conversion required approximately 72 hr. When the reaction was over the condenser was exchanged for a small distilling head and the product was distilled yielding 1.25 g (82%) of tetrakis-(dimethylamino)ethylene, bp 50° (1 mm), $n^{25}\text{D}$ 1.4806, mol wt 200 (mass spectrum), showing no significant impurities in the nmr.

The dibromide derivative was prepared according to Wiberg and Buchler,[6] mp 253°, infrared spectrum identical with that of authentic sample.

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[6] N. Wiberg and J. W. Buchler, *Chem. Ber.*, **96**, 3223 (1963).

The Reaction of Phenyl(trichloromethyl)mercury with Diiodoacetylene

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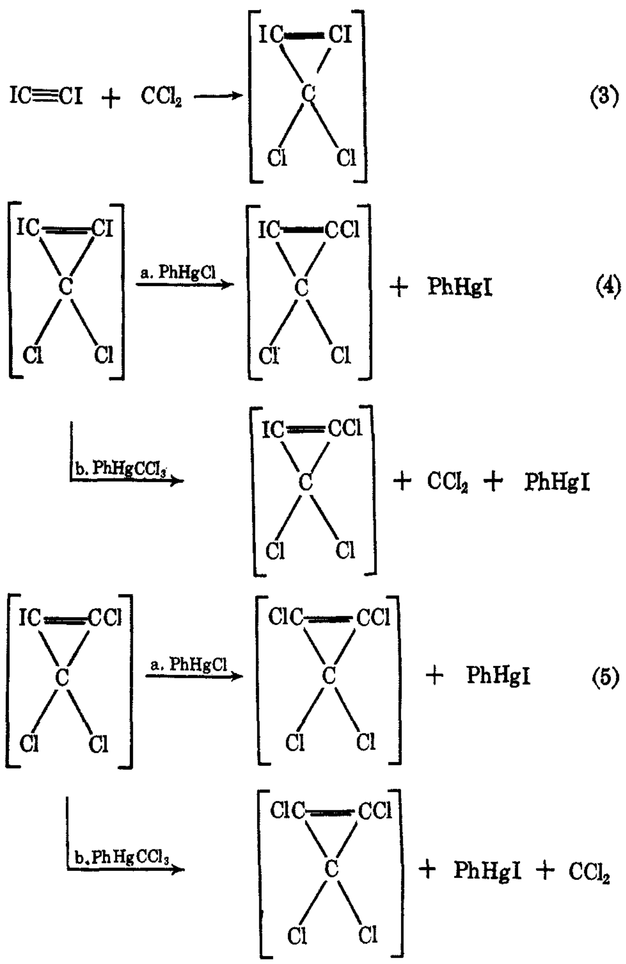
The reaction of phenyl(trihalomethyl)mercurials with a number of olefins has been shown to proceed in good yield even with olefins of low reactivity to carbene reagents.[1] Since a number of acetylenes have been shown to react with carbenes to form cyclopropenes,[2] it appeared likely that phenyl(trichloromethyl)mercury would give a dichlorocarbene adduct with a dihaloacetylene, the simplest type of nonterminal acetylene available. Accordingly, the reaction of phenyl(trichloromethyl)mercury with diiodoacetylene in benzene was studied. No reaction was found to occur at room temperature and little reaction at a temperature less than 80°. However, decomposition of phenyl(trichloromethyl)mercury was complete within 4 hr in refluxing benzene solution in the presence of diiodoacetylene. In the absence of diiodoacetylene, phenyl(trichloromethyl)mercury required 36–48 hr for complete decomposition.[3]

The major products isolated were tetrachlorocyclopropene (13.4%) and 1-iodo-3,3,3-trichloropropyne (12.9%). Also recovered from the reaction mixture were tetrachloroethylene (1.9%), diiodoacetylene (18.7%), and iodobenzene (4.2%). When a 2:1 ratio of phenyl(trichloromethyl)mercury–diiodoacetylene was used, diiodoacetylene was completely consumed. In addition to the products noted above, small amounts of phenyl-substituted cyclopropenes were probably present as indicated by a weak band at 1820 cm^{-1} [4] in the infrared spectrum of each of two constituents. The infrared spectrum of each constituent was otherwise almost identical with that of iodobenzene.

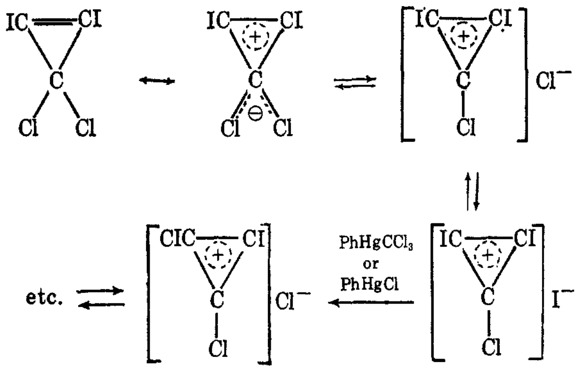
The results can be interpreted by considering the simultaneous reactions (eq 1–5).

$$\text{PhHgCCl}_3 + \text{IC}{\equiv}\text{CI} \longrightarrow \text{PhHgI} + \text{Cl}_3\text{CC}{\equiv}\text{CI} \quad (1)$$

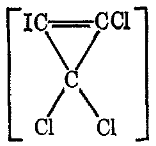
$$\text{PhHgCCl}_3 \longrightarrow \text{PhHgCl} + \text{CCl}_2{}^{5} \quad (2)$$



Reactions 4 and 5 may be facilitated by halogen scrambling *via* a cyclopropenium cation. The proposed mechanism for reactions 4 and 5 would account for the catalytic effect of diiodoacetylene on the thermal decomposition of phenyl(trichloromethyl)mercury since iodide ion is known[6] to effect the complete decomposition of phenyl(trichloromethyl)mercury within 4 hr at 80°. The reaction sequence would also



account for the lack of reaction below 80°, since reaction 2 will not occur to any appreciable extent much below this temperature. Reaction 1 may proceed by direct reaction, or reactions 1 and 4 may proceed *via* a common intermediate as shown below.



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[1] D. Seyferth, J. M. Burlitch, R. J. Minasz, J. Y.-P. Mui, H. D. Simmons, Jr., A. J. H. Treiber, and S. R. Dowd, *J. Am. Chem. Soc.*, **87**, 4259 (1965).

[2] F. L. Carter and V. L. Frampton, *Chem. Rev.*, **64**, 497 (1964).

[3] D. Seyferth, J. M. Burlitch, and J. K. Heeren, *J. Org. Chem.*, **27**, 1491 (1962).

[4] R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2367, 2375 (1961).

[5] D. Seyferth and J. M. Burlitch, *ibid.*, **86**, 2730 (1964).

[6] D. Seyferth, J. Y.-P. Mui, M. E. Gordon, and J. M. Burlitch, *ibid.*, **87**, 681 (1965).

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, $n^{26}\text{D}$ 1.5049 (lit.[11] $n^{27}\text{D}$ 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.

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[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. Eglington 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 recently 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.

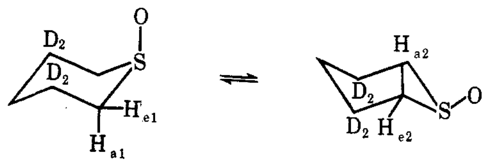
Table I

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.



I II

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]

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[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).

[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*).