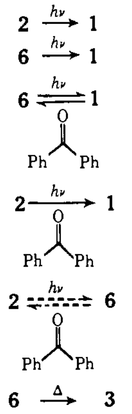
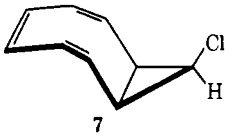
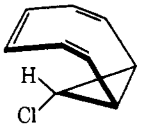
Scheme I



photoconversions exemplified by the irreversible isomerization of **2** to **1** and also by the rearrangement, be it reversible (sensitized excitation) or irreversible (direct excitation), of **6** exclusively to **1**. The specificity of these processes is, we believe, best accounted for in terms of factors relating to conformation. We note, for example, that excited-state conversion of **2** to **1** most likely results from a 1,7 sigmatropic shift of the CHCl bridge which must pivot about the cyclopropane C–C bond common to both reactant and product if the migration is to conform with the restrictions imposed on the systems by orbital symmetry.[12] Clearly, such a process will invert the configuration of the migrating function relative to the remainder of the molecule, *i.e.*, it will allow for interconversion between **1** and **2**. Within this scheme, the actual irreversibility of the stereoisomerization is, we believe, best reasoned in terms of steric restrictions imposed on the migration by different and rather pronounced conformational preferences inherent in the two molecules. Specifically, we suggest that whereas the syn isomer **2** is sterically constrained to the "extended" arrangement shown in **7**, the anti counterpart **1** exists, for reasons we do not yet fully comprehend, predominantly in the "folded" conformation shown in **8**.[13] Brief scrutiny of these forms reveals that while the extended arrangement **7** may readily accommodate a 1,7 pivotal migration of the bridge, the folded form **8** cannot do so without generating a sterically impossible situation in the form of folded **2**; hence, the observed irreversibility.[14] Furthermore, the conformational arrangements shown in **7** and **8** serve to rationally interpret the specificity of the photoinduced behavior of **6** as well, *i.e.*, the occurence of a **6** $\rightleftarrows$ **1** process to the apparent exclusion of a **6** $\rightleftarrows$ **2** interconversion. In brief, it appears that whereas arrangement **8** may properly generate **6** on symmetry-controlled excited-state rupture of the cross-link, conformation **7** is, for obvious reasons, topologically incapable of doing so. Instead, this latter arrangement ought to lead to a *trans,cis,cis,trans*-cyclononatetraene skeleton under the same conditions.[17,18]



7



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The chemistry of **6** is currently under investigation within our laboratories.

Acknowledgments. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. We also thank Mr. R. C. Griffith for useful discussions and Mr. S. W. Eachus for several nmr spectra.

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Received April 1, 1971

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[12] Orbital symmetry considerations demand that the 1,7 process occur suprafacially in the excited state: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

[13] Strongly suggestive nmr evidence for preferred arrangements 7 and 8 for 2 and 1, respectively, derives from the relative positions of the resonances due to the CHCl proton. In the spectrum of **1a** this resonance appears *ca.* 50 Hz upfield from the corresponding signal of **2a**.

[14] It should be noted here that isomerization of 2 to 1 through a sequence involving rupture of a peripheral cyclopropane C–C bond followed by rebonding at the same position *with inversion* also accounts for the observed irreversibility of this process for exactly the same conformational reasons we advanced for the 1,7 shift. For energetic reasons we believe this "topical" stereoisomerization to represent a less likely possibility[15] than the symmetry-controlled 1,7 shift, but cannot, of course, eliminate it entirely as a reasonable mechanistic candidate without further experimentation with properly tagged reactants.

[15] It is interesting to note in this context that 9,9-dimethyl-*cis*-bicyclo[6.1.0]nona-2,4,6-triene, a substance believed[16] for obvious reasons to be rigidly held in the "extended" form, does appear to undergo topical isomerization upon irradiation, the photoproduct being 9,9-dimethyl-*trans*-bicyclo[5.1.0]nona-2,4,6-triene: S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **92**, 7612 (1970).

[16] S. W. Staley and T. J. Henry, *ibid.*, **91**, 1239 (1969).

[17] Operationally, the predicted photoconversion of 7 and 8 to geometrically isomeric 1,3,5,7-cyclononatetraenes may be viewed either as a conformationally controlled unidirectional disrotatory motion, corresponding to an inward and outward movement of the bridge protons in the case of 7 and 8, respectively, or simply as a nonrotatory rupture of the cross-link.

[18] One referee commented as follows with regard to the photosensitized interconversion of **6** and **1**: "Electrocyclization of polyenes has in general been found to be a singlet reaction. The interconversion of **1** and **6** in the presence of benzophenone raises the interesting question whether the sensitized conversion of **6** to **1** might not proceed by way of *trans,cis,cis,cis*-9-chloro-1,3,5,7-cyclononatetraene which could cyclize thermally to **1**." We fully concur with the underlying principles of this statement, but nonetheless wonder whether one should expect a molecule, as thermally labile as 9-Cl-*cis*^{3},*trans*-CNT might be anticipated to be, to electrocyclize with the high degree of regiospecificity and stereospecificity demanded by our results.

Wavelength Dependency in the Photochemistry of 1,3-Cyclohexadienes. *cis*-Bicyclo[4.3.0]nona-2,4-diene to *cis,cis,trans*-1,3,5-Cyclononatriene Valence Tautomerism[1]

Sir:

Very subtle structural differences in homoannular cyclohexadienes have been shown to play an important role in the rearrangement pathway followed by the molecule upon photoexcitation.[2] We now wish to report that energy of excitation can also be a factor in the cyclohexadiene photochemical dichotomy.

Grimme and Vogel[3] have reported that *cis*-bicyclo[4.3.0]nona-2,4-diene (**1**) undergoes rearrangement on

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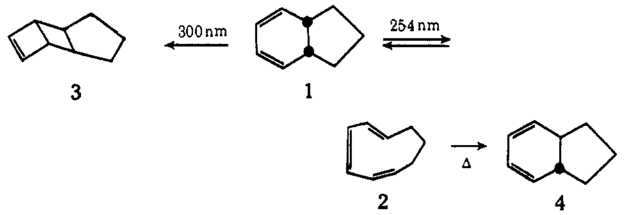
[1] This investigation was supported in part by P.H.S. Grant No. 00709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

[2] (a) D. H. R. Barton, *Helv. Chim. Acta*, **42**, 2604 (1959); (b) R. J. de Kock, N. G. Minnaard, and E. Havinga, *Recl. Trav. Chim. Pays-Bas.*, **79**, 922 (1960); (c) W. G. Dauben, *Chem. Weekbl.*, **29**, 381 (1964); (d) W. H. Schaller, R. N. Moore, J. E. Hawkins, and R. V. Lawrence, *J. Org. Chem.*, **27**, 1178 (1962); (e) G. J. Fonken and K. Mehrotra, *Chem. Ind. (London)*, 1841 (1963); (f) W. G. Dauben and R. M. Coates, *J. Amer. Chem. Soc.*, **86**, 2490 (1964).

[3] E. Vogel, W. Grimme, and E. Dinne, *Tetrahedron Lett.*, 391 (1965).

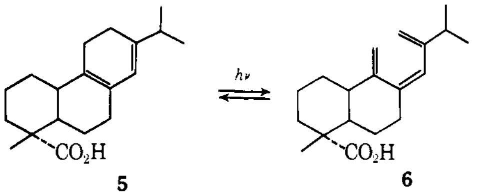
irradiation with a low-pressure mercury lamp to yield *cis,cis,trans*-1,3,5-cyclononatriene (**2**). The triene was isolated *via* its silver nitrate complex and shown to have λ_{max} 290 nm (ϵ 2050). Thermally, **2** rearranged quantitatively to *trans*-bicyclo[4.3.0]nona-2,4-diene (**4**).



When a 1.5 × 10^{-2} *M* solution of **1** in pentane was irradiated at 254 nm in a Rayonet Reactor through Vycor (λ > 220 nm), a photostationary state was reached between **1** and **2**; analysis by uv and glpc indicated 40% of **1** and 60% of **2**.[4] The uv displayed isosbestic points at 235 and 283 nm. Upon continued irradiation, another photoproduct **3** (of short retention time) slowly was formed at the expense of **1** and **2**. A similar experiment at −20° in pentane utilizing a low-pressure resonance lamp gave essentially the same results.

However, when **1** was irradiated with RPR 300-nm lamps (λ 270–330 nm) through Vycor in the Rayonet Reactor, no significant amount of **2** could be detected by uv or glpc, but photoproduct **3** slowly was formed. The new photoproduct **3** was glpc purified and characterized by its spectral properties as tricyclo[4.3.0.0.^{2,5}]non-3-ene. The nmr spectrum (δ, CCl$_4$) exhibited a sharp but finely split multiplet at 6.20 (2 H, cyclobutene vinyl protons), a broad singlet at 2.67 (2 H, allylic bridgehead protons), a broad singlet at 2.43 (2 H, bridgehead protons), and two closely spaced bands at 1.63 and 1.60 (6 H, methylene hydrogens). The infrared spectrum displayed the characteristic cyclobutene overtone absorption at 1550 cm^{-1} and the C–H out-of-plane deformation band at 725 cm^{-1}.[5] The uv spectrum showed only end absorption. Further evidence supporting the assigned structure was obtained by pyrolysis at 250°, in the injection port of the gas chromatograph, to yield **1**, and by hydroboration and oxidation to obtain a compound exhibiting a carbonyl stretch at 1780 cm^{-1} in the ir.

One possible explanation for the wavelength-dependent behavior of this system could be a very efficient photochemical closure of **2** back to **1**. Photochemical cyclizations of hexatrienes to cyclohexadienes are symmetry-allowed processes and have been reported in the literature by several workers.[6,7] In most of these cases the photostationary state existed far on the side of the triene, indicating inefficient cyclization as compared to ring opening.[8a,b,d] Palustric acid (**5**), however, approaches a photostationary state that is about 50% diene and 50% triene **6**.[6c] The rationale given for this observation was inhibition of rotation of the terminal methylene by the isopropyl side chain, keeping **6** in a conformation amenable to cyclization.



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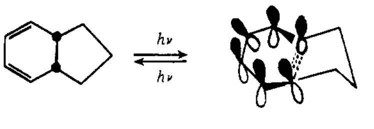
Since at 254 nm the extinction coefficient for **1** is about 30 times that of **2** (ϵ^{254}_{diene} 3800, ϵ^{254}_{triene} 130), the quantum yield for closure of **2** must be about 20 times that for the opening of **1**. At 300 nm the ratio of extinction coefficients drops to about 0.02 (ϵ^{300}_{diene} 50, ϵ^{300}_{triene} 2000), so the photostationary state is greatly displaced to favor **1**, thus allowing the less efficient bicyclo[2.2.2]hexene structure formation to proceed from the diene.

Evidence that cyclization of **2** does readily proceed at 300 nm was obtained by irradiating a solution of **1** in pentane at 254 nm in the Rayonet Reactor until the photostationary state was reached; the irradiation vessel was then cooled to −78° to prevent thermal cyclization while the lamps in the reactor were changed, and the solution containing **2** was irradiated with the 300-nm lamps through Pyrex. Monitoring by uv and glpc showed rapid reversion to **1**.

The remarkable efficiency of this triene photochemical closure is in accord with the spatial orientation of its π system as a Möbius array of orbitals.[8] In a 6π-electron system the Möbius orientation perfectly places the π orbitals for a conrotatory closure, an orbital symmetry allowed excited state process.[7,9] Examination of molecular models indicates such a conformation for the triene is favored, explaining its highly efficient cyclization (Scheme I).

Scheme I



In principle, any combination of substituents that will keep the triene in such a Möbius-like conformation will increase the efficiency of photorecyclization; likewise, any combination of substituents favoring a conformation that is not conducive to a conrotatory closure will accentuate the rearrangement of the triene to other products upon irradiation.[9] From molecular models nine- and ten-membered monocycles containing trans,cis,trans or cis,cis,trans conjugated trienes appear to resist rotation out of the Möbius conformation that is initially formed on photolysis of the cyclohexadiene doubly allylic σ bond, making recyclization geometrically very favorable. An example of this former system has been reported to yield a photostationary state.[10] When the ultraviolet absorption bands of the

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(4) Triene **2** is analyzed as **4** by glpc, thermal rearrangement occurring in the injection port and on the column (10 ft, 10% Carbowax 6000 on 60–80 Chromosorb W at 100°). Irradiation of triene **2** with 300-nm light did not yield any *trans*-diene **4**.

(5) M. V. Evans and R. C. Lord, *J. Amer. Chem. Soc.*, **83**, 3411 (1961).

(6) (a) E. Havinga, R. J. de Kock, and M. P. Rappoldt, *Tetrahedron*, **11**, 276 (1960); (b) G. J. Fonken, *Tetrahedron Lett.*, 549 (1962); (c) W. G. Dauben and R. M. Coates, *J. Org. Chem.*, **29**, 2761 (1964); (d) K. J. Crowley, *ibid.*, **33**, 3679 (1968).

(7) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(8) (a) E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964); (b) H. E. Zimmerman, *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).

(9) For a general review of these reactions, see W. G. Dauben in "Reactivity of the Photoexcited Molecule," Interscience, New York, N. Y., 1967, pp 171–199.

(10) E. J. Corey and A. G. Hortman, *J. Amer. Chem. Soc.*, **85**, 4033 (1963).

related diene and triene occur in different regions of the spectrum, "optical pumping" becomes possible, permitting one to choose the desired direction of the photochemical reaction of a 1,3-cyclohexadiene.

These results demonstrate the possible use of irradiations at specific wavelengths to control the pathway followed by 1,3-cyclohexadienes, particularly when ring opening results in a medium-sized ring compound. It also appears clear that conformations of π systems can play important roles in the photochemistry of unsaturated compounds. A related Möbius array for an 8π-electron system in a ten-membered ring has been reported to undergo reversible closure in the ground state.[11]

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(11) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **92**, 7612 (1970).

(12) National Institutes of Health Predoctoral Fellow, 1969–present.

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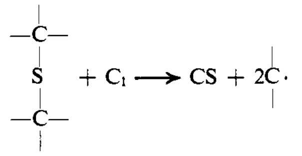
The Chemistry of Atomic Carbon. Desulfurization

Sir:

Previous reports from this laboratory have demonstrated that metastable, singlet carbon atoms are capable of abstracting oxygen from ethers[1] and carbonyl compounds.[2] We now wish to report that arc-generated carbon atoms abstract sulfur atoms from carbon disulfide and thioethers in a manner analogous to deoxygenation. We call this process desulfurization.

The removal of a sulfur atom by atomic carbon from a thioether is approximately 45 kcal mol exothermic on the basis of bond energies.[3] This fact



$$\begin{array}{c} | \\ -\mathrm{C}- \\ | \\ \mathrm{S} \\ | \\ -\mathrm{C}- \\ | \end{array} + C_1 \longrightarrow CS + 2\,\begin{array}{c} | \\ \mathrm{C}\cdot \\ | \end{array}$$

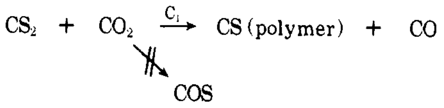
suggested that the reaction would be feasible, although not nearly so exothermic as deoxygenation.[1]

When carbon disulfide and arc-generated carbon vapor are codeposited at a liquid nitrogen cooled surface, a brownish black polymer is formed. This material was thought to be the CS polymer since it is known[4,5] that CS polymerizes very rapidly at low temperature; this material is also reported to be brownish black. When carbon disulfide and carbon vapor are codeposited at a liquid nitrogen cooled surface in the presence of 5 mol % oxygen, carbonyl sulfide is produced in 10% yield based on the total carbon vaporized (25% yield based on CS content). This suggested that CS produced by desulfurization of carbon disulfide was being trapped at low temperature by molecular oxygen. When mixtures of carbon disulfide and small quantities of propylene oxide reacted with carbon vapor, traces of carbonyl sulfide were formed; presumably CS is a mild deoxygenating agent, although there is not sufficient information on this point at present. It should be noted that the chemistry of the CS molecule is unknown. The desulfurization of carbon disulfide may be a convenient source of this material.[6]

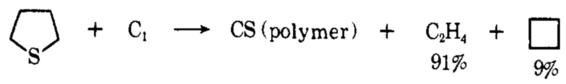
$$CS_2 + C \longrightarrow 2CS \longrightarrow \text{polymer}$$

$$CS_2 + C \longrightarrow 2CS \xrightarrow{O_2} COS$$

When a mixture (1:1) of carbon disulfide and carbon dioxide was cocondensed at a liquid nitrogen cooled surface with arc-generated carbon vapor, both carbon monoxide and CS polymer were formed; no carbonyl sulfide was present in the product mixture. The yield of carbon monoxide from carbon dioxide and carbon vapor is 20% of the carbon vaporized (correcting for the degeneracy of carbon monoxide production), while, in the presence of 50 mol % carbon disulfide, the yield was reduced to 10%. This statistical yield suppression implies that the rates of deoxygenation and desulfuration are essentially equal. The failure to observe carbonyl sulfide production in this system indicates that CS is not able to deoxygenate carbon dioxide.



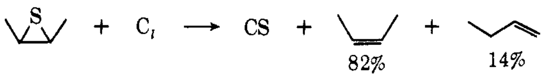
Because of the lower exothermicity of desulfurization reactions, it was of interest to examine the desulfurization of cyclic thioethers since the oxygen analogs were suggested to undergo "hot" reactions.[1] The desulfurization of tetrahydrothiophene gave ethylene as the major product although cyclobutane was formed. This



is in contrast with the deoxygenation of tetrahydrofuran which yields no detectable amount of cyclobutane under these conditions.[1] Similar behavior was observed in the desulfurization of diethyl sulfide where ethane, ethylene, and n-butane were the major products. In

$$Et_2S + C_1 \longrightarrow CS\ (\text{polymer}) + \underset{46\%}{C_2H_6} + \underset{46\%}{C_2H_4} + \underset{8\%}{C_4H_{10}}$$

the deoxygenation of diethyl ether there was no detectable quantity of n-butane produced.[1] Additional evidence that the energetics of desulfurization differ to a measurable degree from those of deoxygenation was found in the desulfurization of *cis*-1,2-dimethyl episulfide. The desulfuration of this material gave both *cis*- and *trans*-2-butene with a cis–trans value of 4.5. The corresponding epoxide deoxygenated to give both 2-butenes but with a cis–trans value of 1.5.[7]



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(1) P. S. Skell, J. H. Plonka, and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 1748 (1967).

(2) P. S. Skell and J. H. Plonka, *ibid.*, **92**, 836, 2610 (1970).

(3) Required bond dissociation energies were taken from B. deB. Darwent, *Nat. Stand. Ref. Data Ser., Nat. Bur. Stand.*, No. **31** (1970).

(4) R. Steudel, *Z. Naturforsch.*, **21**, 1106 (1966).

(5) G. Porter and F. J. Wright, *Discuss. Faraday Soc.*, **14**, 23 (1953).

(6) It has been reported that CS reacts with halogen molecules to yield thionyl dihalides. See ref 4.

(7) J. H. Plonka and P. S. Skell, *Chem. Commun.*, in press.