared spectrum of sulfine exhibits two strong vibration-rotation bands with prominent Q-branches centered at 1170 and 760 cm^{-1}. The former frequency is characteristic of the C=S=O group.[2g,21]



5

The decomposition of sulfine in the gas phase could be conveniently studied by following the disappearance of the sulfine absorption lines in a closed microwave cell. In a cell free of polymeric decomposition products, sulfine at a pressure of 30 μ decayed linearly with a 30-min lifetime. After the cell had been used for several weeks, sulfine's decomposition was exponential in the 30-300 μ pressure range, with a half-life of ca. 1 h (under the latter conditions, the lifetime of thioformaldehyde was found to be ca. 20 s[22]). The principal gaseous decomposition products were CH_2O and SO_2. The reactions and mechanism of decomposition of sulfine are currently under investigation.

It might be noted that since sulfine is the *S*-oxide of thioformaldehyde, which has been established as a constituent of the interstellar medium,[23] sulfine itself might be of some astronomical significance.

Acknowledgment. Support for this research by the Research Corporation (R.E.P) and the National Science Foundation under its Undergraduate Research Participation program is gratefully acknowledged. We thank Mr. W. Garrison and Mr. T. Renken for technical assistance.

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(4) For examples, see (a) A. Jones and F. P. Lossing, *J. Phys. Chem.*, **71**, 4111 (1967); (b) R. Langendries, F. C. De Schryver, P. de Mayo, R. A. Marty, and J. Schutyser, *J. Am. Chem. Soc.*, **96**, 2964 (1974); (c) L. E. Gusel'nikov, N. S. Nametkin, and V. M. Vdovin, *Acc. Chem. Res.*, **8**, 18 (1975); (d) C. M. Golino, R. D. Bush, and L. H. Sommer, *J. Am. Chem. Soc.*, **97**, 7371 (1975).

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(7) The apparatus consisted of a solid probe for an A.E.I. MS-12 mass spectrometer hollowed to accept a length of electrically heated heavy wall 2-mm quartz capillary fitted with a chromel alumel thermocouple. The samples were evaporated at low pressure through the capillary and mass spectra were recorded at low ionizing voltage as a function of temperature. With the compounds studied the growth in intensity of the *m/e* 62 peak (CH_2SO) was coupled with the disappearance of the original parent ion and its fragment peaks.

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(20) The indicated dipole moment can be resolved into a component along the C-S bond of the same magnitude as thioformaldehyde (ca. 1.6 D[8]) plus a 2 D vector oriented along the S-O bond.

(21) An analysis of the photoelectron spectrum of sulfine will be presented elsewhere: H. Bock, P. Rosmus, B. Solouki, and E. Block, manuscript in preparation.

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(24) National Science Foundation Undergraduate Research Participant, 1975.

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Received October 15, 1975

Trimethylsilylpotassium. Deoxygenation of Epoxides with Inversion of Stereochemistry

Sir:

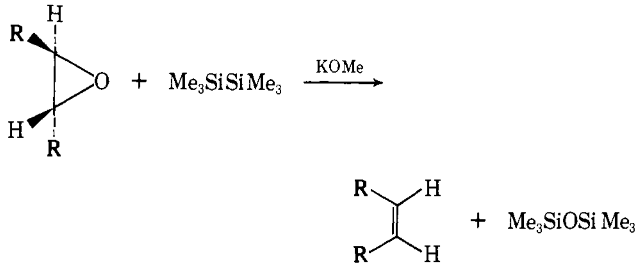
The reactions of silyl anions with appropriately substituted epoxides are potential stereospecific routes to diastereomerically pure erythro and threo-β-alkoxysilanes.[1] We report here that some mono-, di-, and trisubstituted ep-

Table I

Epoxide	Overall yield of olefin, %[a]	Product geometry, %
trans-3-Hexene	99	>99 cis
cis-3-Hexene	86	>99 trans
trans-4-Octene	96	>99 cis
cis-4-Octene	93	>99 trans
2,5-Dimethyl-*trans*-3-hexene	93	>98 cis
2,5-Dimethyl-*cis*-3-hexene	75	>92 trans
trans-3-Methyl-2-pentene	91	>99 cis
cis-3-Methyl-3-pentene	99	>99 trans

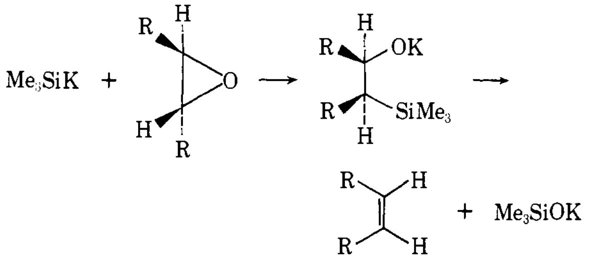
[a] Yields determined by VPC after work-up.

oxides can be deoxygenated[2] in good yields stereospecifically with *inversion* of stereochemistry by trimethylsilylpotassium generated in situ. Reaction of cis and trans epoxides with hexamethyldisilane and potassium methoxide (KOMe) in anhydrous hexamethylphosphoric triamide (HMPT) at 65° under argon for 3 h affords the corresponding trans and cis olefins, respectively. Since olefins can be epoxidized with retention of stereochemistry, this constitutes a new olefin inversion procedure.[4] The yields and stereospecificity of this deoxygenation reaction for several isomerically pure (>99%) epoxides[5] are listed in Table I.



Although the exact nature of this reaction is not known, the results are consistent with the reaction of potassium methoxide and hexamethyldisilane to form trimethylsilylpotassium (TMSK) and trimethylmethoxysilane (eq 1). Backside attack of TMSK on the cis (and trans) epoxides generates the threo- (and erythro) β-alkoxysilanes, respectively. Syn elimination provides the olefin with inverted stereochemistry and potassium trimethylsilanolate (eq 2).

$$\mathrm{KOMe + Me_3SiSiMe_3 \longrightarrow Me_3SiK + Me_3SiOMe} \quad (1)$$



(2)

Elimination reactions of β-hydroxysilanes to olefins are well precedented.[6] However, few preparations of diastereomerically pure β-hydroxysilanes have been reported in the literature.[6d] Recent work by Hudrlik and co-workers has demonstrated that the base-induced elimination of β-hydroxysilanes occurs stereospecifically in a syn fashion.[6e]

The rate of decomposition of β-alkoxysilanes depends to some extent on the choice of metal cation (i.e., K ≫ Na ≫ Mg).[6c,d] Since potassium β-alkoxysilanes are known to undergo rapid elimination at room temperature, we chose trimethylsilylpotassium (TMSK) for the deoxygentation procedure. Methods in the literature for making trimethylsilylpotassium were found not to be convenient. They involve the cleavage of unsymmetrical phenyl-substituted disilanes with potassium metal.[7] In analogy to recent work by Sakurai and co-workers[8a,b] we investigated the reaction of hexamethyldisilane and potassium methoxide as a source of trimethylsilylpotassium.[8c] Besides providing increased solubility of potassium methoxide in the reaction mixture, the entire role of HMPT is not yet known. HMPT is known to complex potassium cations[9] and could conceivably be participating in several steps of the reaction.

Although trimethylmethoxysilane was observed in the reaction mixture, another silicon product, hexamethyldisiloxane, was identified. It is reasonable to assume that potassium trimethylsilanolate from the deoxygenation step was further reacting with either hexamethyldisilane and/or trimethylmethoxysilane to form hexamethyldisiloxane and trimethylsilylpotassium and/or potassium methoxide (eq 3a and 3b, respectively). This suggested that the reaction could either be *initiated* (eq 3a) or *catalyzed* (eq 3b)

$$\mathrm{Me_3SiOK + Me_3SiSiMe_3 \longrightarrow Me_3SiK + Me_3SiOSiMe_3} \quad (3a)$$

$$\mathrm{Me_3SiOK + Me_3SiOMe \longrightarrow KOMe + Me_3SiOSiMe_3} \quad (3b)$$

by less than 1 equiv of KOMe. In fact, we find that the reaction proceeds smoothly with 0.1 equiv of KOMe per equiv of hexamethyldisilane. In this case, the major silicon product is hexamethyldisiloxane.[10] In a formal sense, the epoxide oxygen is being used to regenerate TMSK and/or KOMe.

A typical procedure is as follows. To 0.2 mmol of potassium methoxide[11] in 10 ml of anhydrous HMPT under argon at 65° was added *trans*-4-octene oxide (1.2 mmol) followed by hexamethyldisilane[12] (1.8 mmol) in 5 ml of HMPT. The yellow reaction mixture was allowed to stir for 3 h. Saturated aqueous sodium chloride was added to the reaction mixture and this was extracted twice with pentane. The pentane layers were combined and dried (Na_2SO_4). The product olefins were analyzed by vapor phase chromatography (VPC).[13]

The deoxygenation of epoxides with hexamethyldisilane (1.5 eqiv) and potassium methoxide (0.1 equiv) also proceeds at 65° in anhydrous THF in the presence of 18-crown-6 (0.1 equiv).[14] Research on the scope and limitations of these reactions is currently being investigated.[15]

Acknowledgment. The authors are grateful to the Research Corporation and the National Science Foundation (MPS75-06776) for their generous support of this work. We are grateful for stimulating discussions with Professors David A. Evans and Dieter Seebach during the course of this research.

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(2) Professor Michael Jung at the University of California, Los Angeles, has made similar observations.[3]
(3) Private communication. We thank Professor Jung for informing us of his results prior to publication.
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(10) The yield of $Me_3SiOSiMe_3$ increased as the ratio of $MeOK/Me_3SiSiMe_3$ decreased.
(11) Obtained from Alfa.
(12) Obtained from Columbia Organics and used without further purification.
(13) Cis- and trans-isomer ratios were determined on stationary phases that were independently shown to separate authentic mixtures. Product mixtures were coinjected with authentic olefin samples. Yields were determined after work-up by a weighed amount of internal standard and corrected for detector response (flame ionization detector–electronic integrator).
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(17) National Science Foundation Predoctoral Fellow, 1973–1976.

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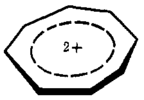
Novel Aromatic Systems. III.[1] The 1,3,5,7-Tetramethylcyclooctatetraene Dication, the First 8C-6π Hückeloid System

Sir:

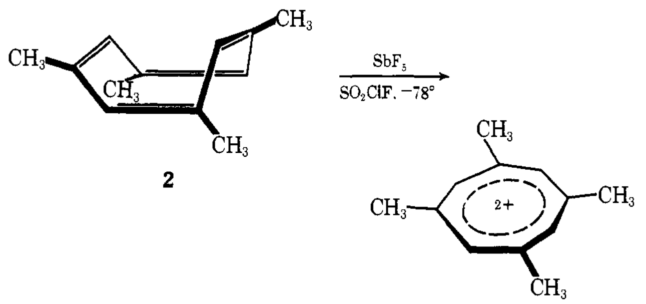
A most significant early triumph of simple MO theory was Hückel's prediction[2] that planar annulenes endowed with $(4n + 2)$ π-electrons should possess relative electronic stability as a consequence of their having closed-shell MO configurations with substantial electron delocalization (resonance) energies. The resultant relative electronic stability (aromaticity) which is achieved has been found to prevail as well, without known exception, in the related annular ions.[3] Notwithstanding their predicted aromatic stabilization,[2-4] several fundamental systems have remained elusive of preparation and experimental study. The most notable Hückeloid absentee is the 8C-6π cyclooctatetraene dication (**1**). Despite repeated attempts,[5] neither **1** nor any of its substituted derivatives have yet yielded to synthesis.



1

We now wish to report the preparation and characterization by ^1H and ^{13}C NMR spectroscopy of the first cyclooctatetraene dication, namely the 1,3,5,7-tetramethyl derivative **3**, showing it to be a fully delocalized, approximately planar, 6π-electron aromatic system.

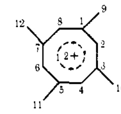
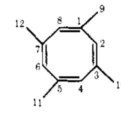
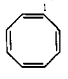
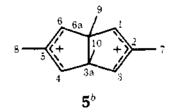
The title substance (**3**) was obtained upon direct two-electron oxidation of 1,3,5,7-tetramethylcyclooctatetraene (**2**)[6] by SbF_5[7] in SO_2ClF solution at −78°.[8] The FT ^1H NMR spectrum (100 MHz) of this solution at −50° consists of two sharp singlets at δ 4.27 and 10.80 of relative area 3:1, respectively (Figure 1, Table I). No spectral change is noted over the temperature range −30 to −100°. Vinylic proton chemical shifts in a series of aromatic molecules have been shown to be a linear function of the π-electron densities of the carbon atoms to which they are bound,



2

3

Table I. Proton and Carbon-13 NMR Parameters of the 1,3,5,7-Tetramethylcyclooctatetraene Dication and Related Compounds[a]

	Proton			Carbon-13			
	H_1	H_2	CH_3	C_1	C_2	CH_3	other
 **3**[b]		10.80 (s)	4.27 (s)	182.7 (s)	170.0 (d, 166.2)	33.5 (q, 134.3)	
 **2**[c]		6.17 (m)	2.40 (m)	138.9 (s)	128.8 (d, 148.4)	23.5 (q, 124.7)	
 *c*	6.42 (m)			132.2 (d, 156.3)			
 **5**[b]	11.33 (s)		C_7H_3, 3.40 (s) C_9H_3, 3.02 (s)	230.6 (d)	164.5 (s)	20.8 (q) 14.6 (q)	C_{3a}, 88.3 (s)
 *d*	11.26 (d)	8.65 (t)		234.7 (d)	145.7 (s)		

[a] Chemical shifts are in parts per million from external capillary Me_4Si, coupling constants are in hertz: s = singlet, d = doublet, q = quartet, m = multiplet. [b] In SbF_5–SO_2ClF solution at −70°. [c] In SO_2ClF solution at −70°. [d] In SbF_5–FSO_3H–SO_2ClF solution at −60°; data taken from ref 21 and converted to ppm from external capillary Me_4Si utilizing δ_{CS_2} 193.7.