propylthioboron bromide[13] in methylene chloride at −78 °C for 3 h to give after quenching with aqueous sodium bicarbonate, extractive isolation, and chromatography on silica gel the macrocycle **14**. This intermediate was identical in all respects (TLC, IR, ^{1}H NMR) with the product obtained from **9** by sodium borohydride reduction and desilylation (as described above); intermediate **14** is convertible to aplasmomycin in two steps, dithiane cleavage and borate complexation.

It is worthy of note that cleavage of the MOM ethers in **13** is not realizable by conventional acid-catalyzed hydrolysis since a six-membered cyclic formal results under these conditions from participation of the neighboring hydroxyl at C(9). In the method of cleavage using diisopropylthioboron dibromide, the C(9) hydroxyl serves to faciliate MOM ether cleavage by formation of a diisopropylthioborate ester which by coordination to the hydroxyl at C(7) catalyzes MOM ether cleavage.[14]

The total synthesis of aplasmomycin reported herein is convergent, stereocontrolled, and efficient. It leads to the natural product without the need for resolution.

Further results on other methods of macrocycle formation and on the extension of this work to the synthesis of boromycin will be discussed in subsequent papers.[15]

Supplementary Material Available: ^{1}H NMR and IR data for compounds **4–14** (2 pages). Ordering information is given on any current masthead page.

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(14) For further examples and a more complete discussion of boron-assisted cleavage of MOM ethers of 1,3- and 1,2-diols see: Corey, E. J.; Seitz, S. *Tetrahedron Lett.*, in press.

(15) This work was assisted financially by a grant from the National Institutes of Health. We are indebted to Professor Hamao Umezawa and Dr. Yoshiro Okami of the Institute of Microbial Chemistry, Tokyo, and to Professor Heinz G. Floss of Purdue University for providing reference samples of aplasmomycin.

Formation of Perthiocarbonate Ligands following the Addition of CS_2 to Binary Mo–S Complexes. Crystal and Molecular Structures of the $(Ph_4P)_2[(CS_4)_2MoS]\cdot$DMF and $(Ph_4P)_2[(CS_4)Mo_2S_4(CS_4)]\cdot{}^1/_2$DMF Complexes

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The hydrogenolysis of organosulfur compounds in petroleum products (hydrodesulfurization) is facilitated by heterogeneous catalysts that often contain "sulfided" molybdenum and cobalt salts supported on alumina. Although it has been proposed that a molybdenum sulfide surface is the catalytic site,[1] little is known about the mechanistic course and intermediates of this important reaction. A basic understanding of the likely interactions between organosulfur compounds and Mo–S surfaces conceivably could be obtained from reactivity studies on well-defined Mo–S complexes. Various binary molybdenum thioanions have been synthesized and structurally characterized in recent years. In compounds such as $[Mo_2(S_2)_6]^{2-}$,[2] $[Mo_3S(S_2)_6]^{2-}$,[3] $[(MoS_4)_2MoS]^{2-}$,[4] $[(S_4)_2MoS]^{2-}$,[5] $[(S_4)Mo_2S_4(S_2)]^{2-}$,[5b,6] and $[(S_4)Mo_2S_4(S_4)]^{2-}$,[5b] the molybdenum atoms are coordinated by sulfide (S^{2-}), persulfide (S_2^{2-}), or tetrasulfide (S_4^{2-}) ligands.

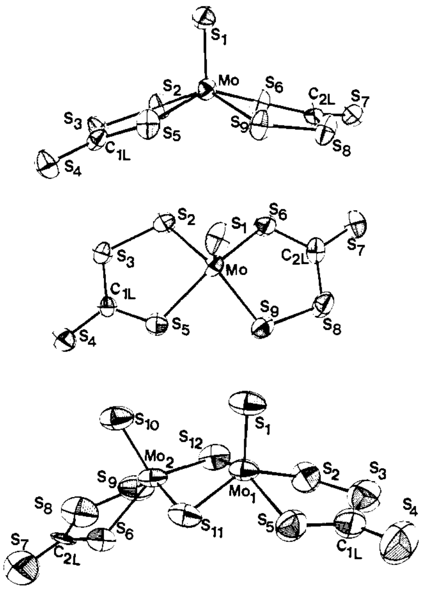

Figure 1. Structures of the $[(CS_4)_2MoS]^{2-}$ and $[(CS_4)Mo_2S_4(CS_4)]^{2-}$ anions showing the atom labeling scheme. Thermal ellipsoids are drawn by ORTEP (Johnson, C. K., ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965) and represent the 50% probability surfaces.

In this communication we report on the reactions of the $(Ph_4P)_2[(S_4)_2MoS]$ (I) and $(Ph_4P)_2[(S_4)Mo_2S_4(S_2)]$ (II) complexes with CS_2 and on the crystal and molecular structures of the CS_2 addition products. The formation and isolation of either I or II, from dimethylformamide (DMF) solutions of $(Ph_4P)_2MoS_4$ and dibenzyl trisulfide (BzSSSBz) in a 1:5 molar ratio at ambient temperatures, depend on the concentration of the reagents. From DMF solutions 0.011 M in $(Ph_4P)_2MoS_4$ and 0.055 M in BzSSSBz, II and $(Ph_4P)_2[(S_4)Mo_2S_4(S_4)]$ (as a minor component) can be isolated as crystalline solids in good yields.[5b] A 4-fold increase in the concentrations of both reagents affords I in excellent yields. Both I and II react with CS_2 (in large excess) in DMF solution at ambient temperatures. Crystalline products are obtained from the reaction mixtures by the addition of diethyl ether to incipient crystallization and standing. Red-orange crystals of $(Ph_4P)_2[(CS_4)_2MoS]\cdot$DMF (III) are obtained from I in 76% yield. Anal. Calcd for $MoS_9P_2ONC_{53}H_{47}$: C, 54.87; H, 4.06; Mo, 8.28; P, 5.35; S, 24.85. Found: C, 54.79; H, 4.26; Mo, 7.79; P. 5.36, S, 24.48. The orange-red, crystalline $(Ph_4P)_2[(CS_4)Mo_2S_4(CS_4)]\cdot{}^1/_2$DMF complex (IV) is obtained from II in 75% yield. Anal. Calcd for $Mo_2S_{12}P_2O_{1/2}N_{1/2}C_{51.5}H_{43.5}$: C, 47.01; H, 3.31; Mo, 14.61; S, 29.21. Found: C, 46.25; H, 3.37; Mo, 14.97; S, 30.12. The visible spectrum of III is characterized by absorptions at 430 nm (ϵ 20,980) and 334 (ϵ 36,200) nm. In the electronic spectrum of IV absorptions are observed at 610, 470, 365, and 314 nm as shoulders on a broad band. In both III and VI the presence of a strong absorption in the infrared at ca. 980 cm^{-1} is attributed to the $C{=}S$ asymmetric stretching vibration of the CS_4^{2-} ligand. Cyclic voltammetry in CH_2Cl_2[7] shows irreversible oxidations at 0.47 and 0.87 V and an irreversible reduction at −0.28 V for III. An irreversible reduction at −1.13 V is found for IV.

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Table I. Selected Distances and Angles

	$[(CS_4)_2MoS]^{2-}$	$[(CS_4)Mo_2S_4(CS_4)]^{2-}$
	Bond Lengths (Å)	
Mo_1–Mo_2		2.840 (3)
Mo–S_1	2.126 (3)	2.108 (1, 5)[a]
Mo–S_2	2.320 (3)	2.390 (6)
Mo–S_5	2.386 (3)	2.418 (6)
Mo–S_6	2.380 (3)	2.408 (5)
Mo–S_9	2.333 (3)	2.393 (6)
Mo_1–S_{11}		2.316 (5)
Mo_2–S_{11}		2.310 (6)
Mo_1–S_{12}		2.311 (6)
Mo_2–S_{12}		2.326 (5)
S_2–S_3	2.101 (1, 5)[a]	2.005 (6, 9)[a]
S_5–C_1L	1.737 (2, 12)[a]	1.78 (4, 2)[a]
S_3–C_1L	1.714 (5, 12)[a]	1.69 (1, 2)[a]
S_4–C_1L	1.651 (11, 11)[a]	1.61 (7, 2)[a]
S_2–S_5	3.223 (8, 5)[a]	3.182 (9, 8)[a]
S_2–S_6	3.091 (19, 5)[a]	
S_5–S_{11}		2.970 (9, 8)[a]
S_2–S_{12}		2.901 (2, 8)[a]
S_{11}–S_{12}		3.584 (7)
	Bond Angles (deg)	
S_2–Mo–S_5	86.3 (4, 1)[a]	82.9 (4, 2)[a]
S_2–Mo–S_6	82.0 (4, 1)[a]	
S_1–Mo–S_2	109.8 (4, 2)[a]	108.4 (9, 3)[a]
S_1–Mo–S_5	107.4 (2, 2)[a]	105.5 (2, 3)[a]
Mo–S_2–S_3	110.83 (3, 13)[a]	110.5 (12, 3)[a]
Mo–S_5–C_1L	114.3 (3, 4)[a]	110.6 (5, 7)[a]
S_2–S_3–C_1L	106.7 (1, 4)[a]	107 (3, 1)[a]

[a] Mean value of the corresponding, independent structural parameters in the two chemically equivalent ligands. The numbers in parentheses represent the standard deviation from the mean and estimated standard deviation, respectively. The labeling in this case represents only one of the two chemically equivalent bonds or angles.

Single-crystal X-ray diffraction and intensity data on III[8] and IV[9] were collected on a Nicolet P3 automatic diffractometer using a θ–2θ scan technique. The data corrected for Lorentz, polarization, and absorption effects were used for the solution of the structures by either direct methods or conventional Patterson and Fourier techniques. Refinement by full-matrix least-squares methods has progressed to conventional R values of 0.046 for III[10] and 0.065 for IV.[11]

The structures of the anions in III and IV are shown in Figure 1. In III the $[Mo(IV){=}S]^{2+}$ unit is coordinated by two nearly planar CS_4^{2-} ligands in a trans arrangement.[12] In the approximate square-pyramidal MoS_5 core the Mo atom is displaced out of the plane of the four equatorial sulfur atoms toward the apical sulfur by 0.749 (1) Å. In IV, the $[Mo(V)_2S_4]^{2+}$ dimeric unit is coordinated by two CS_4^{2-} ligands in a cis arrangement. The two square-pyramidal MoS_5 units in IV are linked by edge sharing in the syn configuration and the Mo atoms are situated above the basal planes (and toward the axial sulfur atoms) at distances of 0.721 (2) and 0.717 (2) Å.

Selected structural parameters for III and IV are shown in Table I. The central MoS_5 and Mo_2S_8 units in III and IV, respectively, are quite similar to the corresponding units in I[5] and II.[5,6] The pronounced asymmetry in the equatorial Mo–S bonding in III has precedent in the structure of I, in which two pairs of Mo–S bonds are observed at 2.387 (1) and 2.331 (1) Å. The mean values of the Mo–S equatorial bonds in III and IV at 2.35 (3) and 2.41 (1) Å, respectively, are almost the same as those in I and II at 2.36 (3) and 2.41 (1) Å. The axial Mo–S bond lengths in III and IV also are within 3σ from the corresponding values in I and II. The similarities in Mo–S bonding between I and III and II and IV indicate that the CS_4^{2-} and S_4^{2-} ligands electronically are very similar.

Differences in the average S–S interligand distances (3.09 (2) Å in III vs. 2.984 (1) Å in I) correlate with differences in the S–S intraligand distances (3.223 (8) Å in III vs. 3.345 (1) Å in I). These correlations support the contention[5,6] that the interligand S–S distances in the MoS_5 cores can be attributed mainly to the S–S intraligand distances (bites) rather than to interligand S–S bonding interactions.

Complexes containing the perthiocarbonate (CS_4^{2-}) ligand are rare, and no structure determination is available for any of the known $[Ni(CS_4)_2]^{2-}$,[13] $[Pt(CS_4)_2]^{2-}$,[13] or $[Ni(CS_4)(CS_3)]^{2-}$[14] complexes. The C–S bonds of the coordinated CS_4^{2-} ligands in III and IV are not significantly different than those reported for the "localized" form of the CS_4^{2-} anion in $K_2CS_4{\cdot}CH_3OH$.[15] Thus in free CS_4^{2-} the distances that correspond to S(5)–C(1), S(3)–C(1), and S(4)–C(1) (Figure 1) are 1.745, 1.728, and 1.659 Å. The S–S bond of the CS_4^{2-} ligand in III at 2.102 (5) Å is significantly longer than the same bond in either IV (2.015 (8) Å) or the free ligand (2.021 Å).[15] The rather long S–S bonds and the associated shorter Mo–S bonds in III may well be a consequence of enhanced Mo–S d_π–p_π bonding in the Mo–S–S units. This type of structural perturbation is apparent also in the structure of I[5] but absent in the structures of either II[6] or IV. In the latter two complexes, the higher formal oxidation states (and weaker reducing character) of the Mo atoms apparently preclude any significant Mo–S d_π–p_π bonding.

The formation of the CS_4^{2-} ligands in III and IV may proceed via electrophilic attack by CS_2 on the coordinated S_4^{2-} ligands with subsequent rearrangement and elimination of S_2. Another mechanism for this reaction could be one in which S_2 dissociation from the coordinated S_4^{2-} ligands allows for the formation of $\overline{\text{Mo–S–S}}$ units.[5b,16] From such units the Mo–CS_4 units may be obtained from CS_2 by electrophilic attack on one of the two sulfur atoms of the disulfide ligand, by insertion into the Mo–S bond and rearrangement, or by a cycloaddition reaction.[17]

Note Added in Proof. Solutions of IV in DMF readily release CS_2 under vacuum, with the formation of the $[(S_2)Mo_2S_4(S_2)]^{2-}$ anion. This anion reforms IV upon the addition of CS_2. The reversible addition of CS_2 to MoS_2 units which apparently occurs with III as well is under study.

Acknowledgment. This research was supported by NSF Grant CHE-8109065. X-ray equipment used in this research was obtained in part by the same grant and by the University of Iowa.

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(8) Crystal and refinement data for $(Ph_4P)_2[(CS_4)_2MoS]{\cdot}DMF$: a = 19.769 (7) Å, b = 13.345 (5) Å, c = 21.647 (8) Å, β = 111.21 (3)°; space group $P2_1/a$; $Z = 4$; $d_{calcd} = 1.42$ g/cm^3, $d_{obsd} = 1.45$ g/cm^3; crystal dimensions (cm) 0.024 × 0.013 × 0.002; $2\theta_{max}$ 50° (Mo radiation); $F^2 > 3\sigma(F^2)$, 2622 reflections used; 5330 unique reflections; 339 parameters.

(9) Crystal and refinement data for $(Ph_4P)_2[(CS_4)Mo_2S_4(CS_4)]{\cdot}{}^1/_2DMF$: a = 10.748 (3) Å, b = 12.262 (4) Å, c = 22.377 (7) Å, α = 75.66 (3)°, β = 87.70 (2)°, γ = 80.49 (3)°; space group $P\bar{1}$, $Z = 2$; $d_{calcd} = 1.52$ g/cm^3, d_{obsd} = 1.51 g/cm^3; crystal dimensions (cm) 0.004 × 0.017 × 0.019; $2\theta_{max}$ 50° (Mo radiation); $F^2 > 3\sigma(F^2)$, 2648 reflections used; 5297 unique reflections; 375 parameters.

(10) In the refinement for III isotropic temperature factors for the C atoms of the Ph_4P^+ cation were employed. All other non-hydrogen atoms were refined by using anisotropic temperature factors. Hydrogen atoms were input at their calculated positions (0.95 Å from the carbon atom) and used in the structure factor calculations but were not refined.

(11) In the refinement process of IV isotropic temperature factors for the C atoms of the Ph_4P^+ cations and anisotropic temperature factors for all other non-hydrogen atoms were employed. The H atoms of the cations and of the DMF solvent molecule were included in the structure factor calculations at their calculated positions but were not refined.

(12) Recently we have isolated and determined the molecular structure of the cis isomer as well.

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(17) The facile reactions of I with activated acetylenes[18] appear to proceed via the latter mechanism.

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Registry No. I, 83463-72-3; II, 82336-38-7; III, 83463-75-6; IV, 83463-78-9.

Supplementary Material Available: Structure factor tables for $(Ph_4P)_2[(CS_4)_2MoS]\cdot DMF$ and for $(Ph_4P)_2[(CS_4)Mo_2S_4(CS)_4]\cdot {}^1/_2DMF$ (40 pages). Ordering information is given on any current masthead page.

Photochemistry of a Triplet Biradical. Cyclization, Cleavage, and Hydrogen Shift in 2-Isopropylidenecyclopentane-1,3-diyl

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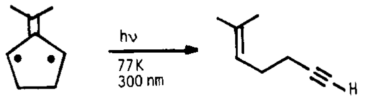
Received July 15, 1982

The literature of photochemistry provides few descriptive examples of the excited-state behavior of non-Kekulé molecules.[3] The present study of 2-isopropylidenecyclopentane-1,3-diyl (**1**) has uncovered a remarkable light-induced rearrangement to 2-methylhept-2-en-6-yne (**2**).



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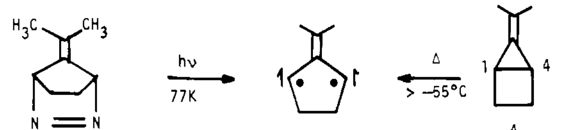
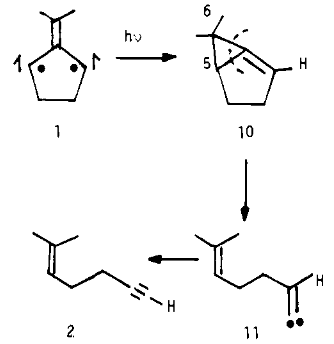
Biradical **1** in its triplet ground state[4,5] is generated by photodeazetation of the diazene **3** in glassy matrices at 77 K,[4] and

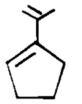


3 1 4

its electron paramagnetic resonance (EPR) signal persists under these conditions for at least 1 h after irradiation is terminated. Melting the matrix produces high yields of dimers of **1**.[4,6,7] In the present experiments, the course of the photolysis of **1** at wavelengths appropriate to the absorption maxima between 299 and 322 nm[8] in glassy preparations at 77 K was monitored either by determining the relative yields of monomeric and dimeric[9] products obtained upon melting the matrix or by following the decline of the EPR signal intensity. In a typical run (diethyl ether–methylcyclopentane glass, 120 min of irradiation with Rayonet "3000 Å" lamps of a sample of **1** that had been prepared by photolysis of **3** with "3500 Å" lamps), an absolute yield of 44% of monomeric products was obtained, which consisted of 93% enyne **2**, identified by isolation and spectroscopic comparison[10] with an independently synthesized authentic sample,[11] and 0.5–1% each of minor products, of which we have identified three resulting from formal disproportionation (1-isopropylcyclopentene, isopropylidenecyclopentane, and 6,6-dimethylfulvene) and two from hydrogen shift (**5** and **6**). Compound **5** also is a product of the pyrolyses of **3** and **2**,[12] but it is noteworthy that the acyclic trienes **7–9** which are prominent bond cleavage products of the latter reactions, did not constitute more than 0.1% of the present photolysis mixtures.

Scheme I





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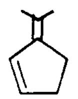

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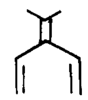

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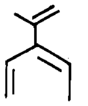

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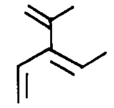

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The most reasonable *formal* mechanism for the deep-seated rearrangement leading to the enyne **2** involves photochemical ring closure of biradical **1** to the bicyclo[3.1.0]hex-1-ene **10** (Scheme I) followed by a vinylidene cycloreversion to give **11**, which then undergoes hydrogen shift. Whether the intermediates **10** and **11** are ground- or excited-state species is not yet clear. For example, the carbene rearrangement **11** → **2** is an amply precedented thermal reaction at ordinary or elevated temperatures,[13] but if the activation barrier of 8.6 kcal/mol calculated[14a,b] for the parent vinylidene → acetylene reaction applies here, the process should be immeasurably slow at 77 K. Either the barrier is lower,[14c] the shift is facilitated by quantum mechanical tunneling, or the overall reaction **10** → **2** occurs without relaxation to the ground vibronic state of **11**. Similarly, the vinylidene cycloreversion step **10** → **11** is a well-known photochemical reaction of methylenecyclopropane,[15] but until recently[12] has had no thermal precedent. Thus, cleavage of **10** may occur before relaxation to the ground state. Alternatively, ground-state bicyclohexene **10** might be formed and

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(1) National Research Service Awardee (Fellowship F32-GM 07997) of the National Institute of General Medical Sciences, 1980–1982.

(2) National Science Foundation Science Faculty Development Awardee, 1981–1982.

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(9) Most of the dimeric product was apparently identical with the dimer mixture obtained when **4** or **3** is thermally decomposed in fluid media. However, under certain conditions, a new set of dimers constituted as much as 40% of the dimeric products. The formation of these "abnormal" dimers was favored by media of high viscosity.

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