from free CO for the stopped exchange peak in the ^{13}C nmr of a 90.5% ^{13}C enriched CO adduct.

Further evidence for the similarity in the O_2 and CO adducts comes from their ^{13}C nmr. The adducts were run at ca. $-50°$ in tubes sealed under 1 atm of gas at that temperature. High-spin Co(salMeDPT) shows irresolvable broad peaks. Relatively sharp resonances with small isotropic shifts are observed for the adducts consistent with the ^{1}H nmr conclusion of slow exchange on the nmr time scale. A definite similarity again exists between the chemical shifts of the ligand resonances in both the O_2 and CO adducts.

The observed cobalt(II) hyperfine coupling constants are ~5 to 20 × 10^{-4} cm^{-1} and comparable to those reported for other adducts of O_2 with cobalt(II) complexes. The unusual esr behavior in the present CO adduct, relative to previously studied five coordinate CO adducts, likely is due to the fact that Co(salMeDPT)·CO is six-coordinate, and, as is the case with the O_2 adduct, the geometry is likely very distorted. There are several possible reasons for the reduced cobalt hyperfine coupling constants in these adducts. They are based on variations in 3d and 4s and 4p atomic orbital contributions in the MO containing the unpaired electron in addition to variations in other crystal field parameters included in the esr analysis.[13] In the past, the reduced value has been interpreted as an indication of O_2^- by comparison to low spin four- and five-coordinate cobalt(II) species.[13-18] The presence of additional ligands in the six-coordinate complexes has a considerable effect on the relative 3d-orbital energies. It is significant to point out that the coordination of methyl isocyanide or CO to this Co^{II}-(salMeDPT) complex results in an esr spectrum similar to that of O_2. The observed isotropic proton nmr shift of the CH$_3$NC ligand (~4 ppm downfield from free CH$_3$NC) and the small ^{13}C shift of the CO ligand preclude the possibility of these fragments being formulated as CH$_3$NC$^-$ or CO$^-$ and provide a precedent for a six-coordinate, low spin cobalt(II) complex with a lower coupling constant than the four-or five-coordinate systems. Subsequent to submission of this manuscript, Wayland, et al.,[19] reported a five-coordinate CO adduct of cobalt(II) tetraphenylporphyrin which behaves quite differently from our CO adduct. This does not alter our conclusions in view of the difference in coordination and geometry.

Since CH$_3$NC is not reduced and it is unlikely that CO is formally reduced in its adduct, we feel it best to describe both the CO and O_2 adduct as Co(II) in nature with the unpaired spin being largely in a cobalt(II) orbital instead of an O_2 π^* orbital (as in O_2^-). The coordinated O_2 is then formulated as a bound singlet state with possible stabilization from metal to O_2 π back-bonding. The spin pairing is caused by the lift-

ing of the degeneracy of the π^* orbitals of $D_{\infty h}$ O_2 upon coordination. Since the reduced cobalt hyperfine was the main evidence for O_2^- in previous studies, there is nothing to suggest that the other reported O_2 complexes of cobalt(II) should not be similarly formulated even though the O_2 adduct reported here may have a very different geometry than those in which part of the ligand set is rigorously planar.

These conclusions are contrary to those recently reported from an ^{17}O labeled study of dioxygen coordinated to a cobalt(II) ammonia complex in a γ Zeolite.[20] The resolution of the ^{17}O hyperfine on these systems is badly obscured by the cobalt, and the spectra do not provide independent support for the O_2^- model advocated by these authors. A recent ^{17}O enrichment study[21] of Co(bzacen)pyO$_2$ in CH$_2$Cl$_2$ solution showed both oxygens equivalent, though the crystal structure shows the geometry of the Co–O$_2$ moiety to be bent with an angle of 126°. Spin densities were calculated from the observed isotropic $\langle a \rangle_{^{17}O}$ = 21.6 G, by assumming that the unpaired electron was in an O_2 π^* MO. Since it was found that both oxygens are equivalent, it is possible that a rapid equilibrium between two σ-bonded structures exists with unpaired spin delocalization arising from the interaction of cobalt d_{z^2} and O_2 sp^2 orbitals (similar to Co(bzacen)py). This situation would put spin directly into the oxygen 2s orbitals and require a very small spin density on the O_2 molecule to produce a 21.6 G hyperfine splitting.

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Singlet Oxygen Reaction. III. "Solvent and Temperature Effects" on the Photosensitized Oxygenation of Vinyl Sulfides and Vinyl Ethers

Sir:

Reactions of singlet oxygen with vinyl ethers have been extensively developed,[1-6] but relatively few studies have been reported in which sulfur substituted ethylenes are oxidized.[7,8] We previously reported that vinyl sulfides, which have an activated double bond as well as allylic hydrogen atoms, give dithiooxalate, thiocarbonate, and disulfide, presumably *via* 1,2-dioxetane intermediates.[9,10] Recently, however, several reports have

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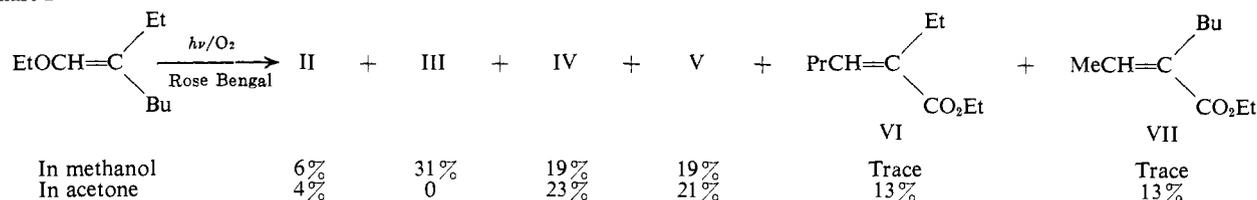
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Chart I

$$\text{EtOCH}=C\overset{\text{Et}}{\underset{\text{Bu}}{<}} \xrightarrow[\text{Rose Bengal}]{h\nu/O_2} \text{II} + \text{III} + \text{IV} + \text{V} + \text{PrCH}=C\overset{\text{Et}}{\underset{\text{CO}_2\text{Et}}{<}} + \text{MeCH}=C\overset{\text{Bu}}{\underset{\text{CO}_2\text{Et}}{<}}$$

VI   VII

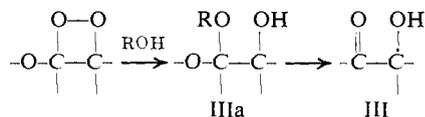|						
In methanol	6%	31%	19%	19%	Trace	Trace
In acetone	4%	0	23%	21%	13%	13%

demonstrated that the dioxetane mode is somewhat sensitive to the surrounding medium,[11-13] although the ene mode is not.[14] We report here that the relative rates of ene and dioxetane modes are sensitive to solvent and temperature in the reaction of singlet oxygen with vinyl sulfides.

1-Ethylthio-2-ethylhexene-1 (I) in methanol was irradiated with a 500-W tungsten lamp for 1 hr, while oxygen was bubbled through the mixture in the presence of Rose Bengal. Evaporation followed by glpc gave diethyl disulfide (4%), ethyl butyl ketone (II) (65%), and hydroxy aldehyde (III) (26%). The structural assignments are based on spectral and analytical data and comparison with authentic samples.

An attractive mechanism for the conversion of the vinyl sulfide into the products, II and III, may involve a 1,2-dioxetane intermediate followed by C–C and C–S bond cleavages as suggested in previous papers.[9,10] The most marked change in going from methanol to acetone solvents is in the formation of vinyl aldehyde derivatives. The reaction of singlet oxygen with the sulfide I in acetone solvent gave the vinyl aldehydes, IV and V, in 19% yield as well as diethyl disulfide (15%), II (49%) and III (12%) (Scheme I). Control experiments showed that under the reaction conditions there is insignificant formation of IV and V from the product III.

The data in Table I may imply that the dioxetane mode is favored exclusively in protic solvents, and is slightly favored over the ene mode in aprotic solvents such as carbon tetrachloride and cyclohexane. Such a solvent effect is more dramatic when the olefin is a vinyl ether. The photosensitized oxygenation of 1-ethoxy-2-ethylhexene-1 in methanol gave dioxetane mode products, II and III[15] in 37% yield, and ene mode products,

$$\underset{\text{IIIa}}{-O-\overset{O-O}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-} \xrightarrow{\text{ROH}} \underset{\text{IIIa}}{-O-\overset{RO}{\underset{|}{C}}-\overset{OH}{\underset{|}{C}}-} \xrightarrow{} \underset{\text{III}}{-\overset{O}{\underset{\parallel}{C}}-\overset{OH}{\underset{|}{C}}-}$$

IV and V in 38% yield, but in acetone gave dioxetane mode products in only 4% yield and ene mode products (IV–VII) in 70% yield (Chart I).

In all cases, protic solvents appear to accelerate the dioxetane mode and the vinyl sulfides have more aptitude to take that course than the corresponding ethers.

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(15) The dioxetane intermediate may combine with alcohol to yield the acetal IIIa, which then converted into aldehyde III under the analytical conditions. The acetal IIIa is often isolated by glpc.

Table I. Solvent Dependence of the Dioxetane and Ene Reaction Modes for 1-Ethylthio-2-ethylhexene-1 (at 20°)

Solvent	Relative yields, %	
	Dioxetane mode	Ene mode
Methanol	100	0
Ethanol	100	0
Isopropyl alcohol	100	0
Acetonitrile	83	17
Benzene	82	18
Dichloromethane	79	21
Acetone	78	22
Cyclohexane	76	24
Carbon tetrachloride	64	36

$$\text{EtZCH}=C\overset{\text{Et}}{\underset{\text{Bu}}{<}} + {}^1O_2 \longrightarrow$$

$$Z = S, O$$

ene mode

A

dioxetane mode

B
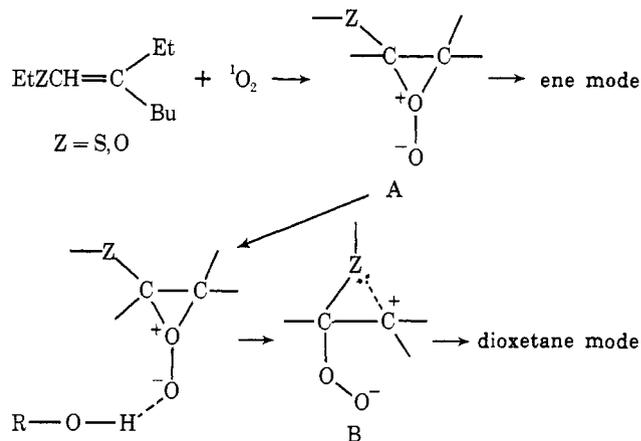
Although the possibility of a concerted mechanism for the ene mode reaction cannot be ruled out, these data may be best explained in terms of the intermediacy of perepoxide structure A, which decomposes by two paths, ene mode reaction by intramolecular proton transfer and dioxetane mode reaction *via* zwitterion structure B. Protic solvent may decrease the negative charge density on oxygen by hydrogen bonding, thus promoting nucleophilic attack by neighboring sulfur or oxygen. One possible explanation of the aptitude of the sulfides may be found in *β-participation of the mercapto group*, in which sulfur vastly excels oxygen, and which stabilizes the polar zwitterion intermediate in dioxetane formation.

Similar studies on the photosensitized oxidation of 1-ethylthiocyclohexene and 1-ethoxycyclohexene showed only small solvent dependence of product distribution, as shown in Scheme II. The reason is not certain, but conformational or steric factors may be responsible.[16-18]

In addition, when the reaction was carried out in acetone under reflux conditions, the vinyl sulfide I led to equal amount of products of the ene and dioxetane modes. At low temperature, only the products from the dioxetane mode are obtained in both acetone and di-

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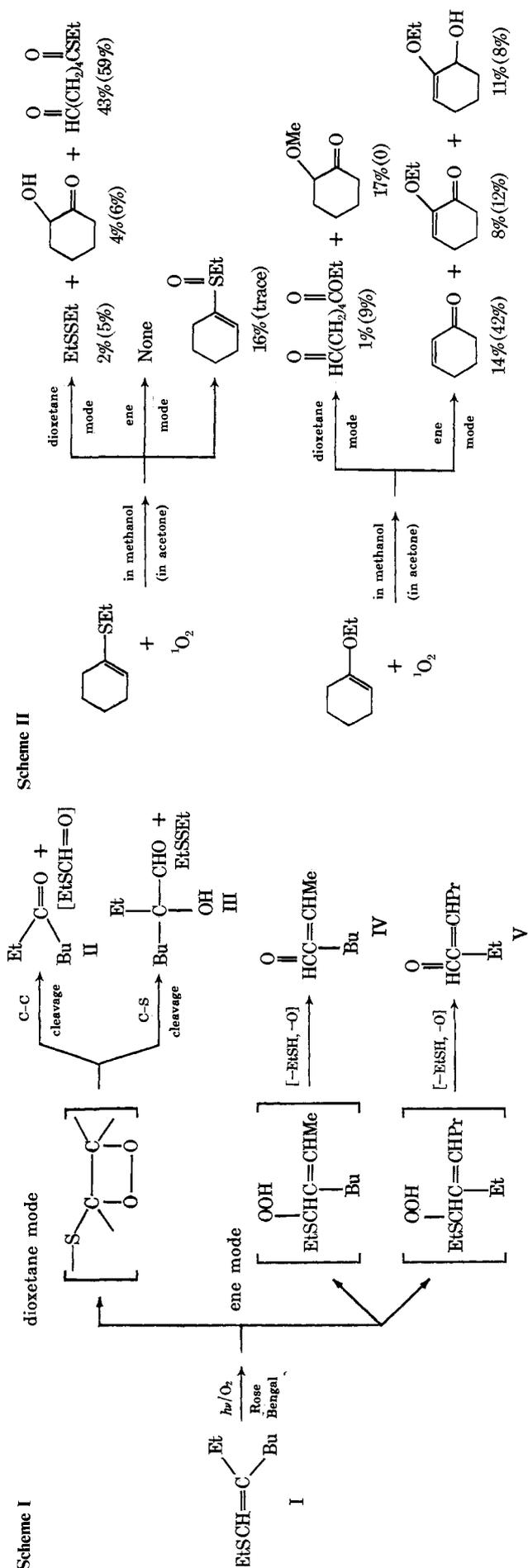(18) K. R. Kopecky and H. Reich, *Can. J. Chem.*, **43**, 2265 (1965).

Scheme II

Scheme I

Table II. Temperature Effect on the Photooxidation of 1-Ethylthio-2-ethylhexene-1 in Acetone

Temp, °C	Relative yields, %	
	Dioxetane mode	Ene mode
56	55	45
20	78	22
−78	100	0

chloromethane (Table II). Under the reaction and analytical conditions, the products are neither isomerized nor destroyed. The surprising temperature dependency for singlet oxygen reaction probably fits a scheme in which the ene mode, which arises from the perepoxide A of vinyl sulfide, stands at higher potential than the dioxetane mode—in contrast to vinyl ether in which dioxetane stands at higher potential than the ene mode by unfavorable stabilization of zwitterion B.

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Matrix Photolysis of 1,2,3-Thiadiazole. On the Possible Involvement of Thiirene

Sir:

The mechanism of the photolysis of 1,2,3-thiadiazole (1) and its derivatives is of considerable interest because of the seemingly unpredictable variation of product structure with changes in substituents[1,2] and the possible involvement of thiirenes[3] in these reactions. Based on chemical trapping experiments, Strausz[3] has concluded that thiirenes are formed as intermediates in the photodecomposition of parent (1) and 5-methyl-1,2,3-thiadiazole. Other workers have proposed that thiadiazole photoproducts arise from reactions of diradicals[1,2,4] and/or thioketenes. This communication describes direct evidence for the formation of thioketene (2) in the photolysis of 1 and implicates thiirene (3) as a precursor to the photoproduct ethynyl mercaptan (4).
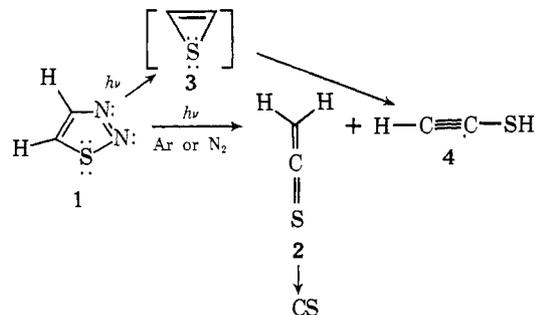

Table I lists the infrared bands observed upon irradiation with a medium-pressure mercury lamp of 50–80-mm samples of 1 (M/R ≡ host/guest ∼500) in an argon or nitrogen matrix using Pyrex filtered light. The most intense band (1760 cm⁻¹) in the spectrum of

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