Although the available evidence argues in favor of a common intermediate, the mechanism for reaction 1 must be regarded as uncertain at this time.

The addition of dichlorocarbene to diiodoacetylene via phenyl(trichloromethyl)mercury is particularly interesting since a number of 1-haloacetylenes have been shown not to add dichlorocarbene generated from potassium t-butoxide and chloroform.[7]

Experimental Section

Analyses were performed by Dr. S. M. Nagy, Microchemical Laboratory, Massachusetts Institute of Technology, Cambridge, Mass. Infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer. An F & M Model 700 gas chromatograph with thermal conductivity detector was used for component isolation and analysis. Reactions involving phenyl-(trichloromethyl)mercury were run in an atmosphere of prepurified nitrogen.

Diiodoacetylene[8] (7.0 g, 25.6 mmoles), phenyl(trichloromethyl)mercury[9] (10.1 g, 25.5 mmoles), and dry benzene (50 ml, distilled from sodium) were heated at reflux for 4 hr. The precipitated solid was filtered off, washed with pentane, and vacuum dried. The yield of phenylmercuric iodide was 7.44 g (72%). Recrystallization of the solid from tetrahydrofuran gave material, mp 274.5–275° (lit.[10] mp 270° for PhHgI), which was identified as phenylmercuric iodide by infrared spectrum and a mixture melting point with those of an authentic sample prepared from phenylmercuric chloride and sodium iodide in ethanol. In a second experiment, a 90% yield of phenylmercuric iodide was achieved.

The filtrate was subjected to a bulb-to-bulb distillation, then analyzed by gas chromatography on a 4-ft SE-30 (10% on Chromosorb P) column using bromobenzene as an internal standard. Tetrachloroethylene and iodobenzene were identified by retention times and comparison of infrared spectra with those of authentic materials. Tetrachlorocyclopropene[11] was identified in the same manner and by refractive index, n^{26}D 1.5049 (lit.[11] n^{27}D 1.5045). 1-Iodo-3,3,3-trichloropropyne was identified by its infrared spectrum, retention time, and elemental analysis.

Anal. Calcd for C_3Cl_3I: C, 13.38; H, 0.00; Cl, 39.50; I, 47.13. Found: C, 13.28; H, 0.08; Cl, 39.00; I, 47.36.

The infrared spectrum of this compound consisted of four bands: 746 (s), 1093 (s), 2151 (m), and 2203 cm^{-1} (m). 1-Bromoacetylenes have been reported[12] to have a strong acetylenic absorption near 2200 cm^{-1}. The retention time (11.2 min; cf. C_2I_2, 9.2 min; C_6H_5I, 9.8 min) and infrared spectrum argued against any structure more complicated than that indicated. Diiodoacetylene was identified by its retention time and melting point.

(7) E. V. Dehmlow, *Tetrahedron Letters*, 2317 (1965).
(8) W. M. Dehn, *J. Am. Chem. Soc.*, **33**, 1598 (1911).
(9) T. J. Logan, *J. Org. Chem.*, **28**, 1129 (1963).
(10) M. Cowper, H. Waite, and E. Warhurst, *J. Chem. Soc.*, 2429 (1958).
(11) S. Tobey and R. West, *Tetrahedron Letters*, 1179 (1963).
(12) G. Eglinton and W. McCrane, *Advan. Org. Chem.*, **4**, 276 (1963).

Equilibrium Conformations of Thiane 1-Oxide (Pentamethylene Sulfoxide)

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The oxide functions in 4-substituted thiane 1-oxides[2,3] and in *trans*-1,4-dithiane 1,4-dioxide[4] have re-

(1) National Science Foundation Undergraduate Research Participant, 1965–1966.
(2) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **86**, 2935 (1964).
(3) J. C. Martin and J. J. Uebel, *ibid.*, **86**, 2936 (1964).

cently been shown to prefer the axial position. Both the assignment of isomers and the determination of the position of thermal equilibrium have been topics of some controversy.[2,3,5,6] By examination of the nmr spectrum of the unsubstituted thiane-3,3,5,5-d_4 1-oxide at low temperatures, we have obtained a direct measure of the conformational free-energy difference for the oxide function on sulfur.

Above −20° (see Figure 1), the α and γ protons give rise to separate AB spectra with rather small chemical-shift differences.[7] As the temperature is decreased, each band broadens and gradually assumes the form of two distinct AB patterns. The pertinent analytical data for the low-temperature spectra are listed in Table I. We shall not be further concerned with the γ-proton resonances, which are more crowded and less susceptible to analysis than those of the α protons.

Table I
Spectral Properties of Thiane 1-Oxide at −90°

Protons[a]	δ_{ae}, Hz	J_{ae}, Hz	δ'_{ae}, Hz	J'_{ae}, Hz
α	52.2	11.7	28.8	13.7
γ	20.4	14.0	24.1	14.3

[a] In this context, the unprimed quantities pertain to whichever AB pattern of the multiplet in question (α or γ) extends to lower field.

We interpret the slow-exchange resonances as arising from the distinct axial (I) and equatorial (II) conformations. The low-field protons (presumably, but not necessarily, equatorial) give four well-separated resonances, which may be used for purposes of
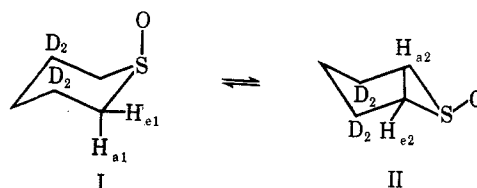
integration, whereas the resonances of the high-field protons (presumably axial) overlap one another. As the temperature is raised, ring inversion becomes rapid with respect to the nmr time scale. Thus, H_{e1} exchanges with H_{a2}, and H_{a1} exchanges with H_{e2}. Because of the "criss-cross" nature of this exchange (axial protons with equatorial protons), the resultant chemical-shift average at fast exchange is quite small.

From integration of the resonances of the low-field α protons, the equilibrium constant between I and II is calculated to be about 1.62 (−90°), corresponding to a free-energy difference of 175 ± 30 cal/mole. The calculations and discussion thus far have not required a designation of the preferred conformation (I *vs.* II).[8]

(4) C.-Y. Chen and R. J. W. LeFèvre, *Australian J. Chem.*, **16**, 917 (1963).
(5) H. B. Henbest and S. A. Khan, *Proc. Chem. Soc.*, 56 (1964).
(6) M. Ōki, private communication.
(7) The low-intensity peaks symmetrically disposed about the principal resonance of the α protons do not arise from spinning effects. The small peak at the position of lowest field arises from the sulfone. Methylene chloride was used as the solvent in these experiments.
(8) Johnson[2] has discussed the alternatives to steric size as the determining factor in the choice of conformation. Other factors may be particularly important at low temperatures, since dimers may predominate (*vide infra*).
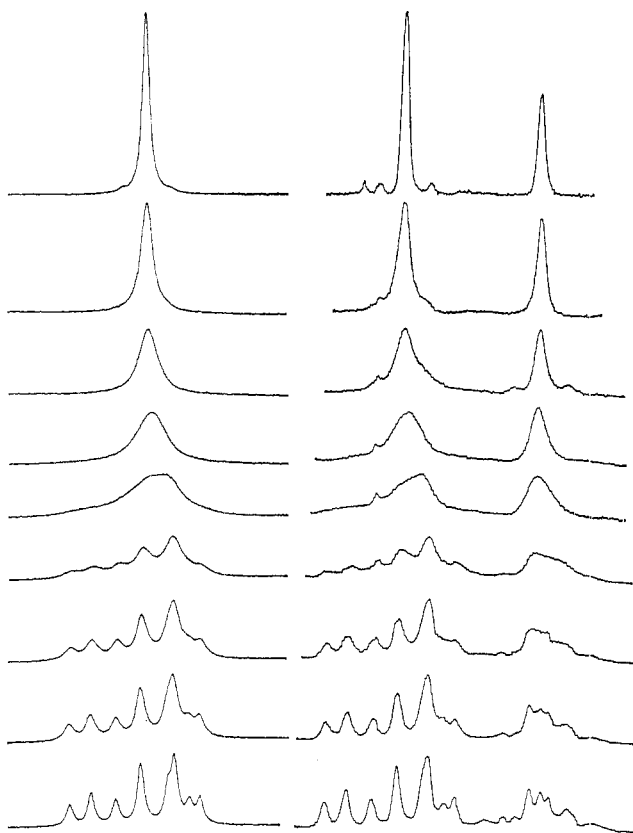
Figure 1.—The 60-MHz spectra (Varian A-60) of thiane-3,3,5,5-d_4 1-oxide as a function of temperature: left, calculated spectra for the α protons; right, experimental spectra for both the α (low-field) and the γ protons. The calculated spectra are all 150 Hz in width. The temperatures for the experimental spectra from top to bottom are -20, -52, -58, -63.5, -70, -76.5, -80, -84, and $-90°$, respectively.

If an axial lone pair enhances $\delta_{ae}(\alpha)$,[9] as in the case of piperidine systems,[10] then the AB pattern that extends to lower field, because of its larger chemical-shift difference [$\delta_{ae}(\alpha) = 0.87$ ppm], belongs to the isomer with an axial lone pair (II). The more intense AB pattern, with the smaller chemical-shift difference [$\delta_{ae}(\alpha) = 0.48$ ppm], would belong to the isomer with an equatorial lone pair (I). This assignment, in which the predominate conformer possesses an axial oxide function, is in agreement with the conclusions of Johnson[2] and Martin.[3]
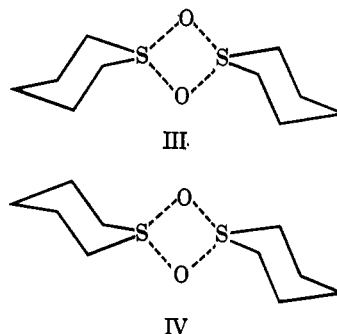
If dimers comprise a significant portion of the population,[11] alternative explanations are admissible. The importance of a monomer–dimer equilibrium, however, is disallowed by concentration experiments, in which no variation of the rate was found when the concentration of solute was decreased in steps up to a factor of 4. Of the three possible dimers (I–I, II–II, and I–II), the mixed dimer is excluded as the sole species, because the apparent conformer ratio would have to be 1. The remaining possibility, an equilibrium among all three dimers, with the resonances of I–II superimposed

on the appropriate resonances of I–I and II–II, is not excluded. If the oxygen atoms are symmetrically disposed between two monomers,[12,13] only two dimers are possible (III, IV). As a consequence of the sym-

III.

IV

metry of dimers of this type, exchange of oxygen between monomeric units would occur. Such an exchange would furnish a mechanism for racemization of optically active sulfoxides. Since sulfoxides are, in general, configurationally stable below room temperature, an explanation of the slow-exchange spectra in terms of III and IV is rather unlikely.[14]

Rates for the ring-inversion process were determined by comparison of the observed spectra with line shapes calculated as a function of the mean lifetime. The calculated line shapes for the α protons are presented in Figure 1. Table II lists the rate data of interest,

TABLE II
RATE PARAMETERS FOR HETEROCYCLES

X	Solvent	T_c, °C[a]	E_a, kcal/mole
SO	CH_2Cl_2	-70	14.2
SO_2	CH_2Cl_2	-63	14.9
S	CH_2Cl_2	-93	11.6
O	CD_3OD	-80	10.7
NH	CD_3OD	-63	14.5

[a] Temperature of coalescence.

together with the data for four related systems. The activation energies for ring inversion of the oxide and the sulfide, being slightly lower than for the other compounds, are close to that of cyclohexane.[15] Variations will be considered in detail in a forthcoming paper.

Experimental Section

Nmr spectra were measured on a Varian A-60 spectrometer equipped with a variable-temperature probe. The temperature for each spectrum was determined from the separation between the methyl and hydroxyl resonances of methanol.

Dimethyl glutarate-2,2,4,4-d_4 was obtained in 85% yield from the corresponding unlabeled material by successive treatment with methanol-d and sodium methoxide. After six such treat-

(9) An extension of the conclusions from the piperidine work is not wholly justified at present. There may be important contributions to $\delta_{ae}(\alpha)$ from the anisotropy of the S–O bond; cf. B. A. Arbouzov and Y. Y. Samitov, *Tetrahedron Letters*, **No. 8**, 473 (1963). The directionality of the lone pair on sulfur is not even known with certainty.

(10) J. B. Lambert and R. G. Keske, *J. Am. Chem. Soc.*, **88**, 620 (1966).

(11) Molecular weight measurements at 37° (osmometry) indicate that the only species in chloroform solution (0.05 M) is the monomer. Unfortunately, this method cannot duplicate the conditions of concentration and temperature used in the nmr experiments.

(12) R. F. Watson and J. F. Eastham, *J. Am. Chem. Soc.*, **87**, 664 (1965).

(13) A. Rauk, E. Buncel, R. Y. Moir, and S. Wolfe, *ibid.*, **87**, 5498 (1965).

(14) Our evidence says little concerning the question of boat conformations, although the necessity of a criss-cross exchange mechanism argues against such species. We do, however, exclude the symmetrical, hydrated sulfoxide, which would possess equivalent protons at temperatures for which ring inversion is fast. The AB pattern did not collapse to a single line even at 60°. Spectra were almost identical for carefully dried solutions and for solutions saturated with water.

(15) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.*, 145 (1964); F. A. Bovey, F. P. Hood, III, E. W. Anderson, and R. L. Kornegay, *ibid.*, 146 (1964); *J. Chem. Phys.*, **41**, 2041 (1964).

ments, 97% of the α protons had been exchanged for deuterium, as determined by nmr spectroscopy.

1,5-Pentanediol-2,2,4,4-d_4 was obtained in 75% yield by the reduction of labeled dimethyl glutarate with lithium aluminum hydride (1.3 moles per mole of ester) followed by hydrolysis with 5% sodium hydroxide. The deuterium content was found by nmr spectroscopy to be 95%.

1,5-Dibromopentane-2,2,4,4-d_4.—Phosphorus tribromide (3 g per gram of diol) was placed in a three-necked flask equipped with a condenser and a dropping funnel. The labeled diol was added dropwise, and the resulting solution was heated on a steam bath overnight. Water (1 ml per gram of diol) was added, and the layers were separated. The aqueous layer was extracted four times with methylene chloride, and the combined organic portions were neutralized with aqueous sodium carbonate. 1,5-Dibromopentane-2,2,4,4-d_4 (87%) was isolated by distillation at reduced pressure. No loss of deuterium occurred during these manipulations.

Thiane-3,3,5,5-d_4.—To a refluxing solution of 2.0 g of sodium sulfide nonahydrate in 25 ml of 50% ethanol were added 2.3 g of 1,5-dibromopentane-2,2,4,4-d_4 and, simultaneously but separately, an additional 2.0 g of sodium sulfide in 25 ml of 50% ethanol. After the solution had refluxed for 2 hr, the ethanol was removed by careful distillation and the residue was steam distilled. The aqueous distillate was extracted with methylene chloride, and thiane-3,3,5,5-d_4 was obtained upon evaporation of the solvent.

Thiane-3,3,5,5-d_4 1-Oxide.—A mixture of 0.29 g of the deuterated sulfide and 0.32 g of 30% hydrogen peroxide was shaken in a sealed tube until only one layer was present. After standing overnight, the solution was extracted three times with methylene chloride. The combined organic portions were dried with magnesium sulfate. The crystalline sulfoxide that was obtained after removal of the drying agent and the solvent under anhydrous conditions possessed the characteristic band at 1020–1060 cm^{-1}. Sulfone bands were absent. Pentamethylene-3,3,5,5-d_4 sulfone could be obtained by the same method, with the use of 0.64 g of hydrogen peroxide. These products were identical with the known, unlabeled compounds.

Thermal Decomposition of Quaternary Ammonium Hydroxides. Synthesis and Properties of Tri(²H₃-methyl)amine

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Completely deuterated trimethylamine was desired for infrared studies on boron hydride–amine adducts. One general synthesis for tertiary amines involves thermal decomposition of quaternary ammonium hydroxides. For example pyrolysis of ethyltrimethylammonium hydroxide yields ethylene and trimethylamine. If the methyl groups are deuterated, it would seem that deuterated trimethylamine could be syn-

thesized by this route. However, both Shiner and Smith[2] and Cope, LeBel, Moore, and Moore[3] have shown hydrogens on α carbons to undergo exchange. The elimination, however, was shown not to proceed by way of a *cis*-ylide mechanism. An E2 elimination of the *trans* hydrogen on the β carbon was established as the mechanism of choice for most compounds undergoing the Hofmann elimination. Cope, *et al.*, clearly demonstrated that exchange of the α protons occurs with the water "pool" prior to elimination. In showing this Cope and co-workers were unable to parallel the results obtained by Weygand, Daniel, and Simon[4] on the exchange of tritium during the pyrolysis of β-tritiated ethyltrimethylammonium hydroxide carried out by blowing high-velocity steam through the melt. Doering and Hoffmann[5] found that tetramethylammonium deuterioxide in deuterium oxide solution is enriched only to the extent of 1.13 atom % deuterium in 358 hr at 100°. Because of this slow exchange rate and the relatively low vacuum generally used for Hofmann eliminations (6 mm by Cope, *et al.*), it seemed reasonable to try the elimination under high-vacuum conditions with the hope that the water "pool" can be reduced to a sufficiently low level to eliminate exchange.

Another route more certain of success is the pyrolysis of completely deuterated tetramethylammonium deuterioxide. As Musker[6] has recently reported, this reaction yields trimethylamine and dimethyl ether as the two major products. It should be noted that Hofmann[7] originally reported trimethylamine and methyl alcohol as products of this reaction. An additional possibility is that tetramethylammonium deuterioxide might lend itself to direct deuteration in case the deuterium exchange reaction studied by Doering exhibits a very favorable anti-Arrhenius temperature dependence.

Results and Discussion

Pyrolysis of ethyltri(²H₃-methyl)ammonium deuterioxide under high vacuum yields tri(²H₃-methyl)-amine and ethylene. When the methyl groups of the original quaternary ammonium salt were 97% deuterated, the trimethylamine obtained contained 94% deuterium. Pyrolysis of the quaternary ammonium hydroxide instead of the deuteroxide yielded trimethylamine containing only 86.5% deuterium. In each case the ethylene obtained was found to contain strong CD stretching bands in the infrared, at times exceeding the intensity of the CH stretching bands. Thermal decomposition of tetra(²H₃-methyl)-ammonium deuterioxide as a dry solid yielded trimethylamine, which contained 99.0% deuterium according to its mass spectrum. The infrared spectrum corroborates the mass spectral data. Deuterated dimethyl ether was obtained as the second major product. In contrast to Chablay,[8] who states that the

(1) (a) Postdoctoral Fellow, Space Program. (b) Participant in Undergraduate Honors Research Program.

(2) V. J. Shiner, Jr., and M. L. Smith, *J. Am. Chem. Soc.*, **80**, 4195 (1958).
(3) A. C. Cope, N. A. LeBel, P. T. Moore, and W. R. Moore, *ibid.*, **83**, 3861 (1961).
(4) F. Weygand, H. Daniel, and H. Simon, *Ber.*, **91**, 1691 (1958).
(5) W. von E. Doering and A. K. Hoffmann, *J. Am. Chem. Soc.*, **77**, 521 (1955).
(6) W. K. Musker, *ibid.*, **86**, 960 (1964).
(7) A. W. Hofmann, *Ber.*, **14**, 494 (1881).
(8) E. Chablay, *Ann. Chim.* (Paris), [9] **1**, 477 (1914).