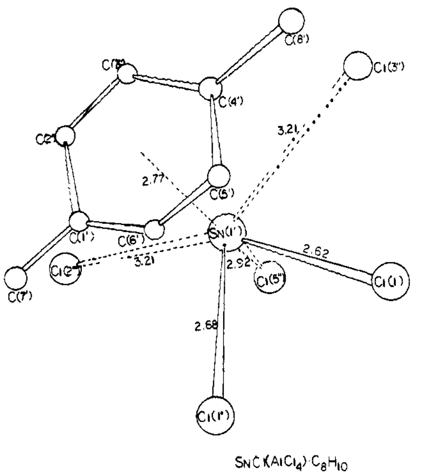

Figure 2. View of the structure of *p*-xylene·SnCl(AlCl$_4$) showing the immediate environment about Sn(II) including the axially symmetric Sn–Ar interaction. Esd's are all approximately three-quarters of those in Figure 1. The angle between the normal to the ring and the Sn center of the ring is 8 ± 1°. For both compounds the rings are planar well within experimental error.

the same length as the shortest Sn–Cl distance found in anhydrous stannous chloride[6] (2.66 Å). Anhydrous stannous chloride may be described as pyramidal Sn(II) forming a chlorine-bridged chain structure. In addition, the Sn–Cl distances in $SnCl_2 \cdot 2H_2O$[7] are 2.59 Å while those in the $SnCl_3^-$ ion are 2.63 and 2.54 Å.[8] (3) The Sn–Cl distances in $C_6H_6 \cdot Sn(AlCl_4)_2(C_6H_6)$[1] are all 2.77 Å or greater. As a consequence, we feel that the 2.61–2.68-Å distance represents a more substantial Sn–Cl bond than any other in the Ar·SnCl(AlCl$_4$) structures and is an important structural feature of these compounds.

The phase diagram of the $SnCl_2 \cdot AlCl_3$[9] system indicates a compound of the composition SnCl(AlCl$_4$). It may well be that the $Sn_2Cl_2^{2+}$ unit is a structural feature of this compound also.

It is to be noted that the Sn–aromatic interaction is essentially axially symmetric and along with $C_6H_6 \cdot Sn(AlCl_4)_2(C_6H_6)$ represents the only known cases of axially symmetric complexes between post-transition metal ions and aromatic moieties.

The overall crystal structure might be described as made up of $(SnAlCl_4)_n$ chains (Figure 1) in which the $AlCl_4^-$ tetrahedra are bonded together by Sn–Cl bonds, Sn–Cl(1), Cl(2''), Cl(4'''). These chains are in turn interconnected *via* the formation of the dimers mentioned above.

Acknowledgment. We are grateful to the National Science Foundation GP-28680 for support.

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(6) J. M. van den Berg, *Acta Crystallogr.*, **14**, 1002 (1961).

(7) B. Kamenar and D. Grdenic, *J. Chem. Soc.*, 3954 (1961).

(8) B. Kamenar and D. Grdenic, *J. Inorg. Nucl. Chem.*, **24**, 1039 (1962).

(9) (a) J. Kendall, E. Crittenden, and H. K. Miller, *J. Amer. Chem. Soc.*, **45**, 963 (1923); (b) R. F. Belt and H. Scott, *Inorg. Chem.*, **3**, 1785 (1964).

M. S. Weininger, P. F. Rodesiler
A. G. Gash, E. L. Amma*
Department of Chemistry, University of South Carolina,
Columbia, South Carolina 29208

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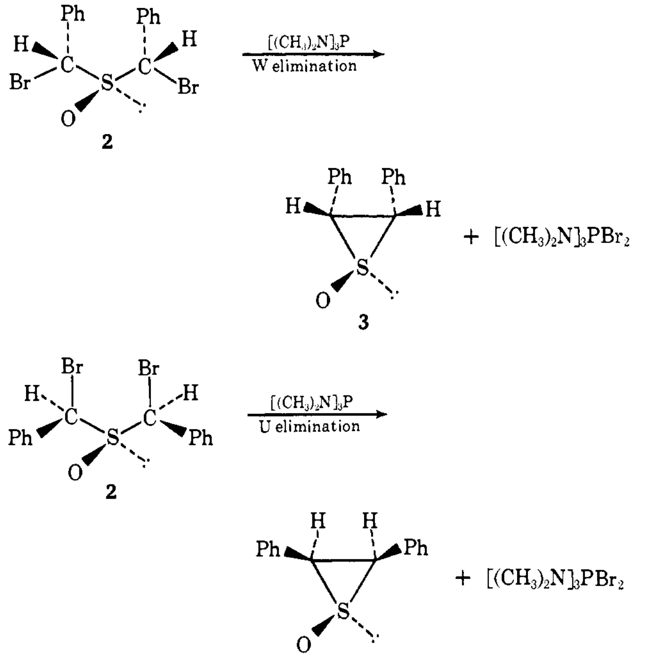
Stereochemistry of 1,3 Eliminations from Dibromo Sulfoxides

Sir:

In general, the 1,3-elimination reactions[1] studied to date have exhibited preferences for W eliminations (inversion at each center)[2–7] and exo sickle eliminations (retention at the carbon atom bearing the electrofugal group and inversion at the carbon bearing the nucleofugal group).[8–10] In the cases of the W eliminations, the systems studied were either rigid polycyclic systems in which the groups were held in the W conformations[4,6,7] or acyclic systems in which the stereochemical results could have been interpreted as being U eliminations[1] (retention at each center) rather than W eliminations. We wish to report a W-1,3 debromination of the dibromo sulfoxides **1** and **2** with hexamethylphosphorictriamide, $(Me_2N)_3P$, wherein the U elimination can be excluded.

Loss of bromine from *meso*-**2** with double inversion would give the *cis,anti*-episulfoxide **3**, while loss with double retention would result in the formation of the *cis,syn*-episulfoxide **4**.



The sulfoxides **1** and **2** were synthesized in a manner analogous to that reported earlier for **1**.[11] Bromination (Br_2–CCl_4) of dibenzyl sulfide followed by oxidation of the crude bis(α-bromobenzyl) sulfide in methylene chloride at 0° with 1 equiv of *m*-chloroperbenzoic acid

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(1) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967).

(2) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *ibid.*, **90**, 5298 (1968).

(3) F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *ibid.*, **92**, 2581 (1970).

(4) L. A. Paquette and R. W. Houser, *ibid.*, **91**, 3870 (1969).

(5) B. M. Trost, W. L. Schinski, and I. B. Mantz, *ibid.*, **91**, 4321 (1969).

(6) R. E. Pincock and E. J. Torupka, *ibid.*, **91**, 4592 (1969).

(7) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

(8) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3915, 3917 (1967).

(9) S. J. Cristol, A. R. Dahl, and W. Y. Lim, *ibid.*, **92**, 5670 (1970).

(10) N. H. Werstiuk, *J. Chem. Soc. D*, 1499 (1970).

(11) L. A. Carpino and H. W. Chen, *J. Amer. Chem. Soc.*, **93**, 785 (1971).

(MCPBA) gave a 60% yield of **1** (75%) and **2** (25%).[12] The diastereomers were separated by a combination of chromatography over silica gel (elution with 5–15% ether–hexane, **1** elutes before **2**), followed by fractional crystallization from methylene chloride–hexane. That **2** is a meso diastereomer was evident from the singlet for the equivalent benzylic protons (τ ($CDCl_3$) 4.63) observed in the nmr spectrum.[13] Also, further oxidation of **2** with MCPBA gives the known[2] *meso*-bis(α-bromobenzyl) sulfone. The *dl* diastereomer **1**[11] upon oxidation with MCPBA gives *dl*-bis(α-bromobenzyl) sulfone.[2] Only one of the possible two *meso*-dibromo sulfoxides was observed in the crude reaction mixture.

The configuration of **2** was established by a single-crystal X-ray diffraction analysis. Cell parameter and intensity data were measured on a Picker FACS-I diffractometer with monochromatic Mo radiation. The crystal data are: monoclinic, $P2_1/c$; $a = 10.09$ (1), $b = 10.243$ (3), $c = 14.74$ (2) Å; $\beta = 108.4$ (1)°; $\rho_{measd} = 1.764$ g cm^{-3}; $\rho_{X\text{-ray}} = 1.783$ g cm^{-3} for $Z = 4$. The intensity data were measured to a 2θ maximum of 40° with a 2θ–θ scan of 2° min^{-1} and 10-sec backgrounds. 1129 of the 1346 unique data were more than two standard deviations above background. The structure was solved using direct methods and it has been refined by the method of full-matrix least squares with anisotropic temperature factors for C, O, S, and Br to an R index of 0.066.[14] Hydrogen atoms were not included in the calculations.

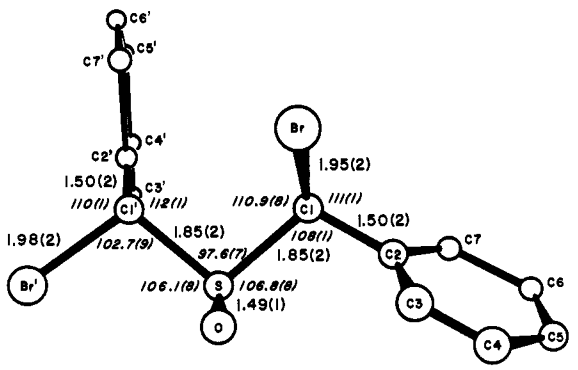
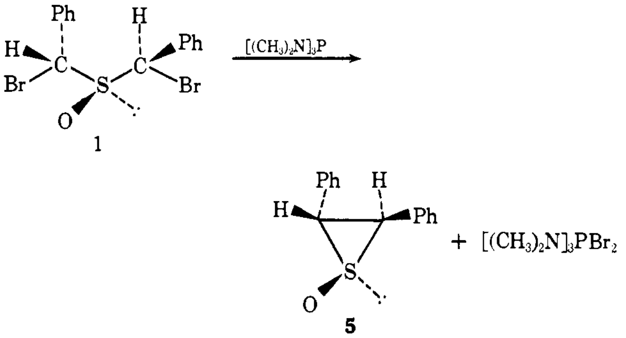


Figure 1. The solid-state configuration of **2** viewed normal to the C–S–C plane. H atoms have been omitted. Bond lengths (angstroms) and angles (degrees) are shown for the central portion of the molecule. The average C–C distances in the primed and unprimed benzene rings are 1.39 and 1.40 Å, respectively.

The configuration is illustrated in Figure 1. Atoms C-2 and Br′ are virtually coplanar with the C–S–C moiety; the disposition of the substituents on C1 and C1′ and the orientation of the benzene rings give an overall configuration in which steric interactions between the rings and the bromine atoms and between these groups and the sulfoxide function appear to minimize.[15] The planar Br-C-S-C arrangement is similar to that reported[2] for *meso*-$PhBrCHSO_2CHBrPh$ and may well be responsible for the clean double inversion observed in solution.

The sulfoxide **1** was treated with $[(CH_3)_2N]_3P$ in benzene at 10° under nitrogen. The resulting phosphine dibromide, $[(CH_3)_2N]_3PBr_2$, was removed by filtration, and pentane was added to the filtrate to precipitate the *trans*-episulfoxide **5** (mp 94.5–96.5°, 65% yield)[12] (nmr τ ($CDCl_3$) 5.70 (1 H), 6.04 (1 H, $J = 11.4$ Hz), 2.4–3.0 (10 H)). The *trans*-episulfoxide **5** was also synthesized by oxidation of *trans*-2,3-diphenylthiirane[16] with 1 equiv of MCPBA in methylene chloride at 0°. The reaction of **2** with $[(CH_3)_2N]_3P$ (benzene, N_2, 10°) gave as the only observable product the *cis,anti*-episulfoxide **3** (mp 92–95°, 70% yield)[12] (nmr τ ($CDCl_3$) 5.48 (2 H) and 2.7–3.2 (10 H)). An authentic sample of **3** was synthesized in 80% yield[17] by oxidation of *cis*-2,3-diphenylthiirane[16] with 1 equiv of MCPBA. The steric influence of the aromatic rings in the *cis*-episulfide should force the oxidizing agent to approach the sulfur atom from the least-hindered side.[18–22]



The conversion of **1** → **5** could have occurred by either double retention (U elimination) or double inversion (W elimination). However, the reaction of **2** → **3** must have occurred with inversion at each carbon center, and we therefore conclude that eliminations in this system as well as the corresponding sulfones[2,3] occur with double inversion.

These results also bear on the question of the conformation of α-sulfinyl carbanions.[23] Theoretical calculations indicate that the lowest energy conformation for α-sulfinyl carbanions is one in which a lone pair of electrons on the sp^3-hybridized α-carbon atom lies on the bisector of the internal oxygen–sulfur lone electron pair angle.[24] However, recent experimental data[25] do not support these theoretical calculations.

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[12] All new compounds gave acceptable elemental analyses.

[13] C. Y. Meyers and A. M. Malte, *J. Amer. Chem. Soc.*, **91**, 2123 (1969).

[14] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[15] C-2 and Br′ deviate by 0.05 and 0.08 Å, respectively, from the C–S–C plane. The angles between the primed and unprimed ring planes and the C–S–C plane are 88.2 and 65.1°; the angle between the C–S–C plane and the S–O bond is 115.4°.

[16] R. Ketcham and V. P Shah, *J. Org. Chem.*, 28, 229 (1963).

[17] None of the cis,syn epimer **4** was ever observed as a product of any of the reactions reported herein.

[18] C. R. Johnson and D. McCants, Jr., *J. Amer. Chem. Soc.*, **87**, 1109 (1965).

[19] J. J. Rigau, C. C. Bacon, and C. R. Johnson, *J. Org. Chem.*, **35**, 3655 (1970).

[20] K. Kondo, A. Negishi, and M. Fukuyama, *Tetrahedron Lett.*, 2461 (1969).

[21] M. Kishi and T. Komeno, *ibid.*, 2641 (1971).

[22] A. G. Schultz and R. M. Schlessinger, *J. Chem. Soc. D*, 1294 (1970).

[23] Like the analogous sulfones[2,3] the dibromo sulfoxides **1** and **2** appear to react stepwise with phosphines to give carbanions followed by loss of bromide ion to give the ring-closed products.

[24] (a) S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **89**, 5710 (1967); (b) A. Rauk, S. Wolfe, and I. G. Csizmadia, *Can. J. Chem.*, **47**, 113 (1969).

[25] (a) B. J. Hutchinson, K. K. Anderson, and A. R. Katritsky, *J. Amer. Chem. Soc.*, **91**, 3839 (1969); (b) T. Durst, R. R. Fraser, M. R. McClory, R. B. Swingle, R. Viau, and Y. Y. Wigfield, *Can. J. Chem.*, **48**, 2148 (1970); (c) M. Nishio, *Chem. Pharm. Bull.*, **17**, 262 (1969); however, see M. Nishio, and K. Nishihata, *J. Chem. Soc. D*, 1485 (1970); (d) M. Cinquini, S. Colonna, and F.Montanari, *ibid.*, 607 (1969); (e) R. Lett, S. Bory, B. Moreau, and A. Marquet, *Tetrahedron Lett.*, 3255 (1971).

Our data, on the other hand, indicate a preference for formation of an α-sulfinyl carbanion whose conformation is that expected from the theoretical calculations.[24]

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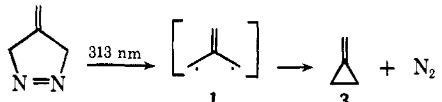
Bruce B. Jarvis,* S. D. Dutkey, Herman L. Ammon
Department of Chemistry, University of Maryland
College Park, Maryland 20742

Received December 14, 1971

Trimethylenemethane. Direct and Benzene-Sensitized Vapor-Phase Photolysis of 4-Methylene-1-pyrazoline

Sir:

As a result of general[1] as well as personal[2] interest in trimethylenemethane (**1**), the vapor-phase photochemistry of 4-methylene-1-pyrazoline (**2**) has been investigated preparatory to flash photolytic experiments designed to detect the intriguing species.

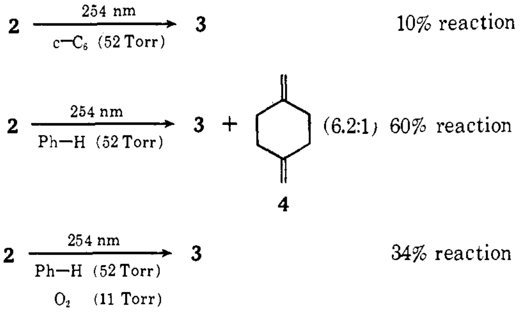


2 1 3

Irradiation of **2** (λ_{max}^{vap} 327 nm)[3] in the vapor phase through Pyrex at room temperature gave methylenecyclopropane (**3**) as the only condensable product at 78°K. Assuming that photochemical reversion to allene and diazomethane followed by photolytic generation of methylene which could add to allene to give **3** does not occur,[4] **1** is a likely intermediate in the reaction. Incomplete photolysis (40% decomposition) of 3,3-dideuterio-**2** (63% *d* on C_3) gave **3** with an *exo*-methylene to ring hydrogen ratio of 0.5 ± 0.05, suggesting that symmetrization of the peripheral carbons in **1** occurred; furthermore, recovered **2** was unchanged.

The quantum yield for the direct photolysis was 0.37 ± 0.1 at room temperature with 1.52 Torr of **2**. The apparatus and technique have been described[5a] and diethyl ketone ($\Phi = 1.0$ at 125°) was the actinometer.[5b] Corrections were made for the relative absorption characteristics of **2** and the actinometer in relation to the emission of the source and Pyrex filter system. There was about 10% decrease in the relative quantum yield upon addition of 570 Torr of nitrogen and a slight increase when the pyrazoline pressure was lowered to 1.14 Torr. The addition of 72 Torr of piperylene had the same effect as nitrogen at that pressure.

Attempts were made to triplet sensitize the reaction of **2** with biacetyl ($E_T = 54.9$ kcal/mol) with no success, presumably because the triplet energy of *cis*-azo compounds is higher than 60 kcal/mol.[6] Because the spectrum of **2** has somewhat of a window at 254 nm (ϵ 80), it was possible to use benzene as a sensitizer. Thus, while direct photolysis of **2** (2.28 Torr) in the presence of 52 Torr of cyclohexane at 254 nm gave 10% reaction to **3**, replacement of the cyclohexane with benzene (52 Torr) gave 60% decomposition under the same conditions. Furthermore, not only was **3** formed but also 1,4-dimethylenecyclohexane (**4**) in a 6.2:1 ratio, respectively, as determined by nmr and mass spectrometry.[7] At lower pressures of **2** less **4** was formed (*e.g.*, at 0.42 Torr of **2** the **3**:**4** ratio was 14). Importantly, 254-nm irradiation of **2** (2.2 Torr) with benzene (52 Torr) and 11 Torr of oxygen under the same conditions resulted in only 34% decomposition giving only **3**.



These results suggest that (a) direct photolysis of 4-methylenepyrazoline (**2**) gives a singlet trimethylenemethane species, **1**, which closes to methylenecyclopropane (**3**); (b) benzene-sensitized photolysis of **2** is both triplet and singlet sensitized possibly leading to **4** and **3**, respectively; (c) oxygen quenches triplets of **2** or **1** before production of dimer; and (d) oxygen partly quenches benzene singlets.

Since most pyrazolines and cyclic azo compounds appear to decompose from their singlet states upon direct excitation, suggestion a is reasonable. However, unclear is whether **3** is formed *via* electronically excited states of **1** or a vibrationally excited ground state of **1** like the orthogonal biradical apparently involved in the thermal self-interconversions of **3**. It is of interest that direct photolysis of 3-methylenecyclobutanone in furan at 15° gave **3** with small amounts of **4**.[8] In addition, the amount of **4** produced increased with decreasing temperature, and, of course, at very low temperatures Dowd[9] elegantly demonstrated by esr that the triplet of **1** was produced. Thus, Dowd's solution experiments may indicate that intersystem crossing of singlet **1** to triplet **1** occurs competitively with a thermally activated process of closure of singlet **1** to **3**, which is consistent with the expectation of a 13-kcal/mol activation energy[2] for closure of the orthogonal singlet ground state of **1**. It should also be noted that Borden[10] has suggested on theoretical grounds that electronically excited **1** can close only to excited states of **3** although conversion of excited **1** to the ground state of **3** is not an unexpected process.[11]

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(1) (a) For a review, see F. Weiss, *Quart. Rev., Chem. Soc.*, **24**, 278 (1970); (b) see also M. J. S. Dewar and J. S. Wasson, *J. Amer. Chem. Soc.*, **93**, 3081 (1971).

(2) J. J. Gajewski, *ibid.*, **93**, 4450 (1971).

(3) (a) P. Dowd, *ibid.*, **88**, 2587 (1966); (b) R. J. Crawford and D. M. Cameron, *ibid.*, **88**, 2589 (1966).

(4) Photolysis in the presence of cyclopentene gave no bicyclo[3.1.0]-hexane, thus lending support to this assumption.

(5) (a) H. Webster III and E. J. Bair, *J. Chem. Phys.*, **53**, 4532 (1970); (b) K. O. Kutschke, M. H. J. Wijnen, and E. W. R. Steacie, *J. Amer. Chem. Soc.*, **74**, 714 (1952).

(6) P. S. Engel, *ibid.*, **89**, 5031 (1967).

(7) All products were stable to the photoconditions, and all reactions proceeded quantitatively.

(8) P. Dowd, G. Sengupta, and K. Sachdev, *J. Amer. Chem. Soc.*, **92**, 5726 (1970).

(9) P. Dowd, A. Gold, and K. Sachdev, *ibid.*, **90**, 2715 (1968).

(10) W. T. Borden, *Tetrahedron Lett.*, 259 (1967).

(11) G. S. Hammond, *Advan. Photochem.*, **7**, 373 (1969).