ternal motions in a wide variety of compounds containing two or three aromatic rings attached to a central atom. This systematic approach has disclosed that some of the data reported in the literature are consistent with several interconversion mechanisms not previously considered.

We are of the opinion that only a complete and exhaustive analysis is capable of disentangling the often complex web of mechanistic alternatives, and that any approach other than a systematic one is bound to be superficial by comparison, and therefore prone to error. What might be a formidable task is however rendered less arduous through the use of graphical representations.

In order to provide a rigorous treatment, the scope of this study has necessarily been restricted to include a somewhat limited set of compounds. For example, this analysis requires that the aryl rings of the compound under study assume a case III orientation so as to generate a propeller-shaped molecule and that the X and Y ligands have local conical symmetry as described above. In addition, the only allowable torsional mechanisms for interconversions are the flip mechanisms wherein the rotation of one aryl group is concurrent with that of the others. Thus, for any proposed study it must be demonstrated that the class of compounds being investigated actually fulfills the above conditions before the analysis presented here may properly be utilized.

There are many classes of compounds which are obviously similar to those belonging to systems described in this work, but which lack one or more of the attributes required for inclusion within the present framework of analysis.[61] Some examples are certain di- and triaryl compounds with bridged ring systems (*e.g.*, 9-arylfluorenes), and various monoaryl systems such as substituted acetophenones and substituted toluenes. Although these classes of compounds do not strictly fall within the scope of the formal analysis presented here, isomerism and isomerization of such compounds may nevertheless be analyzed in a similar manner. In some cases, only a slight modification of the scheme presented here may be needed, whereas in others, more extensive changes may be required. It must be stressed, however, that the matter of basic importance is not so much the formal analysis as it is the methodology, *i.e.*, the general, systematic, and exhaustive procedure which employs graphical representations where necessary for purposes of clarity and convenience.

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(61) Two classes especially closely related to the systems discussed here are compounds of the type Ar_2 (the biaryls) and Ar_4Z. Biaryls may be readily analyzed using the general procedures outlined in this paper. The maximum number of isomers for the Ar_2 system is four, and the only mechanisms for isomerization are analogous to the zero-ring flip (with a planar transition state), and the one-ring flip (with the two aryl groups perpendicular in the transition state.)[10] Analysis of Ar_4Z systems is considerably more complicated and will be the subject of a later report.

Deoxygenation and Desulfurization of Cyclic Ethers and Thioethers by Carbon Atoms. Intermediates with Excess Energy in a Low-Temperature Matrix[1]

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Abstract: Singlet carbon atoms react with cyclic ethers to give carbon monoxide and diradical species. Cyclic thioethers react with singlet carbon atoms to give carbon monosulfide (CS) and diradicals. While both deoxygenation and desulfurization are facile processes, the deoxygenation reaction is more exothermic; this exothermicity difference is manifest in the more frequent occurrence in deoxygenations of fragmentations and hydrogen expulsion. These energetic reactions take place in a frozen matrix.

Many interesting reactive intermediates have been generated at low temperature by the reaction of carbon atoms with various organic compounds. The removal of oxygen or sulfur from organic compounds by carbon atoms has been a useful reaction in this respect,[1] and both reactions occur with about equal efficiencies.[1a] Deoxygenation is a highly exothermic process (ΔH = 85–100 kcal/mol) on the basis of bond energies. Desulfurization of thioethers is also an exothermic reaction (ΔH = 45 kcal/mol) on the basis of bond energies, but not to the extent of deoxygenation.[1] When dealing with such exothermicities, a pivotal consideration is the fate of the excess energy. In most chemical reactions, the exothermicity is manifest as vibrational excitation of the intermediate species and products. In previously investigated reactions of atomic carbon with carbonyl compounds,[4] no evidence

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(1) Preliminary communications concerning this and related work have appeared; see (a) K. J. Klabunde and P. S. Skell, *J. Amer. Chem. Soc.*, **93**, 3807 (1971); (b) P. S. Skell, J. H. Plonka, and R. R. Engel, *ibid.*, **89**, 1748 (1967); (c) J. H. Plonka and P. S. Skell, *Chem. Commun.*, 1108 (1970); (d) P. S. Skell, K. J. Klabunde, and J. H. Plonka, *ibid.*, 1109 (1970).

(2) University of North Dakota.

(3) National Institutes of Health Predoctoral Fellow, 1967–1970.

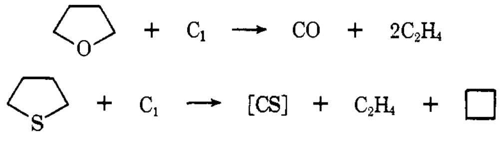
(4) P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 836 (1970).

was obtained for the intermediacy of a vibrationally excited carbene fragment. This result suggested that the excitation of the fragments was either transferred

$$R_1R_2C{=}O + C_1 \longrightarrow CO + R_1R_2C:$$

to the frozen matrix or localized in the carbon monoxide.[5]

In our preliminary work with ethers and thioethers[1] it was observed that the deoxygenation of tetrahydrofuran did not yield cyclobutane as a reaction product; only internal fragmentation yielding two molecules of ethylene was observed. However, the desulfurization of tetrahydrothiophene did produce some cyclobutane as a product.[1a] The presence of the coupling product (cyclobutane) from the sulfur analog but not the oxygen analog implied that the higher exothermicity of deoxygenation was indeed capable of producing different competitive rates of fragmentation in a frozen matrix. A similar and additional variation was observed on deoxygenation of *cis*-2-butene oxide and desulfurization of *cis*-2,3-dimethyl episulfide. The epoxide deoxygenated to give *cis*- and *trans*-2-butenes in a ratio of 1.5 : 1 while the sulfur compound gave a 6.7 : 1 ratio. This observation can be explained by a higher population of excited olefin intermediates thereby resulting in greater isomerization from the more energetic mode of generation.



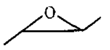
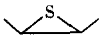
Since "hot" reactions occur in the cyclic ethers and to a lesser extent with the corresponding sulfur compounds, low-temperature condensed phase deoxygenations and desulfurizations were carried out to obtain additional information regarding this difference. This paper reports the results of that investigation.

Results and Discussion

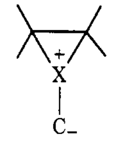
A. Epoxides and Episulfides. When *cis*- and *trans*-2-butene oxide were codeposited at a liquid nitrogen cooled surface with arc generated carbon atoms, a mixture of *cis*- and *trans*-2-butene, carbon monoxide, 1,3-butadiene, and molecular hydrogen was produced. The reaction of *cis*-2,3-dimethyl episulfide with carbon atoms under the same conditions yielded CS polymer and both 2-butenes without the production of butadiene or hydrogen. Table I presents a comparison of the C_4 hydrocarbon yields from the three-membered ring compounds studied. These data (Table I) reveal two differences between deoxygenation and desulfurization: desulfurization is more stereoselective, and the elimination of molecular hydrogen to form butadiene is only observed in deoxygenation.

Deoxygenation and desulfurization are envisioned as occurring from ylide intermediates I produced by the interaction of the electrophilic carbon atom and a pair of nonbonded electrons from the heteroatom. The leaving molecule (CO or CS) results from the decomposition of I.[6] Application of the orbital symmetry rules to the decomposition of I[7] requires that the eventual olefin formation, in which the carbon–heteroatom bonds of the ring are broken, occur in a stepwise manner. This mechanism would yield a geometrically distorted olefin which then produces the observed isomerization. The lower degree of isomerization in the sulfur case would be attributed to a shorter lifetime for the open-chain intermediate II and/or a lower energy content of the excited olefin species III.

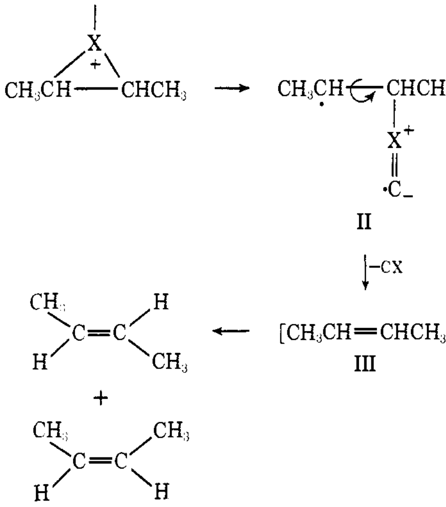
Table I. Epoxides and Episulfides with Carbon Atoms

Substrate	Absolute yields of products shown[a]	Distribution: *cis*-2-Butene	Distribution: *trans*-2-Butene	Distribution: Butadiene
	58[b]	39	55	6
	62[c]	53	40	7
	85	87	13	0

[a] mmol of products/mmol of C_1 assuming 40% of the carbon vaporized is monatomic (*cf.* ref 4 and references therein and Experimental Section). [b] 62% carbon monoxide, 8% hydrogen. [c] 70% carbon monoxide, 8% hydrogen.



I, X = O or S



The presence of butadiene and hydrogen in the product mixture suggests that the "hot" intermediate (II or III) contains sufficient energy to expel molecular hydrogen more rapidly than it can transfer excess energy to the condensed reaction medium. The expulsion of hydrogen from hydrocarbons has an activation energy of 60 kcal/mol.[8] While this value is less than the exothermicity of deoxygenation (85–100 kcal/mol), it is

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(5) The first possibility is most likely. We have observed that cyclopropylcarbenes may fragment at a rate which is competitive with the rate of energy transfer to the frozen matrix when such species are produced under deoxygenative conditions. Ring strain must be important in increasing the rate of fragmentation. Similar findings are pointed out later in this paper. For further discussion *cf.* P. S. Skell and J. H. Plonka, *Tetrahedron*, **28**, 3571 (1972).

(6) Recently a similar reaction where X = NH has been observed: J. Villaume and P. S. Skell, *J. Amer. Chem. Soc.*, **94**, 3455 (1972).

(7) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

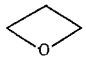
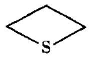
(8) D. W. Vanus and W. D. Walters, *J. Amer. Chem. Soc.*, **83**, 1324 (1961).

greater than the estimated exothermicity of the corresponding desulfurization (45 kcal/mol). By this reasoning, desulfurization should not lead to hydrogen expulsion while deoxygenation may; this is the observed behavior. The ability of the reaction exothermicity to persist in the condensed phase is interesting. Good mechanical coupling to the medium could lead to deexcitation in 10^{-13} sec. It appears that in the condensed phase reactions discussed in this work there is sufficient energy content in the intermediate species, and sufficiently poor coupling to the surrounding medium that the rate of deexcitation and decomposition can be competitive.

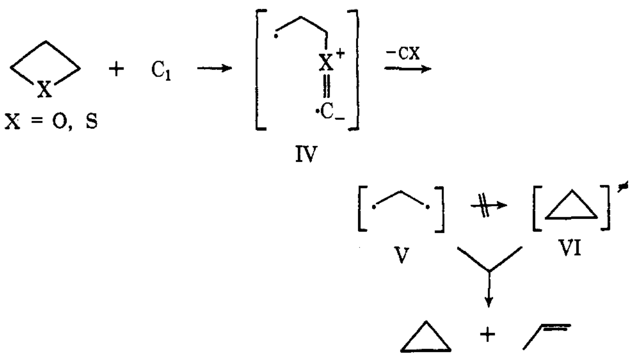
To eliminate the possibility that these reactions were occurring in a dense vapor layer just outside the frozen matrix, *trans*-2-butene oxide was frozen to the walls of the reaction flask and, with a pressure of 4×10^{-5} Torr in the reactor, carbon atoms were impinged on the surface. This layering experiment yielded very similar results compared with the normal simultaneous deposition experiments, and butadiene was still a product (5%), as was 2-butene (trans:cis, 53:42%, respectively). Thus, within experimental error deoxygenation of a frozen matrix of *trans*-2-butene oxide was identical with that found in a continuous deposition experiment with its ill-defined temperature gradient at the condensation surface.

B. Trimethylene Systems. The deoxygenation of trimethylene oxide and the desulfurization of trimethylene sulfide both proceed *via* trimethylene species.[1d] As in the examples presented above, evidence for the intermediacy of an excited species (in this case trimethylene) was obtained. Table II indicates the yields of the two important products from these studies, cyclopropane and propylene. The cyclopropane:propylene ratio from deoxygenation was 4.0 while this ratio for desulfurization was 10. Since the conversion of cyclopropane to propylene has an activation energy of 65 kcal/mol,[9] it would be expected that considerable conversion to propylene would take place in the case of trimethylene oxide, but not in the case of desulfurization. Of course, the question of exact mechanism is of interest here, and the formation of an excited cyclopropane (VI) is not a requirement since propylene could be formed as a consequence of rearrangement in IV or V. To obtain information bearing on this question, two additional four-membered ring compounds were synthesized and reacted with carbon atoms. These compounds are 3,3-dimethyltrimethylene oxide and 3,3-dimethyltrimethylene sulfide. The rationale was that if an excited cyclopropane was formed in these cases, it could cleave two different ways to yield different olefins. (Of course 1,1-dimethylcyclopropane would be an important product in any case, so it is not included in Scheme I.) Table III shows that only 2-methyl-1-butene (VII) and 1,1-dimethylcyclopropane were formed. The other pentene isomers were not formed. Therefore VIII must not be formed.

Table II. Trimethylene Oxide and Sulfide with Carbon Atoms

Substrate	Absolute yields of products shown[a]	Distribution: $c\text{-}C_3H_6$	Distribution: $H_2C{=}CHCH_3$
 O	39	80	20
 S	48	91	9

[a] *Cf.* footnote *a*, Table I.



Scheme I

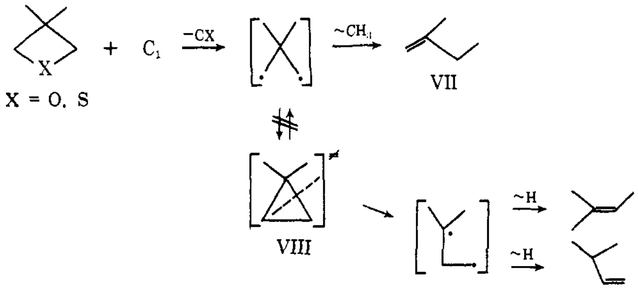
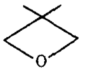
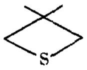


Table III. 3,3-Dimethyltrimethylene Oxide and Sulfide with Carbon Atoms

Substrate	Absolute yields of products shown[a,b]	Distribution: 1,1-Dimethylcyclopropane	Distribution: 2-Methyl-1-butene
 O	7.4	96.5	3.5
 S	7.5	100	Trace

[a] *Cf.* footnote *a*, Table I. [b] These yields are low because small amounts of substrate were available, and therefore high dilution experiments were not carried out.

Note from Table III that the cyclopropane:olefin ratio is higher for desulfurization, again expected in accord with exothermicity considerations.

Since it was of interest to determine the stereochemistry of cyclopropane formation, *trans*-2,4-dimethyltrimethylene oxide and sulfide were synthesized and allowed to react with carbon atoms.[1d] The results are shown below and were somewhat predictable. Cyclopropane formation from deoxygenation is nonstereospecific, while a bit more stereospecificity was found for desulfurization. Hydrogen elimination must be quite facile with these systems since the 1,3-pentadienes were

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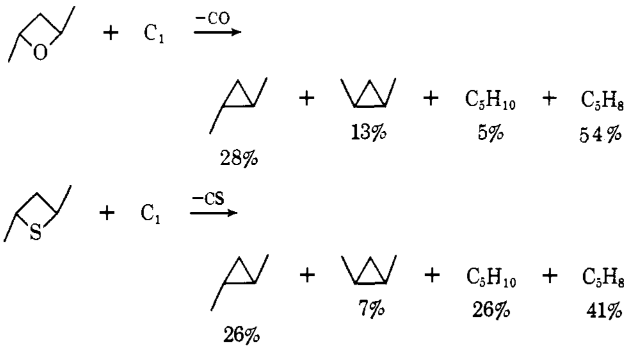
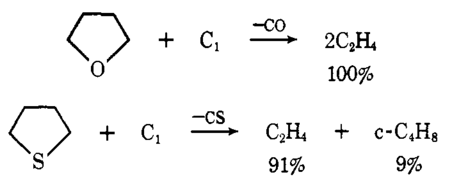
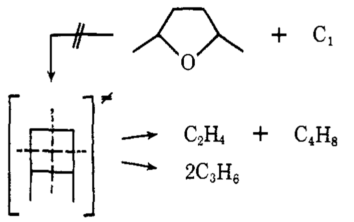
[9] W. E. Falconer, T. F. Hunter, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 609 (1961).

the major products from deoxygenation, less from desulfurization, but still substantial.[10]



C. Tetramethylene Systems. Previous work has demonstrated the difference between tetrahydrofuran (THF) and tetrahydrothiophene (THT) with carbon atoms.[1a,b] These reactions proceed through tetramethylene species to yield ethylene although desulfurization does give a small amount of cyclobutane. In this system it was of interest to determine if "hot" cyclobutane was formed.[11] This possibility was examined through the deoxygenation of 2,5-dimethyltetrahydrofuran since, if a "hot" cyclobutane were involved, ethylene and 2-butene as well as propylene would appear in the product mixture. When 2,5-dimethyltetrahydrofuran and carbon vapor were condensed at liquid nitrogen temperature simultaneously with carbon atoms, only propylene was produced as a product of deoxygenation. This result excludes the intervention of "hot" cyclobutane molecule in the deoxygenation of tetrahydrofurans and supports the intermediacy of a tetramethylene.

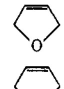
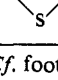




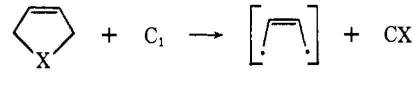
The stereochemistry of olefin formation from tetramethylene cleavage was probed by deoxygenating *cis*-2,3-dimethyltetrahydrofuran. When this ether and carbon atoms were codeposited at a liquid nitrogen cooled surface, ethylene, *cis*- and *trans*-2-butene, and carbon monoxide were produced; the cis:trans ratio was 1:2. This result is consistent with the intermediacy of a tetramethylene species which has sufficient lifetime to undergo rotation about the C_1–C_2 axis before cleavage of the bond between the C_2–C_3 positions, or an open intermediate to which CO is still attached. The high degree of fragmentation observed here may not be totally attributable to exothermicity since recent calculations suggest that the conversion of tetramethylene to two olefin molecules has a very low activation energy barrier.[12]

The technique of deoxygenation and desulfurization may be utilized to generate dehydrotetramethylenes from dihydrofuran and dihydrothiophene. A comparison of the carbon atom chemistry of these two materials provides an excellent example of the role played by excitation of the intermediate species. Table IV presents the product distributions resulting from the reactions of 2,5-dihydrofuran and 2,5-dihydrothiophene with carbon atoms. These reactions, by analogy to the THF series, yield the butenediyl diradical. In the oxygenated system, the expected butadiene was formed, but not as the major product. Instead, the excited dehydrotetramethylene decomposed to give two molecules of acetylene and a molecule of hydrogen. In the sulfur compound, only butadiene was present as a product of desulfurization.[13,14] Cyclobutene was not found in either of these investigations.

Table IV. Dihydrofuran and Dihydrothiophene with Carbon Atoms

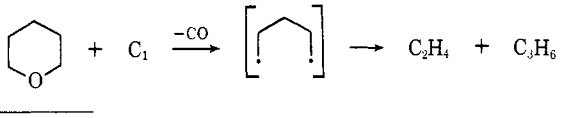
Substrate	Absolute yields of products shown[a]	Distribution	
		C_2H_2	C_4H_6
	$37^{b,13}$	75	25
	43^{13}		100

[a] *Cf.* footnote *a*, Table I. [b] 40 mol % CO, 46 mol % H_2.



X = O, S

D. Pentamethylene Systems. The pentamethylene diradical was generated by the deoxygenation of pentamethylene oxide (PMO) and the desulfurization of pentamethylene sulfide (PMS). Table V presents a comparison of the product yields from the reactions of PMO and PMS with carbon atoms. A noticeable distinction exists in the major product forming pathway. The deoxygenation of PMO led to internal cleavage which yielded ethylene, propylene, and cyclopropane.



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(10) Total product yields were not considered reliable and are not reported since small amounts of substrates were available and, thus, ratios of substrate to carbon could not be maintained 50:1 or greater.

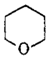
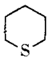
(11) The activation energy for cyclobutane–ethylene conversion is 62.5 kcal/mol; see R. W. Carr and W. D. Walters, *J. Phys. Chem.*, **67**, 1370 (1963). As seen above, such a barrier is not insurmountable under deoxygenative conditions.

(12) R. Hoffmann, S. Swaninathan, B. G. Odell, and R. Gleiter, *J. Amer. Chem. Soc.*, **92**, 7091 (1970).

(13) Because C_2 is produced simultaneously with C_1 in the arc technique, some of the acetylene (and ethylene) present was derived from C_2 (see P. S. Skell and J. H. Plonka, *J. Amer. Chem. Soc.*, **92**, 5620 (1970)); however, the yield of acetylene from C_2 is reasonably constant over a variety of substrates. Thus, acetylene produced in excess of 21% of the carbon vaporized (weight %) was attributed to deoxygenation in the case of 2,5-dihydrofuran. In this study the total yield of acetylene was much higher than for any other substrates. Similar considerations put the C_2 ethylene yield at 2%. Corrected yields are used.

(14) The photolysis of 3,4-cyclopentenone, a reaction which may also involve the same diradical, yields only butadiene, a decarbonylation product with no mention of acetylene formation: see L. D. Hess, Ph.D. Thesis, University of California at Riverside, 1965.

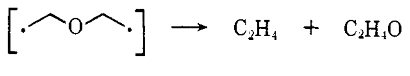
Table V. Pentamethylene Oxide and Pentamethylene Sulfide with Carbon Atoms

Substrate	Absolute yield of products shown[a]	Distribution C_2H_4[18]	C_3H_6	C_5H_8	c-C_5H_{10}	C_5H_{10}	C_5H_{12}
	38	73	17[b]	4[c]	2	3[e]	1
	15	50	9[b]	14[d]	6	20[f]	2

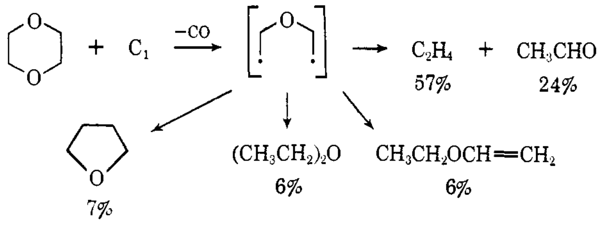
[a] *Cf.* footnote *a*, Table I. [b] Combined propylene and cyclopropane. The ratio of propylene:cyclopropane for pentamethylene oxide was 5.4; for pentamethylene sulfide, 3.5. We do not understand why the C_3H_6 yield was so much smaller than the C_2H_4 yield. Other known reaction pathways that use up the C_3H_6 fragment are probable. However, the C_3H_6 yields are still quite large when compared with other arc carbon studies, and it is certain that much fragmentation took place to yield these products. [c] Trans:cis = 4.2. [d] Trans:cis = 1.6. [e] 67% 1-pentene, 8% *trans*-2-pentene, 24% *cis*-2-pentene. [f] 94% 1-pentene, 3% *trans*-2-pentene, 3% *cis*-2-pentene.

The sulfur compound (PMS) underwent a smaller amount of cleavage and gave more cyclopentane, the diradical coupling product. Also, the sulfur substrate yielded much more pentene, which was almost all 1-pentene, presumably from 1,4-hydrogen transfer in the diradical or in the open form intermediate with CX attached, and more pentadiene. Thus, in the more energetic deoxygenation to produce pentamethylene, cleavage of the intermediate is more important than in the desulfurization reaction.[15]

The deoxygenation of *p*-dioxane should produce the 3-oxapentamethylene diradical which, by analogy, would be expected to undergo a β-scission reaction to



form ethylene and acetaldehyde.[16] Indeed, when *p*-dioxane was codeposited with carbon atoms on a liquid nitrogen cooled surface, ethylene and acetaldehyde were the major reaction products. However, the yields of these two materials should have been the same, but they were not. It is possible that the oxygen containing fragment yielded other products that were not detected in this work (perhaps scavenging by unsaturated species in the system yielded nonvolatile products).[13]



Conclusions

The exothermicity inherent in carbon atom deoxygenations and desulfurization leaves its imprint on product distribution. Reactive diradical intermediate species, *to which CO or CS may or may not be attached*, have long enough lifetimes in a low-temperature matrix to allow various energetic fragmentation reactions to occur.

Experimental Section

The reactor system and methodology employed for arc carbon reactions have been previously described[17,18] and are not repeated here. The substrates were vaporized under vacuum and deposited on the inside of a liquid nitrogen cooled cylindrical glass reactor while carbon electrodes were intermittently touched together manually so that arcing (16 V) took place. The carbon vapor deposited in the same region as the substrate. Usually 1–2 mg of carbon was vaporized per minute while 0.2–1.0 g of substrate was deposited. If small amounts of substrate were available, slower depositions were employed, resulting in smaller substrate to carbon ratios; under these conditions (less than 50:1) absolute product yields were unreliable and low. Table VI summarizes the experimental conditions for each substrate, and thus complements the data presented in the tables in the text. It should be noted that any absolute yields presented throughout the paper are corrected for reactor geometry (only 70% of the carbon vaporized reaches the reactor zone due to the obstructions by electrode supports, etc.), and the fact that 40% of the carbon is C_1.

Table VI. Reaction Conditions for Carbon Atom Reactions (−196°)

Substrate	Amount, g	Carbon vaporized, mg	Approximate reaction time, min
cis-2,3-Dimethyl episulfide	4.0	35	20
Trimethylene oxide	5.0	20	20
Trimethylene sulfide	5.0	73	25
trans-2,4-Dimethyltrimethylene oxide	1.5	20	30
trans-2,4-Dimethyltrimethylene sulfide	0.1	18	15
3,3-Dimethyltrimethylene oxide	1.2	28	15
3,3-Dimethyltrimethylene sulfide	1.4	29	15
Tetrahydrothiophene	5.0	29	25
Dihydrofuran	10.0	22	25
Dihydrothiophene	3.0	32	15
cis-2,5-Dimethyltetrahydrofuran	8.0	23	25
cis-2,3-Dimethyltetrahydrofuran	3.0	18	15
Pentamethylene oxide	8.0	25	30
Pentamethylene sulfide	8.0	42	20
p-Dioxane	8.0	29	20

Products were isolated by trap-to-trap distillation under vacuum followed by gas chromatography. Their identification was ac-

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(15) The photodecarbonylation of cyclohexanone is also known to yield ethylene and propylene in a reaction which may involve the intermediacy of pentamethylene: see R. Srinivasan, *Advan. Photochem.*, **1**, 83 (1963).

(16) The nature of the initially formed C_2H_4O species is not known. If it is a vibrationally excited ethylene oxide, it isomerizes to acetaldehyde more rapidly than it is stabilized under these conditions. No ethylene oxide was ever found in these reactions, although an authentic sample of this material could be quantitatively recovered under the conditions employed.

(17) For a description of the reactor, see P. S. Skell, L. D. Wescott, Jr., J. P. Golstein, and R. R. Engel, *J. Amer. Chem. Soc.*, **87**, 2829 (1965).

(18) For a description of the reaction procedure, see P. S. Skell and J. H. Plonka, *ibid.*, **92**, 5620 (1970).

complished by a comparison of the retention times and spectral properties with those of authentic samples. After PV measurements, C_2–C_4 hydrocarbon gases were vpc analyzed on a 30 ft × 0.25 in. hexanedione column at 0°, while C_5 hydrocarbons were analyzed on a 10 ft × 0.25 in. propylene carbonate column at 0°. A 10 ft × 0.25 in. silicone rubber column at 25° was used for higher boiling materials, and in some cases a Carbowax column at 80° was employed.

Permanent gases were collected, measured, and identified in two different ways. The first technique employed a sealed evacuated reactor which was connected to a $-196°$ trap followed by another $-196°$ trap filled with thoroughly degassed silica gel followed by a Toepler pump. Upon carbon arcing and formation of some permanent gases the pressure in the reactor would go up, and then several minutes would elapse before the silica gel would absorb these gases and bring the vacuum back down to the 10^{-3}–10^{-4} Torr range. Then another short arcing sequence would be carried out. After about 10 cycles, the reactor was shut off and the silica gel trap heated in hot water, the CO and CH_4 given off were collected by the Toepler pump, and PV measurements were carried out. Vpc analysis was carried out on a 5-Å molecular sieve column. Although this method was quantitative and satisfactory for many purposes, there were these disadvantages: (1) it was very slow, (2) reactor pressure became quite high, sometimes 60×10^{-3} Torr, and (3) hydrogen could not be determined this way since the silica gel would not absorb it quantitatively. Therefore a second method was developed.

The second method of collecting and measuring permanent gases employed the normal reactor system connected to a $-196°$ trap followed by an oil diffusion pump, followed by a small mechanical pump (30-cc pump oil capacity). The vent of the mechanical pump was fitted with vacuum tubing leading to a Toepler pump. The vent side of the mechanical pump and the Toepler pump were initially evacuated along with the reactor using another pump. Pressure in the reactor remained in the 10^{-4} Torr range even when 1 mmol of gas was generated in the space of *ca.* 1 hr. And these gases, including hydrogen, could be quantitatively collected if the pump oil was well degassed before initiation of the reaction, and if the amount of gas generated was not an extremely large quantity. Even better results were obtained if a large volume bulb (1–3 l.) was connected into the line just following the small mechanical pump. This volume served as a storage area for gases awaiting entrance into the Toepler pump. This technique will be described in more detail elsewhere.[19]

The substrates were purchased from the Aldrich Chemical Co., with the exception of the trimethylene sulfide, which was obtained from the Eastman Chemical Co. These were purified as required. The following substances were not commercially available and references to their preparation are presented.

***cis*-2,3-Dimethyl episulfide** was prepared from the corresponding epoxide by the method of Bordwell and Anderson.[20]

3,3-Dimethyltrimethylene Oxide. The method of Case and Schmoyer was satisfactory.[21]

3,3-Dimethyltrimethylene Sulfide. The method of Searles was used.[22]

***trans*-2,4-Dimethyltrimethylene Oxide.** This compound was obtained in poor yield from 2,4-pentanediol by adaptation of the procedure used for the preparation of 2-methyltrimethylene oxide.[23] The product was isolated by spinning band distillation on an 18-in. column (bp 75°): nmr (A60) in CCl_4 τ 5.26 (sextet, $J_{H-CH_3,CH_2} = 6.7$ Hz, 2 H), well-resolved triplet 7.71 ($J_{H-CH} = 6.9$ Hz, 2 H), doublet 8.68 ($J_{H-CH} = 6.0$ Hz, 6 H).

***trans*-2,4-Dimethyltrimethylene sulfide** was obtained in poor yield by the method of Trost and coworkers.[24]

***cis*-2,3-Dimethyltetrahydrofuran.** This compound was prepared by the catalytic hydrogenation (PtO_2, 1 atm) of 2,3-dimethyl-4,5-dihydrofuran.[25] Analysis by vpc indicated the sample to be greater than 95 mol % as named. No trans isomer was present: nmr spectrum in CCl_4 τ 9.02 (two doublets overlapping, 6 H, $J_{H-CH_3} = 6.5$ Hz), 8.0 (multiplet, 3 H), 6.3 (multiplet, 3 H).

2,5-Dihydrothiophene. A Birch reduction of thiophene was carried out and the properties of the compound obtained are in accord with those reported.[26] Purification was carried out on an 18 in. Teflon spinning band.

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(21) L. G. Case and L. F. Schmoyer, U. S. Patent 3,006,926; *Chem. Abstr.*, **56**, 59346 (1962).

(22) S. Searles, Jr., H. R. Hayes, and E. F. Lutz, *J. Org. Chem.*, **27**, 2828 (1962).

(23) S. Searles, K. A. Pollart, and F. Block, *J. Amer. Chem. Soc.*, **79**, 954 (1957).

(24) B. M. Trost, W. L. Schminiski, F. Chen, and I. B. Mantz, *ibid.*, **93**, 676 (1971).

(25) D. E. McGreer, M. G. Vinji, and R. S. McDaniel, *Can. J. Chem.*, **43**, 1417 (1965).

(26) P. K. Kower, P. J. Van Der Haak, H. Steinberg, and T. J. DeBoer, *Recl. Trav. Chim. Pays-Bas*, 82, 129 (1965).

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[19] P. S. Skell, K. J. Klabunde, W. Brent, and O. Lauver, to be submitted for publication.