

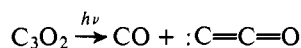
The Reaction of Carbonylcarbene with Cyclic Ethers. Competition between Deoxygenation and Insertion into the Carbon–Oxygen Bond

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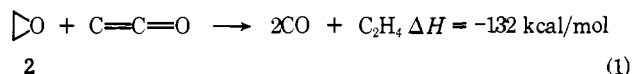
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Abstract: The gas-phase reaction of carbonylcarbene (**1**), generated by photolysis of carbon suboxide, with tetrahydrofuran (THF) proceeds by two competing pathways. One path is the deoxygenation of THF leading to the tetramethylene biradical which closes to cyclobutane and cleaves to two molecules of ethylene. There is also an insertion of **1** into the carbon–oxygen bond of THF which leads, after loss of carbon monoxide, to cyclopentanone. Studies of the reaction of **1** with oxetane have established that carbon–oxygen insertion competes with deoxygenation in this system as well.

The gas-phase photolysis of carbon suboxide at wavelengths between 200 and 300 nm is a convenient method of generating carbonylcarbene (**1**).¹ Carbene **1** is an energetic intermediate which generally reacts with organic substrates to yield products in which the carbon monoxide has been lost. Reactions of **1** with saturated hydrocarbons to yield alkenes² and with olefins to give cumulenes³ have been reported.

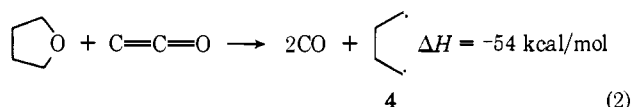


An interesting reaction of **1** is the deoxygenation of oxirane (**2**) to produce ethylene and two molecules of carbon monoxide (eq 1).⁴ Oxetane (**3**) is also deoxygenated in a reaction that is



thought to yield two CO molecules and a vibrationally excited cyclopropane.⁴

Although other carbenes can effect the deoxygenation of oxirane,⁵ this is usually a minor reaction in competition with C–O and C–H insertion. The large thermodynamic driving force for deoxygenations by **1** is undoubtedly the transformation of C₂O to two molecules of CO which releases 156 kcal of energy per mol of C₂O (1Δ) consumed.⁶ An additional impetus for the deoxygenation of **2** is the relief of ring strain accompanying oxygen loss. In view of the marked tendency of **1** to effect deoxygenation, it was of interest to evaluate the efficiency of this reaction in a nonstrained cyclic ether such as THF. The deoxygenation of THF is also a possible route to the interesting tetramethylene biradical, **4**⁶ (eq 2). We now report



an investigation of the gas-phase photolysis of carbon suboxide in the presence of THF. We also present additional facts concerning the mechanism of deoxygenation of oxetane by **1**.

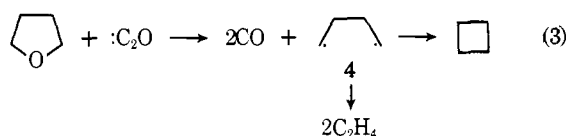
Results and Discussion

Photolysis of Carbon Suboxide in the Presence of THF.

Table I shows the results of the gas-phase photolysis of carbon suboxide and THF under several conditions. Photolysis of THF and C₃O₂ with a medium-pressure mercury lamp through a Vycor filter for 8 h gave ethylene and cyclobutane in a 5:1 ratio along with carbon monoxide. This result is consistent with deoxygenation of THF by **1** to yield the tetramethylene biradical, **4**. Biradical **4** has been observed to cleave to two eth-

ylene molecules in competition with its cyclization to cyclobutane.⁷

However, an examination of the cyclobutane:ethylene ratio as a function of photolysis time indicates that the situation is more complicated than depicted in eq 3. The data in Table I



show that the cyclobutane:ethylene ratio increases with photolysis time, a result which indicates that there must be more than one pathway to cyclobutane and/or ethylene. In accordance with this interpretation, interruption of the photolysis after 1 h leads to the isolation of rather large amounts of cyclopentanone along with smaller yields of ethylene and cyclobutane (Table I).

These results can be rationalized in terms of the reaction sequence in Scheme I involving both deoxygenation and insertion into the C–O bond. An insertion of **1** into the carbon–oxygen bond would initially produce ketene **5** which is expected to photolyze to 2-oxacyclohexanone (**6**) under the reaction conditions. Foster and Agosta⁸ have generated carbene **6** by tosylhydrazone sodium salt thermolysis and report that it rearranges to cyclopentanone and dihydropyran along with small amounts of 4-pentenol. In the present study, cyclopentanone is unstable under the reaction conditions and is photolyzed further to **4** and carbon monoxide. The photolysis of cyclopentanone has been well studied and it is known that the major process is loss of CO to yield ethylene and cyclobutane.^{7,9} In addition, we have established that photolysis of cyclopentanone in an atmosphere of THF, under the reaction conditions, produces ethylene and cyclobutane whose ratio is independent of photolysis time (Table I). Hence, cyclobutane and ethylene are formed by direct deoxygenation of THF and by a car-

Scheme I

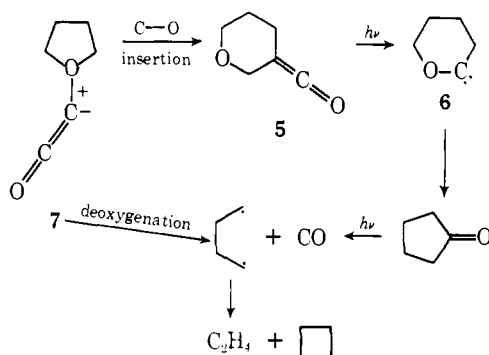








Table I. Product Yields in the Photolysis of Carbon Suboxide with THF

reactants	pressure, mm	photolysis time, h	CO	product yields, mmol			
				C ₂ H ₄			
C ₃ O ₂ + THF ^a	77	8	2.4 × 10 ⁻¹	9.96 × 10 ⁻³	1.44 × 10 ⁻³		0.196
C ₃ O ₂ + THF ^a	77	4		6.14 × 10 ⁻³	1.10 × 10 ⁻³		0.179
C ₃ O ₂ + THF ^a	77	2		5.1 × 10 ⁻³	7.4 × 10 ⁻⁴		0.145
C ₃ O ₂ + THF ^a	77	1		4.5 × 10 ⁻³	5.6 × 10 ⁻⁴	6.4 × 10 ⁻³	0.124
C ₃ O ₂ + THF ^b	44	8	2.0 × 10 ⁻¹	7.8 × 10 ⁻³	1.02 × 10 ⁻³		0.131
 + THF ^c	73.7	1.5		3.34 × 10 ³	1.07 × 10 ⁻³		0.32
 + THF ^c		3		4.94 × 10 ⁻²	1.53 × 10 ⁻²		0.31
 + THF ^c		8		1.08 × 10 ⁻¹	3.46 × 10 ⁻²		0.32

^a Initial quantities: THF = 2.05 mmol, C₃O₂ = 1.9 × 10⁻¹ mmol. ^b Initial quantities: THF = 1.17 mmol, C₃O₂ = 1.08 × 10⁻¹ mmol. ^c Initial quantities: THF = 2.05 mmol, cyclopentanone = 9.9 × 10⁻² mmol.

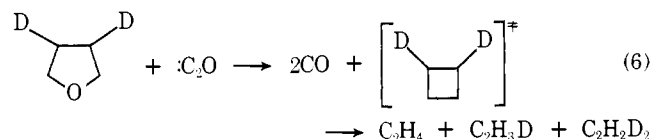
bon-oxygen insertion followed by production of cyclopentanone which subsequently photolyzes.

The possibility that the change in the cyclobutane:ethylene ratio with photolysis time was due to a simple pressure effect was investigated. In both the photolysis of cyclopentanone and the deoxygenation of THF, the cyclobutane:ethylene ratio was observed to increase with increasing pressure and to be represented by the relationship in eq 5 where P is the total pressure

$$\frac{\text{cyclobutane}}{\text{C}_2\text{H}_4} = -\frac{a}{P} + b \quad (5)$$

and a and b are constants. Since the deoxygenation is carried out in a large excess of THF, the total pressure increases only 2% during an 8-h photolysis. A consideration of eq 5 for deoxygenation ($a = 9.3 \times 10^{-3}$ atm, $b = 0.288$) indicates that the cyclobutane:ethylene ratio would increase 1% as a result of increasing pressure during an 8-h photolysis. Since the data in Table I show a 58% increase in this ratio over a 7-h period, a pressure effect alone cannot be responsible and dual mechanisms must be operative.

In Scheme I, direct deoxygenation of THF is postulated to yield biradical **4**. An alternative to the production of **4** is formation of a vibrationally excited cyclobutane which subsequently cleaves to two ethylenes. Since deoxygenation of THF by **1** releases more energy ($\Delta H = -112$ kcal/mol) than is required for cyclobutane cleavage ($\Delta H^\ddagger = 62.5$ kcal/mol),¹⁰ this is a viable mechanism. In order to determine if this mechanism is operative, we have reacted **1** with THF-3,4-*d*₂. Equation 6



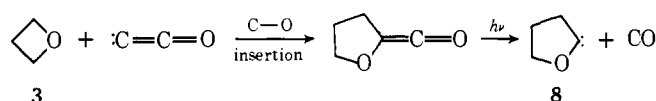
shows that ethylene, ethylene-*d*₁, and ethylene-*d*₂ should be produced if an excited cyclobutane is involved in ethylene formation. However, when carbon suboxide is photolyzed in the presence of THF-3,4-*d*₂, no ethylene-*d*₂ is detected by mass spectrometry. Although these experiments rule out the production of ethylene from an excited cyclobutane, the data do require the intermediacy of biradical **4**. The results are equally consistent with a mechanism involving formation of ethylene and cyclobutane by direct decomposition of ylide **7**. A study of the photolysis of cyclopentanone-2,2,5,5-*d*₄ has established that the ethylene produced does not result from an excited cyclobutane at pressures similar to those in the present study.¹¹

Since these results establish that both direct deoxygenation and insertion into the carbon-oxygen bond are important processes in the reaction of **1** with THF, we have reinvestigated the photolysis of carbon suboxide in the presence of oxetane

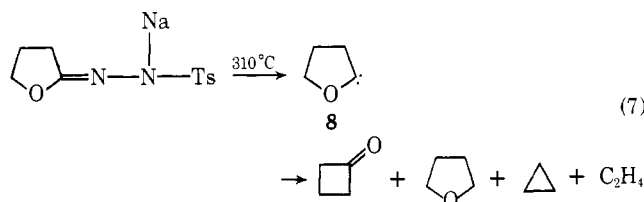
in order to assess the importance of C-O insertion in this system.

Photolysis of Carbon Suboxide in the Presence of Oxetane.

An earlier study of Baker, Kerr, and Trotman-Dickenson⁴ has established that deoxygenation of oxetane to propene and cyclopropane occurs. If a competitive C-O insertion by **1** were operative in this system, it would lead to 2-oxacyclopentanylidene (**8**) after loss of carbon monoxide. Carbene **8** has been

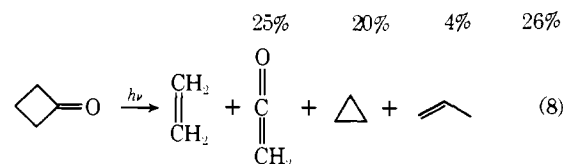


generated by tosylhydrazone sodium salt pyrolysis and observed to rearrange to cyclobutanone and 2,3-dihydrofuran as well as decarbonylate to cyclopropane and fragment to ethylene (eq 7).⁸ Hence, major products of CO insertion by **1**



are expected to be cyclobutanone and ethylene. Indeed, large yields of ethylene were observed previously but cyclobutanone was not reported.⁴

Since cyclobutanone is photolabile under the reaction conditions, its detection presents a problem similar to that encountered in the THF system. The photolysis of cyclobutanone has been well studied and the major products are ethylene, ketene, cyclopropane, and propene (eq 8).¹² Photolysis of cy-







clobutanone in an atmosphere of oxetane under our reaction conditions also yields the products shown in eq 8 (Table II).

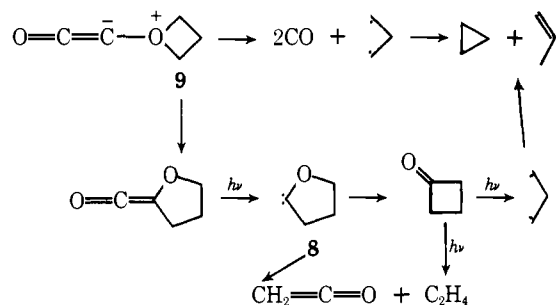
Thus, if cyclobutanone is produced in this system, its photolysis should yield large amounts of ketene and ethylene along with propene and cyclopropane. The propene and cyclopropane will also be produced by direct deoxygenation. Although Baker, Kerr, and Trotman-Dickenson⁴ report high ethylene yields in reaction of **1** with oxetane, they state that ketene would not have been detected if formed under the conditions of their reactions.

In the present study, we have fractionated the reaction

Table II. Product Yields in the Photolysis of Carbon Suboxide with Oxetane

reactants	pressure, mm	photolysis time, min	product yields, mmol					
			CH ₂ =C=O	C ₂ H ₄				
C ₃ O ₂ + oxetane ^a	58.3	30	3.22 × 10 ⁻²	8.5 × 10 ⁻²	4.4 × 10 ⁻³	6.8 × 10 ⁻³	5 × 10 ⁻³	0.66
C ₃ O ₂ + oxetane ^a	58.3	60	4.2 × 10 ⁻²	1.0 × 10 ⁻¹	1.5 × 10 ⁻²	1.33 × 10 ⁻²		1.13
C ₃ O ₂ + oxetane ^a	58.3	90	3.3 × 10 ⁻²	1.7 × 10 ⁻¹	2.6 × 10 ⁻²	2.2 × 10 ⁻²		1.17
cyclobutanone + oxetane ^b	58.4	60	3.2 × 10 ⁻²	6.7 × 10 ⁻²	5.6 × 10 ⁻²	1.5 × 10 ⁻³		3.51

^a Initial quantities: oxetane = 1.43 mmol, C₃O₂ = 2.86 × 10⁻¹ mmol. ^b Initial quantities: oxetane = 1.57 mmol, cyclobutanone = 1.43 × 10⁻¹ mmol.

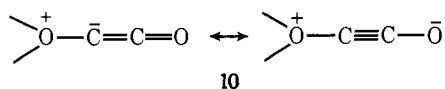
Scheme II

mixture on a vacuum line and conclusively identified ketene by IR spectroscopy. Although the ketene is photolabile, it has been quantitated by IR and its yield along with that of the other products is shown in Table II. The detection of ketene in this system provides good evidence for the formation of carbene **8**. Since **8** has been shown to fragment to ethylene and (presumably) ketene,⁸ it is of interest to know if cyclobutanone is actually formed in this system or if the ethylene and ketene are simply a result of fragmentation of **8**.

When the photolysis is stopped after 0.5 h, cyclobutanone is conclusively identified by GC-mass spectrometry (Table II). Thus the cyclopropane and propylene produced in this system should arise by two competing processes: direct deoxygenation and photolysis of cyclobutanone. If this is the case, the two processes should have different energetics and yield different ratios of cyclopropane:propylene. Since the ratio of cyclopropane:propylene is larger for the direct photolysis of cyclobutanone than for the reaction of **1** with **3**, this ratio is expected to increase as photofragmentation of cyclobutanone becomes more important. The data in Table II show that the cyclopropane:propylene ratio increases with increasing photolysis time as predicted. We propose the sequence shown in Scheme II for the reaction of **1** with oxetane.

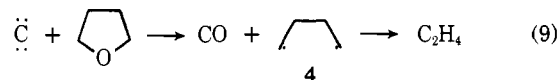
It has recently been pointed out¹³ that the three pathways by which carbenes react with ethers are C-H insertion, C-O insertion, and cleavage of one of the groups from the ether. In the present study, C-O insertion and deoxygenation via cleavage of both of the ether bonds predominate. Products of C-H insertion are not observed.

In Schemes I and II we have depicted both deoxygenation and C-O insertion as arising from a common ylide intermediate (**7** and **9**). Similar ylides have been implicated in the reactions of other carbenes with ethers.^{13,14} The corresponding sulfur ylides have been isolated when carbenes are reacted with sulfides.¹⁵ Carbene **1** should readily accept electrons from an ether oxygen to form an ylide in which the negative charge is delocalized (e.g., **10**). The stability of ylides **7** and **9** may ex-



plain the preference of **1** for attack on oxygen over C-H insertion.

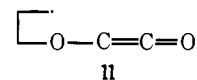
The deoxygenations observed in these experiments are reminiscent of deoxygenations of cyclic ethers by atomic carbon.¹⁶ Skell, Plonka, and Engel¹⁷ report that carbon atoms deoxygenate THF to yield ethylene and carbon monoxide (eq 9). The absence of cyclobutane as a product of the carbon



deoxygenation was ascribed to the large exothermicity of the reaction ($\Delta H = -122$ kcal/mol for C(¹D)) which results in the production of a hot biradical in which cleavage is favored over closure.¹⁸ That the ratio of cleavage to closure in these reactions is dependent on the exothermicity was demonstrated by Klabunde and Skell,¹⁹ who observed that the carbon atom desulfurization of tetrahydrothiophene, which is 59 kcal/mol less exothermic than the deoxygenation, resulted in a 0.1:1 ratio of cyclobutane:ethylene.

Since the deoxygenation of THF is carried out in the gas phase in the present study and in the condensed phase at -196 °C in the carbon atom reactions, the ratio of cleavage to closure in the different systems cannot be directly compared. However, the deoxygenation in Scheme I is the least exothermic of the three reactions and shows the smallest percentage of cleavage.

The ratio of cyclopropane:propene of 1.13 observed here for a 1-h photolysis of carbon suboxide and oxetane at a pressure of 58 mm is in agreement with that reported previously for a photolysis at 50 mm for an unspecified length of time (cyclopropane:propene = 1.0).⁴ However, deoxygenation of oxetane by atomic carbon gives a far higher cyclopropane:propene ratio (4.0) than is observed here.¹⁸ The reason for this difference is not clear at this time. Deoxygenation of oxetane by **1** is a complex process and could well involve a biradical intermediate such as **11** which may undergo a substantial amount of cleav-



age to propylene and two molecules of carbon monoxide.

Experimental Section

General. Infrared spectra were recorded on gaseous samples with a Perkin-Elmer Model 621. Mass spectra were recorded on a Du Pont 491 B spectrometer. NMR spectra were measured on a Varian EM-390 spectrometer. THF, oxetane, cyclopentanone, and cyclobutanone were commercial samples which were degassed and vacuum transferred prior to photolysis.

Carbon suboxide was prepared by the P₂O₅-promoted dehydration of malonic acid.²⁰ It was found that C₃O₂ could be efficiently purified by vacuum distillation from -78 to -115 °C. The material trapped at -115 °C was pumped until its IR spectrum showed that it was free of carbon dioxide.

Tetrahydrofuran-3,4-d₂. This material was prepared by diimide reduction of 2,5-dihydrofuran. Dipotassium azocarboxylate²¹ (70 g, 0.35 mol), 2,5-dihydrofuran (5 g, 0.07 mol), and dry Me₂SO (300 mL) were placed in a 1-L three-necked flask. To this stirred mixture, under N₂, was added 70 g (1.16 mol) acetic acid-*O-d* over a period of 3 h. The reaction mixture was filtered and distilled at 25 mm to a pot

temperature of 80 °C. The NMR spectrum of the distillate showed that THF-3,4-*d*₂ comprised 68% of the sample and that the remainder was mainly 2,5-dihydrofuran.

The mixture of THF-*d*₂ and 2,5-dihydrofuran (~1.5 mL) was dissolved in 10 mL of octane and 1 mL of pyridine. This mixture was brominated at 0 °C by the dropwise addition of 12 mL of a 20% solution of Br₂ in octane. The THF-*d*₂ was then separated from the 3,4-dibromotetrahydrofuran by vacuum transfer. Distillation of the THF-*d*₂ through a 6-in. Vigreux column followed by vacuum distillation from -40 to -196 °C gave a material shown to be pure THF by its NMR spectrum. The NMR showed this THF to be 78% deuterated at the 3,4 positions.

Photolysis of Carbon Suboxide and THF. The appropriate quantities of reagents were vacuum transferred to a 499-mL photolysis flask and irradiated at ambient temperature with Vycor-filtered light from a Hanovia 200-W medium-pressure mercury arc.

After photolysis, the flask was cooled to -196 °C and the carbon monoxide pumped into an activated charcoal trap at -196 °C. The CO was then quantitated by GC on a 12-ft 13X molecular sieves column at room temperature. The remaining products were then pumped through a 2 ft X 0.25 in. column containing 20% AgNO₃/ethylene glycol on 40/60 firebrick at 0 °C (this removes THF and C₃O₂) and analyzed for ethylene and cyclobutane by GC on a 20-ft dimethylsulfolane (DMS) column at room temperature.

In runs where cyclopentanone was analyzed, cyclohexanone was added as an internal standard immediately after photolysis. The reaction mixture was passed, under vacuum, into a trap at -115 °C. The material not volatile at this temperature was analyzed by gas chromatography on an SE-30 column. The GC was interfaced with a mass spectrometer and cyclopentanone was identified by comparison of its mass spectrum with that of an authentic sample. Although 3,4-dihydropyran and 4-pentenal could be separated from other products by gas chromatography, neither was detected in the reaction mixture. The 3,4-dihydropyran was found to be stable to photolysis under the conditions of the reaction. The 4-pentenal, however, was photolabile under the reaction conditions and would not have been detected if formed in quantities of less than 2×10^{-3} mmol.

In addition to the experiments summarized in Table I, the effect of pressure on the cyclobutane:ethylene ratio over a range of 0.05-0.1 atm was measured. In this pressure range, the cyclobutane:ethylene ratio was given by eq 5 where $a = 9.3 \times 10^{-3}$ atm and $b = 0.288$.

Photolysis of Carbon Suboxide and THF-3,4-*d*₂. This reaction was carried out as described for the undeuterated compound using 1.22 mmol of THF-3,4-*d*₂ and 4.5×10^{-1} mmol of C₃O₂ in an 8-h photolysis. The fraction containing the ethylene was separated as described above and analyzed by mass spectrometry. The mass spectrum showed a large peak for C₂H₃D at *m/e* 29 but no C₂H₂D₂ at *m/e* 30.

Photolysis of Cyclopentanone and THF. This photolysis was carried out under identical conditions with those described for THF and C₃O₂.

The ethylene and cyclobutane were analyzed as described above. The results of several experiments are listed in Table I. An investigation of the effect of total pressure over the range 0.05-0.1 atm showed that the cyclobutane:ethylene ratio was given by eq 5 where $a = 6.5 \times 10^{-3}$ atm and $b = 0.376$.

Photolysis of Carbon Suboxide and 3. This photolysis was carried out as described above. Products were distilled from -115 to -196 °C under vacuum. The products volatile at 115 °C were analyzed for ketene and ethylene by IR and for propylene and cyclopropane by GC on a 20-ft DMS column. The material not volatile at -115 °C was analyzed for cyclobutanone by GC-mass spectrometry as described above.

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A CIDNP Study of the Decomposition of Aryldiazenes

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Abstract: Phenyl diazene (**1a**) and *p*-nitrophenyl diazene (**1b**) have been prepared by sodium borohydride reduction of the corresponding aryldiazonium salts, by decarboxylation of aryldiazene carboxylic acids, and by a new method involving hydride transfer from cycloheptatriene to diazonium ions. The decompositions of **1a** and **1b** are accompanied by nuclear polarization (CIDNP). An analysis of the CIDNP signals indicates that spin selection occurs in an aryl radical-arylhydrazyl singlet radical pair. The precursor to this radical pair is postulated to be a pair consisting of an aryldiazanyl radical and an arylhydrazyl radical formed by hydrogen atom transfer between two molecules of aryldiazene.

Aryldiazenes (ArN=NH, **1**) are interesting labile intermediates which have recently been prepared by a number of techniques. Methods of synthesizing **1** include the decarbox-

ylation of aryldiazene carboxylic acids,¹ sodium borohydride reduction of diazonium ions,² oxidation of hydrazines,³ displacement from metal complexes,⁴ and base-induced decom-