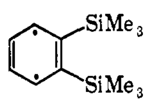
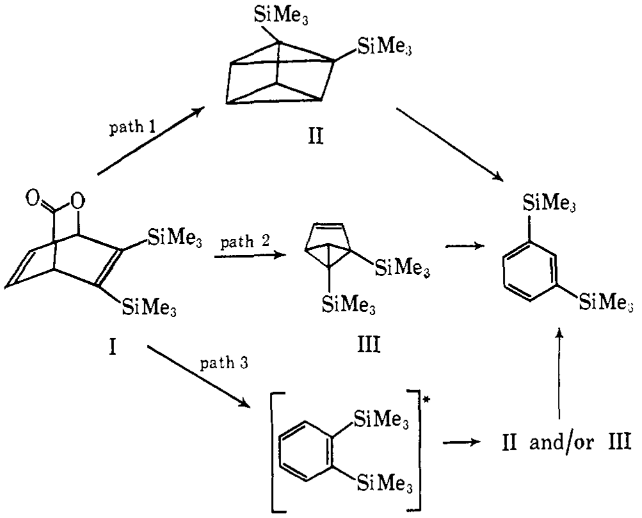
possibly could be involved in the formation of II and III. Since this reaction was carried out in solution,



IV

route 3 seems the least likely. However, route 3 is a formal analog of Burgstahler's photoisomerization of *o*-di-*t*-butylbenzene to a mixture of the *meta* and *para* isomers,[5] for which a prismane,[5] interconvertible Dewar structures,[6] and a benzvalene[6] have been suggested as intermediates. This analogy suggested that one might observe similar isomerization of *o*-bis(trimethylsilyl)benzene upon irradiation. Such was the case: when 3.43 mmoles of this compound in 50 ml of diethyl ether was irradiated in a Rayonet photochemical reactor, a 12.4:1 mixture of *o*- and *m*-bis(trimethylsilyl)benzene, as well as a trace amount of the *para* isomer, was present after a 24-hr reaction time. That such isomerization did occur (presumably *via* II and/or III) suggests that the paths we list above for the thermal Diels–Alder reaction are possible and even plausible routes to the observed *meta* isomer.

**Chart I**



There remains the problem of why α-pyrone and $\mathrm{Me_3SnC{\equiv}CSnMe_3}$ react to give *o*-bis(trimethyltin)benzene, while in the corresponding reaction of $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ the *meta* isomer is produced. In this connection it is noteworthy that attempts to photoisomerize *o*-bis(trimethyltin)benzene thus far have been unsuccessful. Perhaps then the excited state of this molecule is less sterically strained than is that of its silicon analog, and this in turn may have some implications with respect to the thermal Diels–Alder reaction of bis(trimethyltin)acetylene and its silicon analog with α-pyrone. In general, steric effects associated with $\mathrm{Me_3M^{IV}}$ groups decrease with increasing size of $\mathrm{M^{IV}}$: C > Si > Ge > Sn. However, other factors may be of importance in the excitation of these *ortho*-disubstituted benzenes.

Further studies of α-pyrones and 5,5-dimethoxytetrachlorocyclopentadiene[7] with $\mathrm{Me_3M^{IV}C{\equiv}CM^{IV}Me_3}$ compounds ($\mathrm{M^{IV}}$ = C, Si, Ge, Sn, Pb) are being carried out with the aim of determining which factors are of importance with respect to the question of isomerization *vs.* absence of isomerization in these Diels–Alder reactions, as are more detailed investigations of $o$-$\mathrm{(Me_3M^{IV})_2C_6H_4}$ compounds and their photochemical transformations.

**Acknowledgments.** The authors are grateful to the National Science Foundation for generous support of this work (Grant GP 6466X). This work was supported in part by Public Health Service Fellowship 5-F1-GM-20, 099 (to A. B. E.).

---

(5) (a) A. Burgstahler and P.-L. Chien, *J. Am. Chem. Soc.*, **86**, 2940 (1964); (b) A. Burgstahler, P.-L. Chien, and M. O. Abdel-Rahman, *ibid.*, **86**, 5281 (1964).

(6) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *ibid.*, **87**, 675 (1965).

(7) Note the reaction of this compound with bis(trimethyltin)acetylene, which gives 1,2-bis(trimethyltin)tetrachlorobenzene: D. Seyferth and A. B. Evnin, *ibid.*, **89**, 1468 (1967).

(8) National Institutes of Health Predoctoral Fellow, 1963–1966.

**Dietmar Seyferth, David R. Blank, Anthony B. Evnin**[8]
*Department of Chemistry, Massachusetts Institute of Technology*
*Cambridge, Massachusetts 02139*

*Received June 14, 1967*

## On the Mechanism of the Photochemical Decomposition of Cyclobutanone in the Gas Phase[1]

*Sir:*

The photochemical decomposition of cyclobutanone in the gas phase yields ethylene and ketene or cyclopropane, propylene, and CO,[2,3] and only a negligible amount of the expected rearrangement product (3-butenal?) has been detected.[4,5] Recently a pressure-dependence study of the ratio of propylene to cyclopropane led to the conclusion that propylene is a secondary product arising from the unimolecular decomposition of an excited cyclopropane,[6,7a] and a theoretical model for internal energy distribution in the photochemical excitation and the unimolecular decomposition processes has been developed.[7b] As far as the photochemical intermediate responsible for the observed decomposition products is concerned, it has been suggested to be an acyl diradical of the type $\dot{\mathrm{C}}\mathrm{H_2{-}CH_2{-}CH_2{-}}\dot{\mathrm{C}}\mathrm{O}$.[2,3,8]

We have shown that the benzene-photosensitization technique[9,10] can be very useful for a mechanistic diagnosis of the gas-phase photochemical reactions of 4-pentenal[11] and cyclopentanone.[12] The singlet–singlet

---

(1) This research has been supported by a National Science Foundation grant (GP 6924).

(2) S. W. Benson and G. B. Kistiakowsky, *J. Am. Chem. Soc.*, **64**, 80 (1942).

(3) F. E. Blacet and A. Miller, *ibid.*, **79**, 4327 (1957).

(4) R. Srinivasan, *ibid.*, **81**, 5541 (1959).

(5) See, for a review of the photochemistry of cyclic ketones, R. Srinivasan, *Advan. Photochem.*, **1**, 84 (1963).

(6) R. G. Klemm, D. N. Morrison, P. Gilderson, and A. T. Blades, *Can. J. Chem.*, **43**, 1934 (1965).

(7) (a) R. J. Campbell, E. W. Schlag, and B. W. Ristow; (b) R. J. Campbell and E. W. Schlag, private communication, to be published.

(8) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 2758 (1960). The trimethylene diradical, an assumed decomposition product of this acyl diradical intermediate, has been reported to react with excess ethylene to yield $\mathrm{C_5}$ olefins as trapped products, but attempts to confirm this result have so far failed (see ref 6 and 7a).

(9) (a) H. Ishikawa and W. A. Noyes, Jr., *J. Am. Chem. Soc.*, **84**, 1502 (1962); *J. Chem. Phys.*, **37**, 583 (1962); (b) W. A. Noyes, Jr., and I. Unger, *Advan. Photochem.*, **4**, 49 (1966).

(10) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

(11) E. K. C. Lee and N. E. Lee, *J. Phys. Chem.*, **71**, 1167 (1967).

(12) E. K. C. Lee, *ibid.*, **71**, 2804 (1967).

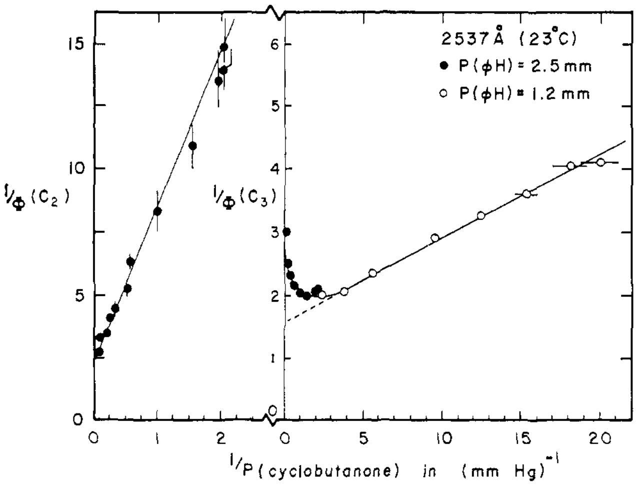


Figure 1. The inverse pressure dependence of the inverse quantum yields: left, the singlet sensitization; right, the triplet sensitization.

energy transfer predominates at relatively high acceptor pressures while the triplet–triplet energy transfer predominates at lower pressures since the $^1B_{2u}$ state benzene intersystem-crosses to the $^3B_{1u}$ state.[9–14] Now we wish to report the results of the benzene photosensitized decomposition and direct photochemical decomposition of cyclobutanone in the gas phase and to present a mechanistic and energetic interpretation of the decompositions of excited cyclobutanones.

The experimental procedures and the kinetic treatment used in this work are described elsewhere in detail.[11,12] The most significant finding from this work is that two distinct primary photochemical processes in the direct photolysis of cyclobutanone can be explained as follows: (1) the decomposition of the excited singlet cyclobutanone to give ethylene and ketene, and (2) the intersystem crossing of the excited singlet cyclobutanone to its low-lying triplet state from which an excited cyclopropane and CO result by the subsequent decomposition. This mechanistic interpretation is based on the data present in Figure 1, in which the inverse sensitization quantum yields of ethylene ($C_2$) and of cyclopropane plus propylene ($C_3$) are plotted against the inverse cyclobutanone pressure.

From this Stern–Volmer type plot, then, a limiting value for the sensitized quantum yield of ethylene is found to be ~0.5 by extrapolation to the infinite cyclobutanone pressure. The quantum yield of ethylene is one-half of this limiting value at 3.0 mm of cyclobutanone pressure. This and our other observation that 50% of the fluorescence emission by the $^1B_{2u}$ benzene is quenched by 3.0 mm of cyclobutanone provide sufficient evidence for a singlet–singlet energy-transfer process in which an excited singlet cyclobutanone is formed with an effective cross section of ~1.3 A$^2$. The subsequent decomposition of the excited singlet cyclobutanone yields ethylene and ketene as characteristic singlet decomposition products.

The yield of the $C_3$ hydrocarbons is monotonically decreased by an increasing amount of *cis*-2-butene, and this implies that these products are characteristic decomposition products of the excited triplet cyclobutanone, since *cis*-2-butene is capable of quenching the long-lived triplet benzene intermediate.[9,10] Our measurements show that cyclobutanone is only one-fourth as effective as *cis*-2-butene in competing for the triplet benzene sensitization. The deviation of the triplet sensitization quantum yield from the straight-line behavior of the Stern–Volmer type plot at high cyclobutanone pressures in Figure 1 is expected, since the diminution of the intersystem crossing of the $^1B_{2u}$ benzene due to more efficient singlet–singlet energy transfer at this pressure lowers the $^3B_{1u}$ benzene population.[12] The limiting value of the triplet quantum yield is ~0.7, which is the maximum value expected in the triplet benzene sensitization,[10] and the half-pressure for this sensitization is 0.10 mm of cyclobutanone. It has been shown previously that the ratio of propylene to cyclopropane is a measure of internal energy of the excited cyclobutanone.[6,7] The observed ratio of propylene to cyclopropane in *triplet* benzene photosensitization indicates that, on the average, 80–85 kcal/mole of excitation energy is transferred to cyclobutanone from the triplet benzene, as compared to about 99 kcal/mole in the *singlet* benzene photosensitization of cyclopentanone.[12]

In view of the fact that the thermal decomposition of cyclobutanone in gas phase yields mainly ethylene and ketene,[15] it is not so surprising to find these as decomposition products of the photochemically excited singlet cyclobutanone. However, it is very interesting to note that cyclopropane with a substantial quantum yield in the direct photolysis (0.14 at 3130 A and 0.29 at 2654 A where $t$ = 100–300° and $p$ = 100–150 mm)[3] presumably arises from the triplet cyclobutanone decomposition. The ratio of the $C_3$ yield to the $C_2$ yield in direct photolysis is indicative of the extent of the intersystem crossing of the excited singlet cyclobutanone to the low-lying triplet state. Our measurements of this ratio at various excitation wavelengths at about 10-mm pressure of cyclobutanone and at 23° are as follows: 0.41 ± 0.02 at 3200 A, 0.64 ± 0.03 at 2800 A, 0.79 ± 0.04 at 2537 A, and 0.93 ± 0.04 at 2480 A. A comparable experimental set of data such as these has been obtained in another laboratory.[7] These results then strongly suggest that the intersystem crossing of the excited singlet cyclobutanone increases with increasing photoexcitation energy and that it plays a very important role in direct photolysis of cyclobutanone. A similar interpretation can also be given for the intersystem crossing of the $^1B_{2u}$ benzene.[16,17] Both examples are worthy of further study. Recent studies of the trimethylene diradical produced by the addition of the triplet methylene to ethylene show that the trimethylene diradical ring-closes to cyclopropane if collisionally deexcited,[18,19] and this analogy favors a mechanism for the formation of cyclopropane *via* a triplet

---

(13) J. W. Donovan and A. B. F. Duncan, *J. Chem. Phys.*, **35**, 1389 (1961). The lifetime of the $^1B_{2u}$ benzene has been measured to be ~0.6 μsec.

(14) C. S. Parmenter and B. L. Ring, *ibid.*, **46**, 1998 (1967). The lifetime of the $^3B_{1u}$ benzene at 20-mm benzene pressure has been measured to be ~26 μsec.

(15) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Am. Chem. Soc.*, **76**, 6271 (1954).

(16) G. B. Kistiakowsky and C. S. Parmenter, *J. Chem. Phys.*, **42**, 2942 (1965).

(17) S. Strickler and R. J. Watts, *ibid.*, 44, 426 (1966).

(18) C. McKnight, E. K. C. Lee, and F. S. Rowland, *J. Am. Chem. Soc.*, **89**, 469 (1967).

(19) R. J. Cvetanović, H. E. Avery, and R. S. Irwin, *J. Chem. Phys.*, **46**, 1993 (1967).

acyl diradical in the photochemical decomposition of cyclobutanone in the gas phase. Further investigation in this direction will be reported in more detail.

**Acknowledgment.** The authors thank Professor E. W. Schlag and his collaborators of Northwestern University for making their papers available to us prior to publication.

**H. O. Denschlag, Edward K. C. Lee**
*Department of Chemistry, University of California*
*Irvine, California 92664*

*Received June 28, 1967*

## The Structure and Configuration of "Neutral Plasmalogens"[1]

*Sir:*

Previous reports suggested the occurrence of minute amounts of aldehydogenic neutral lipids in various mammalian tissues.[2] Small quantities of "neutral plasmalogens" have also been found in man.[3]

We have detected neutral plasmalogens in flesh, liver, and eggs of the shark *Hydrolagus colliei* ("ratfish") and have separated them by adsorption chromatography from the major lipid constituents of these tissues, *viz.*, O-alkyldiglycerides and triglycerides.[4] The total lipids of ratfish liver contained about 5% of neutral plasmalogens and thus constituted a convenient source. A pure fraction (**1**) was obtained by repeated chromatography of ratfish liver lipids on layers of silicic acid.[5] Fraction **1** yielded O-alkyldiglycerides (**2**) upon catalytic hydrogenation. Treatment with hydrochloric acid[4] did not affect **2**, whereas **1** yielded a mixture of aldehydes and diglycerides. Reaction of **2** with methanolic hydrogen chloride at 80° yielded alkyl glycerol ethers and methyl esters of fatty acids; **1** afforded dimethyl acetals of aldehydes and methyl esters. Upon reaction with lithium aluminum hydride in diethyl ether and subsequent acid-catalyzed hydrolysis, **2** afforded alkyl glycerol ethers and alcohols, **1** afforded aldehydes and alcohols. In contrast, decomposition of the lithium alumino complex obtained from **1**, by water, gave alcohols and alk-1-enyl glycerol ethers. The latter compounds migrated on adsorbent layers slightly ahead of alkyl glycerol ethers and could be cleaved to aldehydes and glycerol by acid-catalyzed hydrolysis.

These findings indicated that the fraction (**1**) isolated from ratfish liver lipids consisted of O-alk-1-enyldiglycerides. The quantity we have prepared was sufficient to determine the position of the alk-1-enyloxy group, the optical configuration of the glycerol moiety, and the geometric configuration of the enolic double bond.

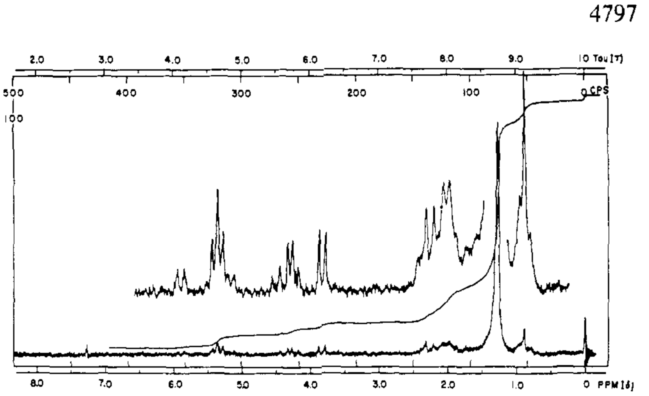


Figure 1.

The alkyl glycerol ethers derived from **1** could be cleaved with sodium metaperiodate and formed isopropylidene ketals with acetone. These reactions and the optical activity of both **1** and **2** proved that these compounds were derivatives of alkyl 1-glycerol ethers, *i.e.*, the asymmetrical isomers. The specific optical rotation[6] of **1** was $[\alpha]^{25}\mathrm{D}$ +2.0° (*c* 1.9); that of **2** was $[\alpha]^{25}\mathrm{D}$ −2.8° (*c* 1.8), which is in numerical agreement with the specific optical rotation found for a synthetic L-alkyldiglyceride[7] ($[\alpha]^{25}\mathrm{D}$ +4.0° (*c* 2.6)). Thus, **1** can be assigned to the D series to which all naturally occurring alkyl 1-glycerol ethers belong.[8,9]

The infrared absorption spectrum[10] of **1** is rather similar to that of **2** and to a synthetic O-alkyldiglyceride.[7] Additional bands associated with the enol ether grouping are those near 1668–1666 and 732–730 cm$^{-1}$, which are due to a stretching vibration of the carbon double bond in the position α to the ether linkage and to a C–H out-of-plane deformation of the same group, respectively. Both bands were found also in spectra of naturally occurring alk-1-enyl acyl glycerophosphatides and were shown to be strictly associated with the *cis*-alk-1-enyl ether linkage, whereas the spectra of *trans*-alk-1-enyl ethers are known to exhibit doublets near 1670 cm$^{-1}$ and a band near 930 cm$^{-1}$.[11,12]

The nuclear magnetic resonance spectrum[13] of **1** (see Figure 1) shows a doublet centered at δ 5.89 ppm which accounts for the olefinic hydrogen at the carbon in the position α to the ether linkage. This doublet is associated with the hydrogen at the *cis* enol ether bond, whereas the *trans* isomer would show a doublet near 6.20 ppm (and a pair of triplets near 4.78 ppm).[12] The signal of the olefinic hydrogen at C-2′ near 4.5 ppm is partially embedded in the multiplet centered at 4.30

---

[1] This investigation was supported in part by Public Health Service Research Grants GM 05817 and HE 08214 from the National Institutes of Health.

[2] M. L. Karnovsky, S. S. Jeffrey, M. S. Thompson, and H. W. Deane, *Biophys. Biochim. Cytol.*, 1, 173 (1955); J. Eichberg, J. R. Gilbertson, and M. L. Karnovsky, *J. Biol. Chem.*, **236**, PC15 (1961); J. C. M. Schogt, P. H. Begemann, and J. Koster, *J. Lipid Res.*, **1**, 446 (1960); J. R. Gilbertson and M. L. Karnovsky, *J. Biol. Chem.*, **238**, 893 (1963).

[3] H. H. O. Schmid, N. Tuna, and H. K. Mangold, *Z. Physiol. Chem.*, **348**, 730 (1967).

[4] H. H. O. Schmid and H. K. Mangold, *Biochim. Biophys. Acta*, **125**, 182 (1966).

[5] Plates coated with layers of silica gel H (Merck), 2 and 0.5 mm thick, were developed twice with hexane–diethyl ether (95:5, v/v). Diethyl ether was used to elute the material from the adsorbent.

[6] Optical rotations were measured at 25° with a Bellingham and Stanley polarimeter, using chloroform as solvent.

[7] W. J. Baumann and H. K. Mangold, *J. Org. Chem.*, **29**, 3055 (1964); W. J. Baumann and H. K. Mangold, *Biochim. Biophys. Acta*, **116**, 570 (1966).

[8] E. Baer and H. O. L. Fischer, *J. Biol. Chem.*, **140**, 397 (1941).

[9] Alk-1-enyl acyl glycerophosphatides ("plasmalogens") recently were shown to possess the D configuration as well: J. C. Craig, D. P. G. Hamon, K. K. Purushothaman, S. K. Roy, and W. E. M. Lands, *Tetrahedron*, 22, 175 (1966).

[10] Infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer. Carbon disulfide served as solvent, except in the ranges 2400–2000 and 1650–1400 cm$^{-1}$, where tetrachloroethylene was used.

[11] W. T. Norton, E. L. Gottfried, and M. M. Rapport, *J. Lipid Res.*, **3**, 456 (1962); H. R. Warner and W. E. M. Lands, *J. Am. Chem. Soc.*, **85**, 60 (1963).

[12] J. C. Craig and D. P. G. Hamon, *J. Org. Chem.*, **30**, 4168 (1965).

[13] Nuclear magnetic resonance spectra were taken in $CDCl_3$ with tetramethylsilane as the internal standard using a Varian A-60A spectrometer.