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]

(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

$$\begin{array}{c} -\overset{|}{C}- \\ | \\ S \\ | \\ -\overset{|}{C}- \\ | \end{array} + C_1 \longrightarrow CS + 2\overset{|}{C}\cdot$$
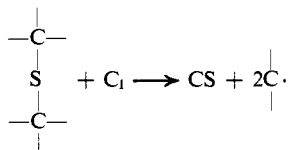
suggested that the reaction would be feasible, although not nearly so exothermic as deoxygenation.[1]

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

$$CS_2 + C \longrightarrow 2CS \longrightarrow polymer$$

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

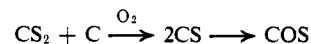(1) P. S. Skell, J. H. Plonka, and R. R. Engel, *J. Amer. Chem. Soc.*, **89**, 1748 (1967).

(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).

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]

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

When a mixture (1:1) of carbon disulfide and carbon dioxide was cocondensed at a liquid nitrogen cooled

$$CS_2 + CO_2 \xrightarrow{C_1} CS\,(polymer) + CO$$
$$\searrow$$
$$COS$$
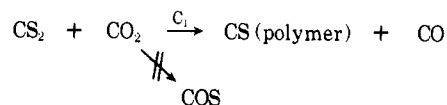
surface with arc-generated carbon vapor, both carbon monoxide and CS polymer were formed; no carbonyl sulfide was present in the product mixture. The yield of carbon monoxide from carbon dioxide and carbon vapor is 20% of the carbon vaporized (correcting for the degeneracy of carbon monoxide production), 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

$$\underset{S}{\bigcirc} + C_1 \longrightarrow CS\,(polymer) + \underset{91\%}{C_2H_4} + \underset{9\%}{\square}$$
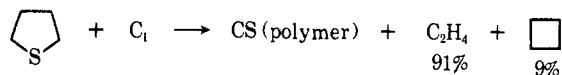
is in contrast with the deoxygenation of tetrahydrofuran which yields no detectable amount of cyclobutane under these conditions.[1] Similar behavior was observed in the desulfurization of diethyl sulfide where ethane, ethylene, and *n*-butane were the major products. In

$$Et_2S + C_1 \longrightarrow CS\,(polymer) + \underset{46\%}{C_2H_6} + \underset{46\%}{C_2H_4} + \underset{8\%}{C_4H_{10}}$$
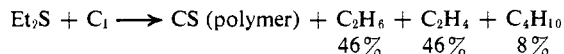
the deoxygenation of diethyl ether there was no detectable quantity of *n*-butane produced.[1] Additional evidence that the energetics of desulfurization differ to a measurable degree from those of deoxygenation was found in the desulfurization of *cis*-1,2-dimethyl episulfide. The desulfuration of this 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]

$$\underset{S}{\bigvee} + C_1 \longrightarrow CS + \underset{82\%}{\bigvee} + \underset{14\%}{\diagdown\diagup}$$
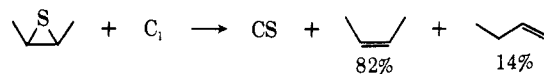
(6) It has been reported that CS reacts with halogen molecules to yield thionyl dihalides. See ref 4.

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

Desulfurization appears to be a general process whose chemistry parallels that of deoxygenation although the energetic difference between the reactions is manifest in the examples presented above.

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Flash Photolysis of N-Nitrosopiperidine. The Reactive Transient

Sir:

The photoreactions of N-nitrosopiperidine in the presence of a mineral acid are outlined in the following scheme. Pathway a has been postulated, from certain
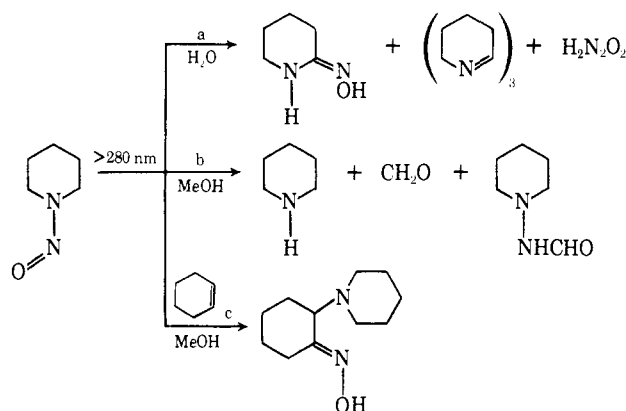
evidence, to occur by eliminating HNO in the primary photoprocess,[1-3] and is termed as photoelimination. Photoaddition pathway c has been shown to give 1-nitroso-2-piperidinocyclohexane as the primary adduct.[4-7] In addition it is now found that N-nitrosopiperidine also photolytically reacts with methanol to give piperidine hydrochloride, formaldehyde, and N-piperidinoformamide[8] shown as pathway b. The latter is therefore referred to as photoreduction. We have carried out flash photolysis experiments which indicate that a common reactive transient derived from a singlet excited state of the N-nitrosopiperidine–acid complex is responsible for the observed photoreactions.

The 1- and 0.4-μsec flash photolysis apparatus[9] used in this investigation was an improved version of that reported previously.[10,11] Flash photolysis,

(1) Y. L. Chow, *Can. J. Chem.*, **45**, 53 (1967); Y. L. Chow, *Tetrahedron Lett.*, 2333 (1964).
(2) E. M. Burgess and J. M. Lavanish, *ibid.*, 1221 (1964).
(3) T. Axenrod and G. W. A. Milne, *Tetrahedron*, 4443 (1967).
(4) Y. L. Chow, *Can. J. Chem.*, **43**, 2711 (1965).
(5) Y. L. Chow, C. J. Colón, and S. C. Chen, *J. Org. Chem.*, **32**, 2109 (1967).
(6) Y. L. Chow, S. C. Chen, and D. W. L. Chang, *Can. J. Chem.*, **48**, 157 (1970).
(7) Y. L. Chow, C. J. Colón, and D. W. L. Chang, *ibid.*, **48**, 1664 (1970).
(8) P. A. S. Smith and N. W. Kalenda, *J. Org. Chem.*, **23**, 1599 (1958).
(9) Both flash photolysis apparatus used two independent, synchronously triggered, capacitor–spark gap lamp circuits. The 1-μsec apparatus used two 0.3-μ F 25-kV capacitors (one in each circuit). In the 0.4-μsec apparatus, two 0.05-μF 35-kV capacitors were used. The lamp configuration and the procedure were the same as that used previously (ref 10).
(10) R. W. Yip, W. D. Riddell, and A. G. Szabo, *Can. J. Chem.*, **48**, 987 (1970).

through a Vycor filter, of degassed or oxygen-saturated aqueous solutions containing 1×10^{-4} M N-nitrosopiperidine and 0.01 M HCl, produced a transient[12] whose absorbance changes indicated first-order kinetic decay with a lifetime ($\tau_{obsd} = 1/k_{obsd}$) of 54 $\pm$ 2 μsec. The similar photolysis of degassed or undegassed methanol solutions containing 6×10^{-5} M N-nitrosopiperidine and 0.01 M HCl produced a transient which, while having the same absorbance characteristics as the transient generated in an aqueous solution, exhibited a first-order kinetic decay with a lifetime of 8 $\pm$ 2 μsec. No transient was observed in the absence of either an acid or N-nitrosopiperidine. Flash excitation of the n $\rightarrow$ π^* transition band in the 340-nm region (5×10^{-3} M N-nitrosopiperidine, 0.01 M HCl, and soft glass filter)[13] produced a weaker transient with the same lifetimes indicating that the transients generated from either the $\pi \rightarrow \pi^*$ or n $\rightarrow \pi^*$ transition band are the same species.

When the concentration of methanol in water was varied, the initial absorbancy $(OD)_0$ of the transient remained virtually constant but the lifetime (τ_{obsd}) was reduced proportionally to the methanol concentration. The second-order rate constant of the reaction of the transient with methanol ($k_r = (4.8 \pm 0.3) \times 10^3$ M^{-1} sec^{-1}) was obtained from the slope of the plot of the pseudo-first-order rate constants (k_{obsd}) vs. the concentration of methanol. In a similar manner, the transient was found to react with cyclohexene in a solvent mixture[14] of methanol and water (2:1, v/v) with a quenching rate constant $k_r = (2.4 \pm 0.1) \times 10^7$ M^{-1} sec^{-1}. The rate of the addition of the transient to cyclohexene is, therefore, about 5000 times faster than that of the reduction of the transient by methanol. This rate ratio explains why photoaddition takes place exclusively without a complication from the photoreduction in methanol as observed previously.[4]

The lowest triplet energy (E_T) of N-nitrosopiperidine is now determined to be about 59 kcal/mol by quenching experiments of the triplet transients[15,18] that are generated by flash photolysis of naphthalene and 2,2'-binaphthyl in aqueous acidic solutions. While the xanthenone $(E_T = 74$ kcal/mol) triplet transient was quenched by N-nitrosopiperidine at nearly the diffusion-controlled rate $(k_q = 1.4 \times 10^9$ M^{-1} sec^{-1}), the photoreactions of N-nitrosopiperidine do not occur with

(11) R. W. Yip, *Rev. Sci. Instrum.*, **40**, 1035 (1969).
(12) The concentration of N-nitrosopiperidine was generally in the vicinity of or lower than 10^{-4} M in order to provide the >300-nm region transparent so that the decay curve of the transient can be recorded at any wavelength in the region of 300–400 nm. N-Nitrosopiperidine exhibits absorptions at 235 nm (ϵ 8300) for π–π^* and 349 (ϵ 88.5) for n–π^* transition bands in methanol.
(13) In this case it was not possible to observe the transient at a wavelength shorter than ~375 nm because of the high concentration of N-nitrosopiperidine required for absorption at 349 nm. The decay kinetics of the transient were monitored at 400 nm.
(14) The mixture solvent allows a wider variation of the lifetimes that can be determined accurately.
(15) The triplet transients of naphthalene and 2,2'-binaphthyl were quenched by N-nitrosopiperidine (<10^{-4} M) with k_q of 1.4 × 10^9 and 7.5 × 10^7 M^{-1} sec^{-1}, respectively. The diffusion-controlled rate constant in methanol at 20° was approximately calculated by the modified Debye equation to be 1.04 × 10^{10} M^{-1} sec^{-1}. The triplet energies quoted in ref 17 and 18 are adopted.
(16) G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961).
(17) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).
(18) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1965, Chapter 5.