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research. We also thank Drs. J. B. Grutzner and J. A. Soderquist for helpful discussions regarding this work.

Registry No. 1, 64045-95-0; 2, 110-86-1; 3, 70338-02-2; 4, 107-10-8; 9-BBN·*i*-$PrNH_2$, 70338-03-3; 9-BBN·Et_2NH, 70338-05-5; 9-BBN·QN, 73178-72-0; 9-BBN·2-EtPy, 70338-11-3; 9-BBN·2-*i*-PrPy, 70338-12-4; 9-BBN·*i*-Pr_2NH, 70338-06-6; 9-BBN·2-MePy, 70338-10-2; *i*-$PrNH_2$, 75-31-0; Et_2NH, 109-89-7; QN, 91-22-5; 2-MePy, 109-06-8; 2-EtPy, 100-71-0; 2-*i*-PrPy, 644-98-4; *i*-Pr_2NH, 108-18-9; 2-*t*-BuPy, 5944-41-2; Et_3N, 121-44-8; $(9\text{-BBN})_2$, 70658-61-6.

Mechanistic Aspects of Gas-Phase Photodecarbonylation Reactions of Bicyclo[3.1.0]hexanones[1]

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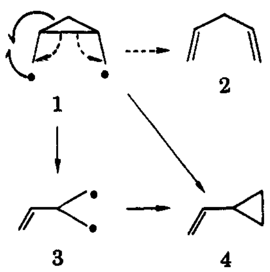
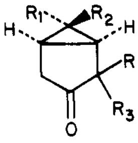
The gas-phase photodecarbonylation and photofragmentation reactions of substituted bicyclo[3.1.0]hexan-3-ones have been studied in detail. Photolysis of these ketones yields 1,3-dienes, vinylcyclopropanes, and 1,4-dienes as detectable products. The possible mechanisms for these reactions are discussed in light of the regiochemical and stereochemical results obtained. In addition, methyl substitution at C-6 and C-2 of these ketones has been shown to have a pronounced effect on both product ratios and overall reaction efficiency. These effects are discussed in terms of stereoelectronic and electronic controls of rates of cyclopropane ring opening of intermediate acylcyclopropylcarbinyl diradicals.

Introduction

Cyclopropyldicarbinyl diradicals (1) have been invoked and discussed as short-lived intermediates in transformations of ground[4] and excited[5] states of polycyclic azoalkanes as well as in the familiar di-π-methane rearrangements of singlet and triplet excited 1,4-dienes.[6] These studies have demonstrated that this diradical species can participate in one of two characteristic reaction pathways, Grob fragmentation producing 1,4-dienes (1 → 2)[7] and di-π-methane-type reactivity resulting in generation of vinylcyclopropanes through a one- (1 → 4) or two-step (1 → 3 → 4) process. Similar types of diradical species having oxygen in place of a carbinyl center have been discussed as reactive intermediates in oxa-di-π-methane rearrangements.[8]



Several years ago Hess and Pitts[9] noted that the major gas-phase photodecarbonylation reactions of bicyclo[3.1.0]hexanone (5) generating 1,4-pentadiene and vinylcyclopropane could be rationalized by invoking the intermediacy of the parent cyclopropyldicarbinyl diradical (1). Although this mechanistic postulate remains speculative, it suggests that the gas-phase photochemistry of bicyclo[3.1.0]hexan-3-ones could potentially serve as a particularly useful method for generation of these diradicals. Our interest in this feature was stimulated by earlier studies[10] which suggested that the stereochemical and regiochemical outcomes of nonconcerted di-π-methane rearrangements might be controlled by factors influencing the pathways chosen for conversion of 1 to vinylcyclopropanes. As a result, we have embarked on an exploratory effort designed to gain information about both the mechanism for photodecarbonylation of bicyclo[3.1.0]hexanones and perhaps the nature of pathways converting cyclopropyldicarbinyl and related diradicals to 1,4-dienes and vinylcyclopropanes. Specifically, we have prepared and



5, R_1 = H; R_2 = H; R_3 = H
6en, R_1 = H; R_2 = CH_3; R_3 = H
6ex, R_1 = CH_3; R_2 = H; R_3 = H
7, R_1 = CH_3; R_2 = CH_3; R_3 = H
8, R_1 = H; R_2 = H; R_3 = CH_3

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[1] Previous accounts of this work have been presented at the 32nd and 33rd Southwest Regional American Chemical Society Meetings in Forth Worth, TX (1976), and Little Rock, AR (1977).

[2] Camille and Henry Dreyfus Foundation Teacher-Scholar Awardee, 1975–1980.

[3] (a) Department of Chemistry, University of Maryland, College Park, MD 20742; (b) EIC Corporation, Newton, MA 02158.

[4] J. A. Berson, S. S. Olin, E. W. Petrillo, Jr., and P. Bickart, *Tetrahedron*, **30**, 1639 (1974).

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[6] S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).

[7] C. A. Grob, *Angew. Chem.*, 81, 543 (1969).

[8] W. G. Dauben, G. Lodder, and J. D. Robbins, *J. Am. Chem. Soc.*, **98**, 3030 (1976); B. Winter and K. Schaffner, *ibid.*, **98**, 2022 (1976).

[9] L. D. Hess and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **89**, 1973 (1967).

[10] (a) P. S. Mariano and J. K. Ko, *J. Am. Chem. Soc.*, **95**, 8670 (1973); (b) P. S. Mariano and R. B. Steitle, *ibid.*, **95**, 6114 (1973); (c) P. S. Mariano, D. G. Watson, and E. Bay, *Tetrahedron*, **33**, 11 (1977); (d) H. E. Zimmerman and G. Epling, *J. Am. Chem. Soc.*, **92**, 1411 (1970); J. S. Swenton, A. L. Crumrine, and T. J. Walker, *ibid.*, **92**, 1406 (1970).

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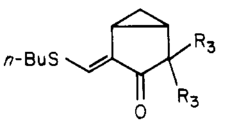
studied the stereo- and regiospecifically methyl-substituted bicyclic ketones **6**–**8**. The results of these investigations are summarized and discussed below.

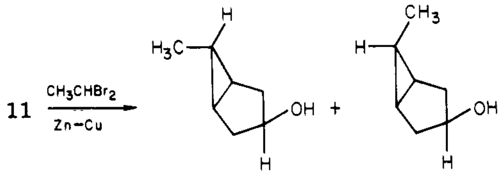
Results

Synthesis of Bicyclo[3.1.0]hexan-3-ones. The bicyclic ketones **6ex**[11] and **7**[12] required for a portion of these studies were prepared by using documented procedures. The method selected for generation of the α,α-dimethylated bicyclohexanone **8** mimicked closely that utilized by Cook and Lyons[13] for production of analogous compounds. Specifically, the parent ketone **5** was converted to its known thioenol ether **9**.[13] Exhaustive methylation (KO-*t*-Bu, CH_3I) followed by removal of the enol ether function of **10** using standard conditions (NaOH, DEG) yielded the bicyclic ketone **8**.



9, R_3 = H
10, R_3 = CH_3

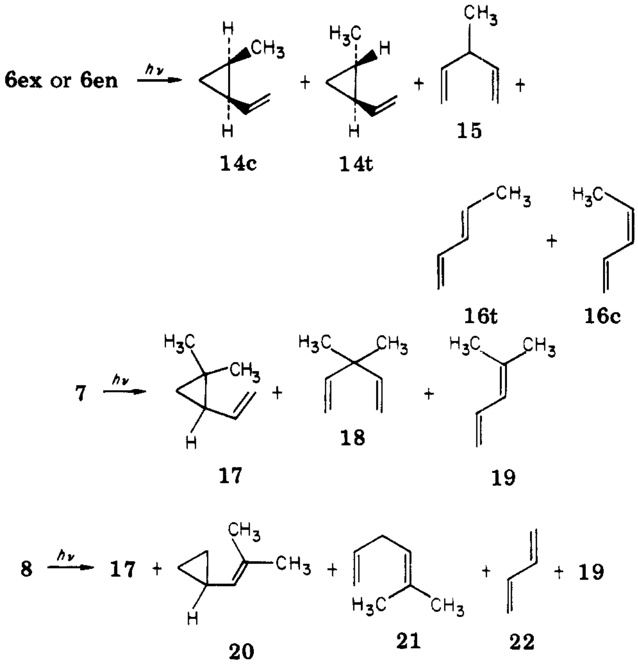
A simple synthetic route mimicking that employed by Winstein and Sonnenberg[15] was selected for preparation of the 6-*endo*- and 6-*exo*-methyl bicyclic ketones **6**. Earlier studies[11] have shown that Simmons–Smith methylcyclopropanation of 3-cyclopentenol (**11**) using the diethylzinc procedure (CH_3CHI_2 + $(CH_3CH_2)_2Zn$ → $CH_3CHIZnCH_2CH_3$)[16] proceeds with complete stereoselectivity to furnish the 6-exo epimer, **6ex**. This observation is in striking contrast to other observations which suggest that transition states for ethylidene transfer using diethylzinc-derived reagents are sterically less crowded than those prepared by using the normal Simmons–Smith techniques.[11] In light of these results and our desire to prepare both of the 6-methyl epimers of **6**, we have investigated the normal Simmons–Smith reactions of **11** using the reagent prepared from ethylidene bromide and zinc–copper couple. Contrary to expectations arising from consideration of the earlier noted trends, we have found that this ethylidene-transfer reaction proceeds with a reduced degree of stereoselectivity when compared to methylcyclopropanations using $CH_3CHI(ZnCH_2CH_3)$ and furnishes a mixture of *exo*- and *endo*-6-methyl bicyclic alcohols (**12ex** and **12en**) in a ratio of 3.3:1.

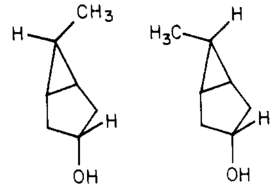


12ex **12en**

The spectral properties (^1H NMR and IR) of the 6-*exo*-methyl-3-*endo*-hydroxy isomer **12ex** were identical with those previously reported.[11] In addition, the ^{13}C NMR and mass spectra of **12ex** (vide infra) were consistent with the previously assigned structure. The structure and stereochemistry of the minor methylcyclopropanation product were assigned by using a combination of methods involving lanthanide-NMR studies and chemical oxidation. First, the minor product displayed similar, but characteristically different, spectral parameters to those of **12ex** (vide infra). Three diastereomers are possible for this compound, i.e., the 6-*endo*-methyl-3-*endo*-hydroxy- (**12en**), 6-*endo*-methyl-3-*exo*-hydroxy- (**13en**), and 6-*exo*-methyl-3-*exo*-hydroxy- (**13ex**) bicyclohexanes. Elimination of **13ex** from consideration as this product was easily accomplished by demonstrating that oxidation of the minor alcohol (CrO_3, pyridine) generated a ketone (**6en**) epimeric to the one obtained from oxidation of the known 6-*exo*-methyl-3-*endo*-hydroxy compound. More definitive proof of the stereochemistry at C-3 is provided by lanthanide NMR studies using $Eu(fod)_3$ which show relative induced downfield shifts of the C-6 methyl, C-6 methine, and C-1 and C-5 methines clearly indicative of the endo hydroxyl disposition and, thus, characteristic of the stereochemistry represented by **12en**.

Scheme I





13en **13ex**

These results demonstrate that the stereochemistry of methylcyclopropanation reactions of olefins using diethylzinc and zinc–copper couple derived ethylidene-transfer reagents is not subject to general classification. Thus, although the normal Simmons–Smith reagent displays a greater degree of stereoselectivity than the ethylzinc reagent in reactions with olefins lacking additional functionality, this situation is perhaps reversed when olefins contain sites which strongly coordinate with the organometallic species. Reasons for this differing behavior do not readily surface and perhaps need to await further studies.

Gas-Phase Photochemistry of Bicyclic Ketones.

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(11) J. Nishimura, N. Kawabata, and J. Furuhawa, *Tetrahedron*, **25**, 2647 (1969).

(12) M. Walkowicz, H. Kucznski, and C. Walkowiz, *Rocz. Chem.*, **41**, 927 (1967).

(13) G. D. Lyon, Ph.D. Dissertation, University of Oregon, Eugene, OR, 1975.

(14) R. E. Ireland and J. A. Marshall, *J. Org. Chem.*, **27**, 1615 (1962).

(15) S. Winstein and J. Sonnenberg, *J. Am. Chem. Soc.*, **83**, 3235 (1961).

(16) J. Furukawa, N. Kawabata, and J. Nishimura, *Tetrahedron Lett.*, 3495 (1968).

Table I. Effect of Varying Temperature and Pressure on Product Yields from Photolysis of 6-*exo*-Methylbicyclo[3.1.0]hexan-3-one (6ex)

temp, °C	ketone pressure, torr	product quantum yields, Φ					total Φ_r
		14c	**14t**	**15**	**16t**	**16c**	
50	50	0.004	0.008	0.11	0.0017	0.0008	0.13
75	50	0.017	0.031	0.33	0.012	0.006	0.40
100	50	0.03	0.06	0.06	0.019	0.008	0.66
100	68	0.032	0.06	0.55	0.019	0.008	0.67
100	84	0.028	0.047	0.53	0.021	0.010	0.64
125	50	0.04	0.09	0.62	0.021	0.008	0.78
150	50	0.06	0.15	0.84	0.027	0.011	1.09

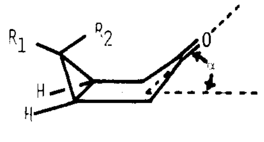
Table II. Effect of Varying Temperature and Pressure on Product Yields from Photolysis of 6-*endo*-Methylbicyclo[3.1.0]hexan-3-one (6en)

temp, °C	ketone pressure, torr	product quantum yields, Φ					total Φ_r
		14c	**14t**	**15**	**16t**	**16c**	
50	50	0.005	0.009	0.034	0.0009	0.0001	0.05
75	50	0.023	0.04	0.12	0.008	0.005	0.20
100	50	0.06	0.12	0.29	0.028	0.013	0.51
100	68	0.052	0.11	0.27	0.029	0.015	0.48
100	84	0.053	0.12	0.26	0.032	0.015	0.48
125	50	0.075	0.15	0.33	0.029	0.012	0.60
150	50	0.10	0.23	0.42	0.033	0.014	0.80

Gas-phase photolyses of the bicyclic ketones **6**–**8** were conducted at a variety of temperatures and pressures by using Pyrex-filtered light and conditions under which hydrocarbon products were both thermally and photochemically stable. No change in the absolute quantities or ratios of the photoproducts could be detected when reaction mixtures were heated at the reaction temperature. Likewise, the individual photoproducts were unchanged when directly irradiated with Pyrex-filtered light or when cyclohexanone was included as sensitizer. In addition, the starting ketones were found to be thermally stable under the photolysis conditions. Analysis of the nonvolatile ketone fraction after irradiation indicated that no isomeric ketones or other oxygen-containing products had been produced. In summary, the photochemical reactions noted for these bicyclic ketones are exceptionally clean and lead exclusively to the products listed in Scheme I.

The 1,4-diene, vinylcyclopropane, and 1,3-diene photoproducts produced in these reactions were identified by comparison of GLC retention times with those of authentic samples which were either commercially available or prepared by known procedures (see Experimental Section). Quantum yields for product formation (Tables I–IV) were determined by using conversion of the parent bicyclic ketone **5** to 1,4-pentadiene[9] (Φ = 0.60 at 118 °C and 35 torr) as the chemical actinometer.

Conformational Analysis of 6-*exo*- and 6-*endo*-Methylbicyclo[3.1.0]hexan-3-ones. The preferred conformations of the ketones **6** were investigated in order to determine if the observed differences in quantum yields for 3-methyl-1,4-pentadiene and 2-methylvinylcyclopropane production from the *exo*- and *endo*-6-methylbicyclohexanones **6** are due to stereoelectronic factors. A preliminary microwave study[17] of the structures of **6en** and **6ex** has enabled evaluation of the dihedral angles (α) between the carbonyl and the remainder of the five-membered ring. These were found to be 8.0 ± 2 and 17.5 ± 2°, respectively, indicating that the presence of the *endo*-6-methyl substituent causes the bicyclic ring conformation to be more planar. This result is as expected if nonbonded interactions between the *endo*-methyl and C-3 carbonyl grouping are more important in controlling the molecular shape than those between methyl and the endo hydrogens located at C-2 and C-4.

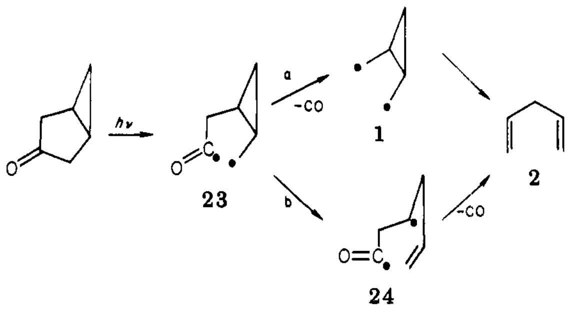


6EN R_1=H , R_2=CH_3
6EX R_1=CH_3 , R_2=H

Table III. Product Yields from Photolysis of 6,6-Dimethylbicyclo[3.1.0]hexan-3-one (7)

temp, °C	ketone pressure, torr	product quantum yield, Φ			total Φ_r
		17	18	19	
100	50	0.17	0.25	0.05	0.47

Scheme II. Mechanisms for 1,4-Pentadiene Production



Discussion

Mechanistic Considerations. Several aspects of the observations reported above including bicyclo[3.1.0]hexan-3-one photodecarbonylation reaction stereochemistry and regiochemistry, substituent dependence on product composition, and temperature and substituent dependence on reaction efficiency require detailed discussion. Each of these features of the bicyclic ketone photoreaction is intimately tied to the mechanistic pathways utilized in the transformation to 1,4-pentadiene, 1,3-butadiene, and vinylcyclopropane products. Several mechanisms for these processes, differing in the timing of carbon monoxide or ketene loss vs. cyclopropane bond cleavage, can be envisaged. Each of the pathways, included in Schemes II–IV,

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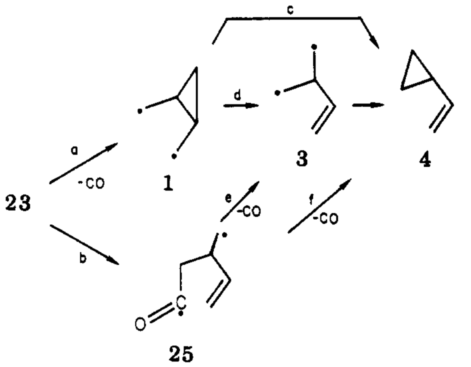
(17) T. Richter, E. Bay, and J. Bevan, unpublished results.

Table IV. Effect of Varying Temperature and Pressure on Product Yields from Photolysis of 2,2-Dimethylbicyclo[3.1.0]hexan-3-one (8)

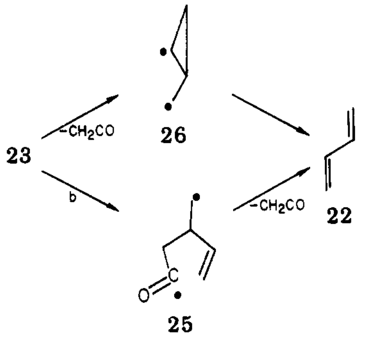
temp, °C	ketone pressure, torr	product quantum yields,[a] Φ					total Φ_r
		17	20	21	22	19	
50	50	0	0.0012	0.18	0	0	0.18
100	50	0.0035	0.007	0.67	0	0.005	0.69
100	60	0.004	0.008	0.69	0	0.004	0.71
100	75	0.0037	0.007	0.66	0	0.004	0.68
150	50	0.013	0.014	0.88	0.0001	0.006	0.91

[a] In this case only was there a difference in extinction coefficient between ketone 8 and the actinometer ketone 5. This difference was accounted for in quantum yield calculations.

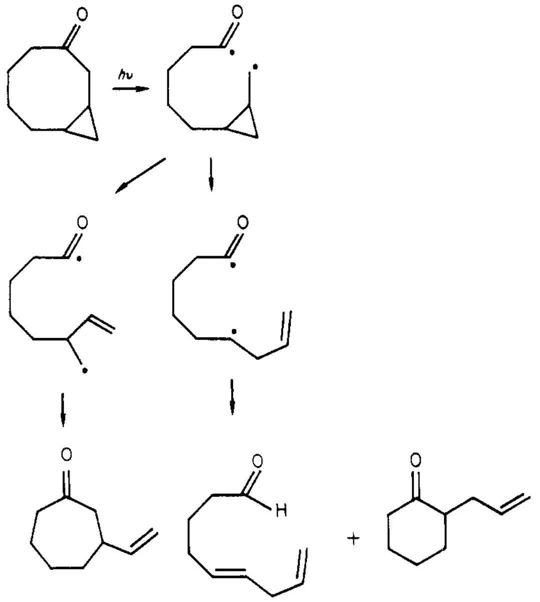
Scheme III. Mechanisms for Vinylcyclopropane Production



Scheme IV. Mechanisms for 1,3-Pentadiene Production



Scheme V



begins with initial α cleavage in the excited ketones. The multiplicity(ies) of the excited state(s) undergoing photodecarbonylation and ketene loss has not been probed. Earlier literature reports suggested that gas-phase α-cleavage reactions of cyclic ketones are singlet processes, but more recent evidence points to the triplet nature of these reactions.[18]

Arguments can be formulated to support the contention that cyclopropane bond cleavage should precede CO loss from the initially produced acyl diradical intermediate **23**. Indeed the large rate constant measured for conversion of cyclopropylcarbinyl to homoallyl radical ($\sim 10^8$ s^{-1} at 25 °C)[19] suggests that pathways b in Schemes II and III should compete favorably with decarbonylation to generate the cyclopropyldicarbinyl diradical (**1**). However, the Arrhenius parameters for this process are not available, thus, preventing a prediction of the rates for cyclopropane ring opening in the gas-phase elevated-temperature system. In comparison, Benson and O'Neal's study[20] of acetone gas-phase photochemistry demonstrates that CO loss from an acyl radical (eq 1) in the temperature and pressure

$$CH_3\dot{C}O \rightarrow \cdot CH_3 + CO \qquad (1)$$

range used in our studies should occur with a rate constant greater than 10^8 s^{-1}.[21] Therefore, it is difficult to derive direct kinetic evidence to serve as a basis for the choice of one of the two general mechanisms suggested for photoconversion of bicyclo[3.1.0]hexan-3-ones to 1,4-pentadienes and vinylcyclopropanes.

Indirect information about these mechanistic questions is found in results from solution-phase bicyclic ketone photochemistry. Acyl diradicals like **23**, resulting from α cleavage of the bicyclo[3.1.0]hexan-3-ones thujone and isothujone, are sufficiently long-lived to undergo rotation and reclosure, accounting for epimerization at C-2 in these systems.[22] Interestingly, solution-phase photodecarbonylation reactions of these[22] as well as other bicyclo[3.1.0]hexan-3-ones[23] lead to the formation of 1,4-pentadienes, exclusively. Whether decarbonylation (path a, Scheme II) or cyclopropane bond cleavage (path b, Scheme II) occurs first in the thujone reactions could not be answered. On the other hand, independent studies of Crandall[24a] and Moon[24b] have demonstrated that solution-phase irradiation of bicyclo[6.1.0]nonan-3-one, con-

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[18] (a) The multiplicity of the excited ketones undergoing reaction has not been probed. Earlier literature reports suggested that gas-phase α-cleavage reactions of cyclopentanones are singlet processes,[18b] but more recent evidence has been provided in support of the triplet nature of these reactions.[18c] (b) For a general discussion see T. Berces, *Compr. Chem. Kinet.*, **5**, Chapter 3 (1972). (c) R. G. Shortridge, C. F. Rusbult, and E. K. C. Lee, *J. Am. Chem. Soc.*, **93**, 1863 (1971).

[19] D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).

[20] H. E. O'Neal and S. W. Benson, *J. Chem. Phys.*, **36**, 2196 (1962).

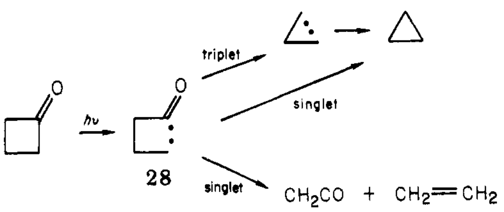
[21] Cyclopropyl stabilization of the developing radical should assist loss of carbon monoxide.

[22] R. S. Cooke and G. D. Lyon, *J. Am. Chem. Soc.*, **93**, 3840 (1971).

[23] J. E. Starr and R. H. Eastman, *J. Org. Chem.*, **31**, 1393 (1966).

[24] (a) J. K. Crandall, J. P. Arrington, and C. F. Mayer, *J. Org. Chem.*, **36**, 1428 (1971); (b) S. Moon and H. Bohm, *ibid.*, **36**, 1434 (1971).

Scheme VI



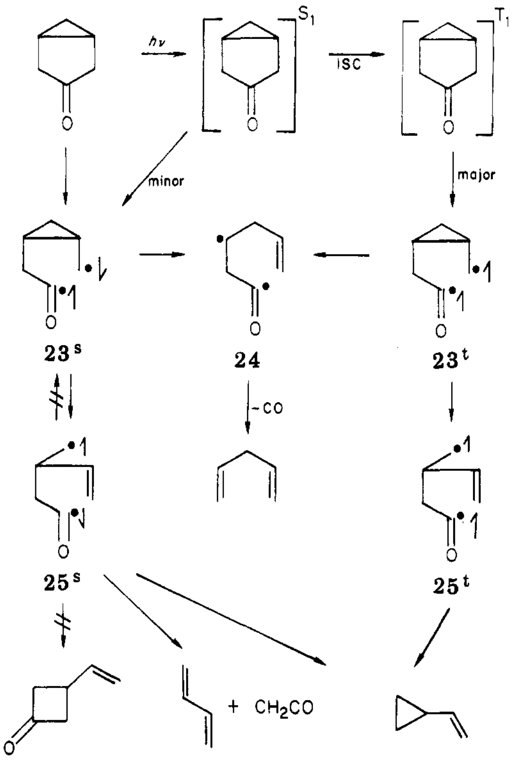
taining a fused cyclopropane ring and carbonyl grouping in the same relative juxtaposition as in the bicyclo[3.1.0] systems, leads to generation of products in which the CO unit is retained while the cyclopropane ring is cleaved (Scheme V). The products obtained most probably result from internal capture of the acyl radical center by the homoallylic moieties arising from the two possible modes of cyclopropylcarbinyl radical cleavage. These results can be used to support mechanisms for transformation of bicyclo[3.1.0]hexan-3-ones to vinylcyclopropanes and 1,4-pentadienes having cyclopropane bond cleavage occurring prior to decarbonylation. However, here again information about the temperature and pressure dependencies of rates of CO loss vs. cyclopropane bond cleavage, needed in order to draw concrete conclusions about preferred mechanisms for the gas-phase processes, is lacking.

In a similar vein, reaction pathways leading from the acyl diradical **23** to 1,3-butadiene products can involve ketene loss prior to or following rupture of the cyclopropane bond. It should be noted that loss of ketene from **23** (path a, Scheme IV) would generate the cyclopropylcarbinyl diradical **26**, similar to **27**, an intermediate postulated by Srinivasan[25] in vapor- or solution-phase photochemical conversion of the piperylenes to 1,3-dimethylcyclopropene (eq 2). Mixtures obtained from irradiation of the 6-methylbicyclohexanones **6** were not found to contain this dimethylcyclopropene,[26] as would have been expected if diradical **27** were an intermediate. Thus, an alternative pathway (path b, Scheme IV) for 1,3-butadiene production is through the acyl diradical **25** which would undergo Grob-type fragmentation to give ketene and conjugated diene. Indeed, singlet diradicals, similar to **25**, generated by gas-phase irradiation of cyclobutanones[27] are known to undergo fragmentation, giving ketenes and olefins, in competition with cyclization and decarbonylation, regenerating cyclobutanones and cyclopropanes, respectively.

27 17 (2)

Other results from investigations of cyclobutanone photochemistry are useful in deriving an understanding of mechanistic pathways operating in bicyclo[3.1.0]hexan-3-one photofragmentations. Triplet diradicals related to **25**, i.e., **28**, derived by benzene-sensitized photolysis of cyclobutanone, undergo loss of CO nearly exclusively, resulting in the formation of cyclopropanes.[27] The nearly complete stereochemical randomization at the center α to the carbonyl in the conversion of triplet cyclobutanones to cyclopropanes suggests that the diradical intermediate(s) in this process (Scheme VI) are long-lived and, thus, rotationally equilibrated. In addition, decarbonylation of **28** in the singlet manifold is reasonably inefficient compared to reclosure and Grob-type fragmentation and leads in a concerted or sequential fashion to cyclopropane products. On the basis of the cyclobutanone photochemical results, it is possible to construct what appears to be a reasonable mechanism for the photofragmentation reactions of bicyclo[3.1.0]hexan-3-ones, as shown in Scheme VII. Reactions through the triplet manifold predominate and lead to exclusive formation of 1,4-pentadiene and vinylcyclopropane products. Our observation of complete stereochemical randomization in the transformation of the 6-methylbicyclohexanones **6** to 2-methyl-1-vinylcyclopropanes is consistent with expectations based upon the intermediacy of triplet acyl 1,4-diradicals, **25**^{t}. The failure to observe detectable quantities of 3-vinylcyclobutanones in mixtures obtained from irradiation of the bicyclic ketones is surprising if a portion of the reaction pathway, as suggested in Scheme VII, funnels through the singlet biradical **25**^{s}.[29] One possible explanation is based upon a more favorable cyclization to generate the initial acyl diradical (**25**^{s} → **23**^{s}) followed by reversion to ground-state ketone. Recovered 6-methylbicyclo[3.1.0]hexan-3-one obtained from irradiation of either the endo or exo isomer contained none of the opposite 6-methyl epimer which would have formed if **25**^{s} and **23**^{s} were interconverting.

Scheme VII



Substituent Effects on Product Ratios. One of the most intriguing aspects of these studies concerns the dependence of quantum efficiencies for formation of 1,3-dienes, 1,4-dienes, and vinylcyclopropanes on the position and stereochemistry of alkyl substituents attached to the bicyclo[3.1.0]hexan-3-one skeleton. The data in Table V show that the quantum efficiencies for formation of 1,3-

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(25) S. Boue and R. Srinivasan, *J. Am. Chem. Soc.*, **92**, 3226 (1970).

(26) 1,3-Dimethylcyclopropene was prepared by the known method.[25] No peak in the GLC chromatogram of reaction mixtures obtained from irradiation of **6ex** or **6en** had a retention time equivalent to that of this olefin.

(27) H. A. J. Carless and E. K. C. Lee, *J. Am. Chem. Soc.*, **94**, 1 (1972); J. Metcalf and E. K. C. Lee, *ibid.*, **94**, 7 (1972); H. A. J. Carless, J. Metcalf, and E. K. C. Lee, *ibid.*, **94**, 7221, 7235 (1972).

(28) D. S. Weiss, M. Haslanger, and R. G. Lawton, *J. Am. Chem. Soc.*, **98**, 1050 (1976).

(29) 3-Vinylcyclobutanones would have been detected in the reaction mixtures since their ultraviolet absorption spectra and photoreaction efficiencies should be similar to the bicyclo[3.1.0]hexanones. No ketone products were observed in the photolysis mixtures.

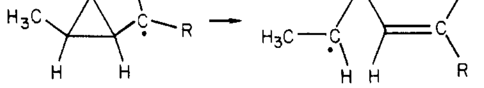
Table V. Substituent Effects on 1,3-Diene, 1,4-Diene, and Vinylcyclopropane Formation Efficiencies

	quantum efficiencies[a]				quantum efficiency ratios		
ketone	total products	1,4-diene	Vi-cPr[b]	1,3-diene	1,3-diene: 1,4-diene	Vi-cPr: 1,4-diene	1,3-diene: Vi-cPr
5	0.84	0.58	0.10	0.018	0.03	0.17	0.18
6ex	0.66	0.54	0.09	0.027	0.05	0.17	0.30
8	0.69	0.67	0.01	0.005	0.01	0.01	0.50
6en	0.51	0.29	0.18	0.041	0.14	0.62	0.23
7	0.47	0.25	0.17	0.05	0.20	0.68	0.29

[a] Quantum yields for reaction of 5 were measured at 118 °C and 35 torr and for reaction of all other ketones at 100 °C and 50 torr. [b] Vinylcyclopropane.

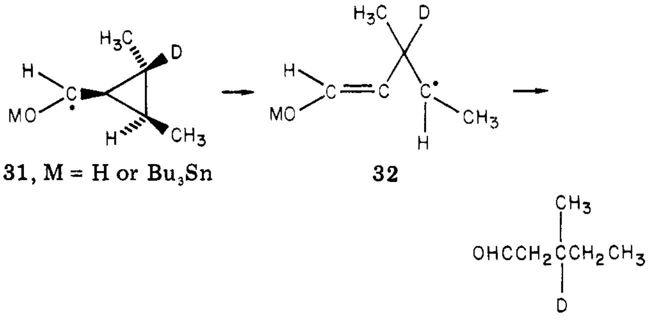
dienes and vinylcyclopropanes increase dramatically in proceeding from bicyclic ketones lacking *endo*-methyl substituents or possessing α-methyl substituents, e.g., **5**, **6ex**, and **8**, to those containing *endo*-methyl substituents, e.g., **6en** and **7**. The opposite effect is observed for 1,4-diene formation. In this case quantum yields decrease in moving from the former class of ketones to the latter. It appears reasonable to expect that the substituent controls of efficiencies for product formation result from variations in the relative rates of cleavage of the external vs. internal cyclopropane bond of the initially formed acyl diradical **23** in transformation to the acyl 1,4- or 1,3-diradicals such as **25** or **24**. Importantly, the effect of methyl substitution on partitioning of diradical **23** is not solely the result of odd-electron stabilizing features since the *endo*- and *exo*-6-methyl ketones display markedly different behavior.

Two factors may be important in controlling substituent effects on the quantum efficiencies of vinylcyclopropane and 1,4-diene production. One is stereoelectronic in nature and arises as a result of preferred conformations about the cyclopropane ring–carbinyl carbon bonds in transition states for conversion of acyl diradicals **23** to **24** or **25**. The other has an electronic origin and involves the influence of alkyl substitution on cyclopropane ring σ bond frontier molecular orbital energies. In order to fully develop this rationalization, it is first necessary to summarize some of our recent work[30] and earlier studies of others[31,32] concerning the ring-opening regiochemistry of cyclopropylcarbinyl to homoallyl radical conversions. The classic work of Dauben and co-workers[31] on lithium–liquid ammonia reductions of rigid cyclopropyl ketones demonstrated that cyclopropane ring opening occurs preferentially on the σ bond which can best overlap with the rigidly oriented carbon p orbital of the anion radical moiety. The selectivity in these cases, as well as in the reductive cleavage of *cis*-2-methylcyclopropyl methyl ketone, has been rationalized in terms of steric control of intermediate radical-anion conformations coupled with the requirement for good overlap between the cyclopropane σ bond and carbinyl carbon p orbital. Related observations have been made by Davies and Pereyre[32] in studies of conversions of cyclopropylcarbinyl radicals **29** to homoallyl radicals **30**. More recently, we have shown, using ESR and product isolation techniques, that ring-opening regiochemistry in the 2,3-dimethyl-substituted cyclopropylcarbinyl radicals **31**, where electronic influences are canceled, favors the *cis*-methyl-substituted σ bond.[30] Specifically, the substituted butenyl radical **32** and aldehyde product **33**, having the deuterium labeling patterns shown, are produced from **31**. In these cases also, the preferences for transition states **34**‡ over **35**‡ are clearly due to minimization of nonbonded interactions between substituents on the carbinyl carbon and the *cis*-methyl group.



29, R = H or CH_3;
X = OH or $OSnBu_3$

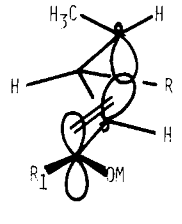
30



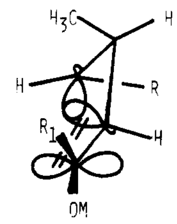
31, M = H or Bu_3Sn

32

33



34‡



35‡

These results are useful in developing an understanding of the substituent dependence of vinylcyclopropane, 1,3-diene, and 1,4-diene formation quantum yields. Both steric and electronic factors should combine to control the direction of ring opening of acyl diradicals **23** and the rates of ring opening which should compete with recombination to generate the starting bicyclo[3.1.0]hexan-3-one systems. Accordingly, transition states for ring opening having the carbinyl p orbital overlapping with the internal cyclopropane σ bond, e.g., **39**‡, should be of lower energy than those with the external bond, e.g., **40**‡, when the endo-C-6 substituent R_1 is hydrogen and when the group R_3 at the carbinyl center is methyl. In these cases stereoelectronically controlled ring opening generates 1,3-acyl diradicals which serve as precursors of 1,4-diene products (Scheme VII). On the other hand, transition states **39**‡ and **40**‡ should be closer in energy when the endo-C-6 substituent R_1 is bulky and R_3 is hydrogen. Efficiencies of 1,4-diene and vinylcyclopropane production from bicyclic ketones with this substitution pattern should be comparable. Indeed, the data in Table V are in accord with this reasoning.

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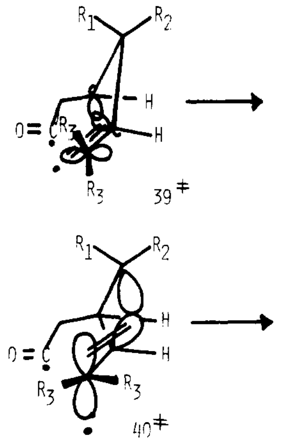
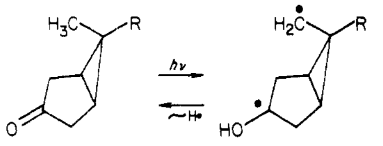
(30) P. S. Mariano and E. Bay, *J. Org. Chem.*, following paper in this issue.

(31) W. G. Dauben, L. Schutte, R. E. Wolf, and E. J. Deviny, *J. Org. Chem.*, **34**, 2512 (1969); W. G. Dauben and R. E. Wolf, *ibid.*, **35**, 374 (1970).

(32) A. G. Davies, B. Muggleton, J.-Y. Godet, M. Pereyre and J.-C. Pommier, *J. Chem. Soc., Perkin Trans. 2*, 1719 (1976).

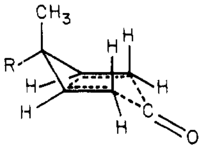


Alkyl substitution at C-6 and C-2 appears to have a marked effect on the total quantum yields for reaction of the bicyclic hexanones. Although these effects are not so readily rationalized, they appear to be consistent with observations made in studies of cyclopropylcarbinyl radical reactions.[30] Several factors could be operating in these cases; a decreased reaction efficiency could be due to enhancement of new modes of excited-state reaction, to decreased rates of excited reaction vs. decay, or to decreased rates of forward reaction of an intermediate relative to return to the ground state of the bicyclic ketone. For example, the data in Table V indicate that **6en** undergoes photodecarbonylation less efficiently than the parent ketone **5**. The presence of an endo-C-6 methyl group could facilitate reversible hydrogen-atom abstraction (eq 3).



(3)

This appears unlikely, however, on the basis of results provided by Turro and co-workers[33] which demonstrated that the C–H bond participating in Norrish type II processes must be oriented correctly in the carbonyl nodal plane.[34] Alternatively, decarbonylation of the excited ketones to yield 1,4-dienes could proceed in part by a concerted mechanism. This would require that CO depart from a direction which allows good overlap between the breaking C–CO and cyclopropane bonds in a manner analogous to thermal chelotropic reactions of diazabicycloheptene[4] and tricyclooctanones.[35] This arrangement is found in the chair-type transition state **41**‡. Accordingly,



41‡

endo-methyl substituents could cause these transition-state conformations to be of higher energy, due to the presence of H–CH_3 1,3-axial interactions, and thus cause the rates of concerted CO loss to be slow. Although this rationale would nicely incorporate the observed interrelationship between reaction and 1,4-diene formation quantum yields, it is inconsistent with the conformational analysis of these systems provided by microwave data.[17] The preferred conformation of the parent bicyclic ketone has been shown to be boatlike.[36] Moreover, *endo*-methyl substitution does not further enhance the preference for the boat over chair conformation as would be required in order for quantum efficiencies for 1,4-diene production to be diminished. As expected, the opposite is the case; the *endo*-methyl group tends to flatten the structure and, thus, most probably perturb the conformational equilibrium in the direction of the chair structures.

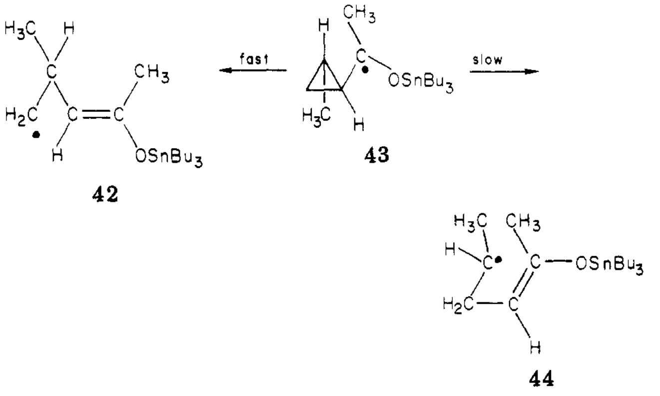
Table VI. Piperylene and Methylvinylcyclopropane Ratios from Irradiation of the 6-Methylbicyclo[3.1.0]hexan-3-ones **6en** and **6ex**

reaction temp,[a] °C	from 6ex		from 6en	
	14c/14t	16c/16t	14c/14t	16c/16t
50	0.50	0.47	0.56	(0.11)[b]
75	0.55	0.50	0.58	0.63
100	0.50	0.42	0.50	0.46
125	0.44	0.38	0.50	0.41
150	0.40	0.41	0.43	0.42

(cis/trans vinylcyclopropane and piperylene ratios)

[a] Pressure 50 torr. [b] Inaccurate due to large error in measurement of the amount of **16c** found.

A more reasonable explanation of the effects of substituents on total reaction quantum yields arises from consideration of the competition between pathways available to the acyl diradical **23** involving cyclopropane ring opening and reclosure to produce starting ketone. Factors which slow ring opening should decrease the reaction quantum yield while those that slow diradical closure should enhance reaction efficiency. On the basis of results arising from studies of cyclopropylcarbinyl radical ring-opening reactions,[30-32] we can postulate that alkyl substitution on the cyclopropane ring of acyl diradicals **23** could decrease the rate of ring opening generating diradicals **24** or **25**. A good example of this phenomenon is found in the preferential (4:1) conversion of **43** to the primary radical **42**.[32] Accordingly, the reaction quantum yield should decrease as the degree of methyl substitution in the cyclopropane ring of bicyclo[3.1.0]hexan-3-ones increases. The data in Table V support this postulate. Furthermore, geminal methyl substitution at the carbinyl center should slow internal radical recombination and enhance reaction efficiency in accord with the results of Weiss' studies[37] on simple cyclohexanones.



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(33) N. J. Turro and D. S. Weiss, *J. Am. Chem. Soc.*, **90**, 2185 (1968); K. Dawes, J. C. Dalton, and N. J. Turro, *Mol. Photochem.*, **3**, 71 (1971).

(34) Additionally, ensuing reactions of the 1,5-diradical produced involving internal coupling or cyclopropane bond cleavage should be fast and would have led to isolable products which were not detected in the photoreaction mixtures.

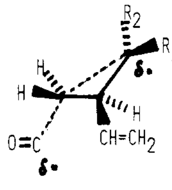
(35) S. C. Clarke and B. L. Johnson, *Tetrahedron*, **27**, 3555 (1971).

(36) J. W. Bevan, A. C. Legon, S. O. Ljunggren, and P. J. Mjoberg, *J. Am. Chem. Soc.*, **100**, 8161 (1978).

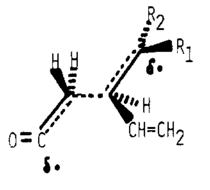
Three additional points are worth mentioning. First, we have postulated above that both 1,3-dienes and vinylcyclopropanes arise via intermediate 1,4-acyl diradicals **25**. As a result substituent effects on the efficiency of formation of vinylcyclopropanes should apply to production of 1,3-dienes if a common mechanism is adhered to and quantum yields are controlled at the cyclopropane ring cleavage stage. Indeed, the data in Table V reveal that this correlation does exist qualitatively. Second, the reasoning employed above to explain the effect of alkyl groups on the quantum yields for total reaction would not apply if CO loss preceded cyclopropane cleavage, i.e., if cyclopropyldicarbinyl diradicals were intermediate in these reactions. Last, although the variations in quantum yields for vinylcyclopropane, 1,4-diene, and 1,3-diene production brought about by substitution are significant, they are due to only small differences in the energetic requirements for competitive reaction pathways initiating from the bicyclic ketone excited states.

Vinylcyclopropane and 1,3-Butadiene Stereochemistry. The cis/trans ratios for 2-methyl-1-vinylcyclopropane and piperylene generated from photofragmentation of the bicyclo[3.1.0]hexan-3-ones **6ex** and **6en** are independent of the 6-methyl stereochemistry of the starting ketone and the reaction temperature (Table VI). Thus, common intermediates serving as precursors for these stereoisomeric products must be present along each reaction pathway. Although vinylcyclopropane production can occur by several pathways (vide supra), these results allow us to rule out processes involving concerted collapse of acyl diradicals **23** or cyclopropyldicarbinyl diradicals **1** directly to cyclopropanes since both mechanisms would occur with inversion of C-6 stereochemistry.[28] Indeed, the mechanism suggested in Scheme VII for photodecarbonylation and fragmentation is in complete accord with C-6 stereochemical randomization via the rotationally equilibrated acyl 1,4-diradical **25**.

An interesting feature of the stereochemical observation is the equivalence and lack of temperature dependence of piperylene and methylvinylcyclopropane stereoisomer ratios from reactions of **6ex** and **6en** (Table VI). This result is suggestive of a common, stereochemically equilibrated intermediate for both 1,3-diene and vinylcyclopropane production, having similar differences in activation energy between pathways leading to cis and trans products. Inspection of transition states for concerted decarbonylation ($45^‡$)[28] and fragmentation ($46^‡$) indicates that similar degrees of crowding between H_1 vs. CH_3 and the vinyl moiety are attained.

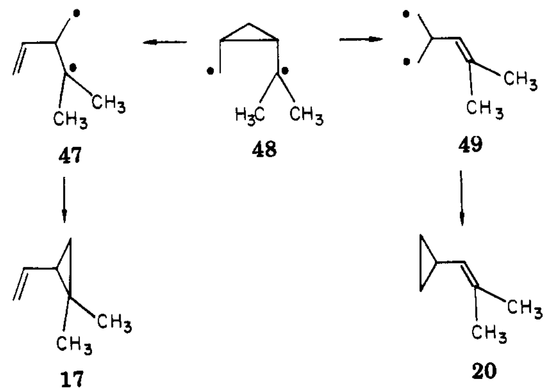


$45^‡$

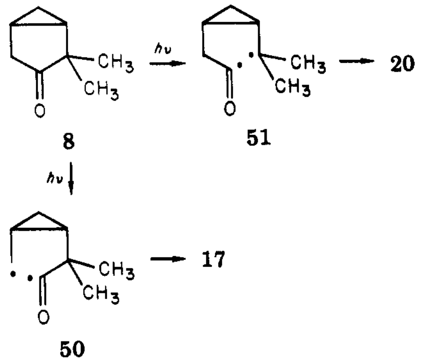


$46^‡$

Regiochemistry of Vinylcyclopropane Formation from 2,2-Dimethylbicyclo[3.1.0]hexan-3-one. Photodecarbonylation of the α,α-dimethylbicyclohexanone **8** leads to production of two vinylcyclopropanes (**17** and **20**) in a temperature-dependent ratio. At 50 °C the reaction generates the dimethylvinyl isomer **20** exclusively while that at 150 °C produces nearly equal amounts of **20** and the dimethylcyclopropyl isomer **17**. The regiochemical course of this process could be determined at several stages depending upon the mechanism followed. For example, in pathways from **8** proceeding via the cyclopropyldicarbinyl diradical **48**, factors governing the direction of ring opening might be similar to those operating in the di-π-methane rearrangement.[6] Zimmerman's theoretical results[5] suggest that reorganization of the singlet ground- or excited-state diradical would prefer the pathway **48** → **49** → **20** in which the donating methyl substituents remain on the vinyl grouping. It is interesting that the mercury-sensitized, di-π-methane rearrangement of 5-methyl-1,4-hexadiene (**21**), contrary to theroretical predictions, generates exclusively the dimethylcyclopropyl isomer **17**.[38]



The regiochemical results are also readily rationalized by the mechanism outlined in Scheme VII. Photoexcited α,α-dimethyl ketone **8** should undergo α cleavage on the most substituted side of the carbonyl producing the tertiary diradical **51**, in preference to the acyl diradical **50**.[39] Accordingly, the ratio of **20** to **17** formed through this mechanism would display the temperature dependence observed, since the pathway of higher activation energy (**8** → **50**) would become more competitive at higher temperatures.



Summary. The results discussed suggest that photodecarbonylation reactions of bicyclo[3.1.0]hexan-3-ones follow mechanistic courses which are more complex than those initially suggested by Hess and Pitts. Moreover, the interesting substituent effects on product ratios and overall reaction quantum yields appear nicely rationalized on the

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(37) (a) D. S. Weiss, *Tetrahedron Lett.*, 1039 (1978). (b) It is not totally clear why ketone **8** reacts less efficiently than the parent compound **5** since the α,α-dimethyl substituents should enhance α cleavage in competition with excited-state decay and slow internal recombination which competes with cyclopropane ring closure.

(38) (a) J. Meinwald and W. G. Smith, *J. Am. Chem. Soc.*, **89**, 4923 (1967). (b) However, 3,3-dimethyl-1,4-pentadiene, another product from mercury-sensitized irradiation of **21**, is known to rearrange to **17**. Thus, the origin of **17** under the di-π-methane rearrangement reaction conditions has not been proven. Also, mercury-sensitized reactions could produce triplet cyclopropyldicarbinyl diradicals whose chemical fate may be different from singlet species.

(39) G. Quinkert, *Pure Appl. Chem.*, **9**, 607 (1964).

(40) L. Schmerling and J. P. West, *J. Am. Chem. Soc.*, **74**, 2885 (1952); R. Ciola and R. L. Burwell, *J. Org. Chem.*, **23**, 1063 (1958).

basis of stereoelectronic and electronic arguments and mechanisms involving the intermediacy of acyl diradicals. Furthermore, the stereochemical and regiochemical aspects of these processes can best be accommodated by mechanisms not involving intermediate cyclopropyldicarbinyl diradicals.

Experimental Section

General Procedures. 3-Methyl-1,4-pentadiene (Chemsampco), *cis*-1,3-pentadiene, *trans*-1,3-pentadiene (Aldrich), 1,3-butadiene (Matheson), 5-methyl-1,4-hexadiene (Chemsampco), 1,1-dibromoethane (Eastman), and diethylzinc (Alfa) were commercially available and used without purification. Bicyclo[3.1.0]hexan-3-one,[15] 6,6-dimethylbicyclo[3.1.0]hexan-3-one,[12] and 3,3-dimethyl-1,4-pentadiene[40] were prepared by known procedures.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. NMR spectra were recorded on Varian HA-100 or T-60 (proton) and JEOL PS-100 (carbon) spectrometers with tetramethylsilane as an internal standard. Infrared spectra were taken with a Beckman IR-8 spectrometer with polystyrene as reference. Solution-phase ultraviolet absorption spectra were measured with a Beckman Acta-III spectrophotometer. Gas-phase ultraviolet absorption spectra were measured with a Cary 17 spectrophotometer. Gas chromatographic analyses of gaseous samples were performed on a Carle AGC-311 flame-ionization chromatograph equipped with a Carle 10-mL gas-sampling loop. Gas chromatographic analyses of liquid samples were performed on a Varian-940 chromatograph with flame-ionization detection. Preparative gas chromatographic work was done on a Varian-2700 chromatograph. Integration of analytical gas chromatographic traces was performed with a Vidar 6300 Autolab digital integrator. Mass spectroscopic data were recorded at 70 eV on a Du Pont 21-490 mass spectrometer. High-resolution mass spectra were taken on CEC-21-110 double-focusing mass spectrometer.

Apparatus and Procedures for Gas-Phase Photolysis. The photolysis apparatus used consisted of one electrically heated quartz cell (2.5 × 30 cm) connected to a manifold for sampling and loading the contents of the cell. This grease- and mercury-free manifold was attached to an oil diffusion pump with a mechanical backing pump. The temperature of the cell was determined by three chrome–alumel thermocouples placed at each end and at the center of the cell. The light source was a 200-W Illumination Industries short-arc high-pressure mercury-vapor lamp. The light was collimated by a Pyrex lens system focused at the center of the cell. Pressures of the various gas samples were measured with a Validyne transducer. The pressure in the low-pressure part of the system was monitored by a Consolidated Vacuum Corp. thermocouple vacuum gauge.

Vapor-pressure studies showed that approximately 55 mg of the bicyclic ketones would remain in the gas phase at 100 °C and exhibit a pressure of about 90 torr. The reactions were carried out by distilling a weighed and degassed sample, usually about 50 mg, of the bicyclic ketone into the room-temperature evacuated cell, closing off the cell, heating to reaction temperature, and photolyzing. The irradiation time was typically 6 h which led to consumption of less than 5% of the bicyclohexanone. After irradiation, the entire contents of the cell was removed and isolated by opening the cell to an evacuated bulb which was cooled by liquid nitrogen. When the pressure of the cell decreased to and remained at 0 torr for 30 min, the bulb was closed off and the cell allowed to cool to room temperature. Ten torr of degassed *n*-hexane was then added to the empty room-temperature cell and this quantity of *n*-hexane frozen into the trapping bulb as an internal standard. The trapping bulb was allowed to warm to room temperature and attached to the gas-sampling loop of the gas chromatograph. The sampling loop was evacuated and filled with approximately 5-torr samples to be injected for analysis (25 ft × $^1/_8$ in., 30% dimethyl sulfolane, 60–80 mesh Chromosorb P, 40 °C, inlet pressure of 40 psig).

Quantum Yield Measurements. Quantum yields were determined by comparing the production of photoproducts from the methylated bicyclohexanones to the known quantum yield for the production of 1,4-pentadiene from bicyclo[3.1.0]hexan-3-one ($\Phi = 0.60$ at 118 °C and 35 torr).[9] The ultraviolet spectra, taken in *n*-pentane, of all the bicyclic ketones studied were characteristically equivalent to that of bicyclo[3.1.0]hexan-3-one. The gas-phase ultraviolet spectra of both *endo*- and *exo*-6-methylbicyclo[3.1.0]hexan-3-one were also identical.

2-((*n*-Butylthio)methylene)-4,4-dimethylbicyclo[3.1.0]hexan-3-one (10). A mixture of 530 mL of dry *tert*-butyl alcohol and 8.9 g (0.23 mol) of potassium metal was stirred until the potassium dissolved. A solution of 17.8 g (0.091 mol) of 2-((*n*-butylthio)methylene)bicyclo[3.1.0]hexan-3-one,[13] 20 mL (0.32 mol) of iodomethane, and 175 mL of dry *tert*-butyl alcohol was added dropwise over a 30-min period. The solution became dark red and a precipitate formed. After 2 h of being stirred, the reaction mixture was heated to a gradual reflux and another 20 mL (0.32 mol) of iodomethane was added in one portion. The slow reflux was continued for 2 h more, during which time the red color turned tan and more precipitate formed. The reaction was cooled and stirred at room temperature overnight. Water was then added until the precipitate dissolved, and the resultant solution was extracted with ether. The ethereal extracts were dried (sodium sulfate), concentrated in vacuo, and distilled (bulb-to-bulb with a Kugelrohr) at 175 °C (0.3 torr) to yield 18 g (89%) of the thioenol ether **10** as a light yellow oil: ^{1}H NMR (CCl$_4$) δ 0.26 (m, 1 H), 1.02 (s, 3 H), 1.09 (s, 3 H), 0.86–1.72 (m, 9 H), 2.44–2.90 (m, 3 H), 6.93 (s, 1 H); ^{13}C NMR (CDCl$_3$) δ 206.15 (s, C-3), 137.35 (d, methylene), 135.47 (s, C-2), 47.06 (s, C-4), 39.77, 38.83, 31.31, 28.19, 26.73, 24.44, 16.57, 14.16, 13.69; mass spectrum *m/e* (relative intensities) 224 (15), 178 (38), 167 (18), 139 (10), 137 (10), 122 (34), 91 (22), 57 (100); high-resolution mass spectrum, *m/e* 224.123002 (C$_{13}$H$_{20}$OS required 224.123482).

2,2-Dimethylbicyclo[3.1.0]hexan-3-one (8). The method of Ireland and Marshall was employed to remove the (*n*-butylthio)methylene blocking group.[14] A mixture of 18 g (0.08 mol) of the dimethyl *n*-butylthioenol ether **10**, 80 mL of 25% aqueous potassium hydroxide, and 80 mL of diethylene glycol was refluxed for 6 h and the resultant solution steam distilled. The aqueous distillate was extracted with ether. The ethereal extracts were combined and dried (sodium sulfate). A careful distillation using a Snyder column at atmospheric pressure was performed to remove the ether. Final purification was done by preparative GLC (15 ft × $^5/_{16}$ in., 20% SE-30, 60–70 mesh ABS Anakrom, 130 °C, inlet pressure of 10 psig), yielding 1.4 g (14%) of the dimethyl bicyclic ketone **8**: ^{1}H NMR (CCl$_4$) δ −0.13 (m, 1 H), 0.97 (s, 3 H), 1.09 (s, 3 H), 0.45–1.58 (m, 4 H), 1.98 (d, 1 H, J = 18 Hz), 2.67 (dq, 1 H, J = 18 and 2 Hz); ^{13}C NMR (CDCl$_3$) δ 9.00 (d, C-5), 11.25 (t, C-6), 20.75 (q, CH$_3$), 25.44 (d, C-1), 26.57 (q, CH$_3$), 39.76 (t, C-4), 47.14 (s, C-2), 220.92 (s, C-3); UV max (*n*-pentane) 297 nm (ϵ 27.3); IR (liquid film) 2975, 1730, 1445, 1060, 790 cm^{-1}; mass spectrum, *m/e* (relative intensities) 124 (8), 96 (40), 83 (80), 81 (100), 67 (28), 53 (25), and 41 (49). Anal. Calcd for C$_8$H$_{12}$O: C, 77.38; H, 9.74; O, 12.88. Found: C, 77.52; H, 9.90; O, 12.57.

***exo*- and *endo*-6-Methyl-*cis*-bicyclo[3.1.0]hexan-3-ols (12ex and 12en).** To a slurry of zinc–copper couple, prepared from 40 g of zinc dust by Winstein's procedure B,[15] in 100 mL of anhydrous ether under nitrogen was added in one portion 37.6 g (0.30 mol) of 1,1-dibromoethane and 8.4 g (0.10 mol) of cyclopenten-4-ol[15] followed by 60 mL of anhydrous ether. After a short induction period, an exothermic reaction occurred which lasted for several minutes. After self-reflux subsided, the solution was heated at gentle reflux for 4 h, cooled, and stirred at room temperature overnight. The reaction mixture was then suction filtered through a Celite pad into 500 mL of water. The resulting emulsion was extracted continuously with ether. The ethereal extracts were dried (sodium sulfate) and concentrated by careful distillation. The yellow, oily pot residue was then purified by preparative GLC (16 ft × $^3/_8$ in., 6% SE-30, 60–70 mesh ABS Anakrom, inlet pressure of 10 psig, temperature programmed to increase at 4 °C/min starting at 110 °C and ending at 150 °C), yielding 2.6 g (23%) of the *exo*-methyl bicyclic alcohol **12ex** and 0.8 g (7%) of the *endo*-methyl bicyclic alcohol **12en**. This mixture of isomeric alcohols was also found to be separable by silica gel column chromatography using the following procedure. The mixture (1.0 g) was placed on a column (1.5 × 75 cm) and slurry packed with silica gel (Davison grade 923, 100–200 mesh) in pentane. Elution was with 1 L of pentane, 2 L of 5% ether–pentane, 2 L of 20% ether–pentane; 20-mL fractions were collected. Fractions 191 through 208 gave the exo isomer **12ex** and fractions 212 through 235 gave the endo isomer **12en** after concentration in vacuo using careful fractional distillations. ^{1}H NMR and IR spectra for the exo alcohol **12ex** were identical with those previously reported.[11] **12ex:** ^{13}C NMR (CDCl$_3$) δ 17.88 (d, C-3), 18.94 (t, C-2 and C-4), 25.76 (d, C-1 and C-5), 38.57 (d, C-6), 74.33 (q, CH$_3$); mass spectrum *m/e* (relative intensities) 112 (4), 94 (54), 79 (57), 68 (100), 57 (61), 55 (43), 41 (37). **12en:** ^{1}H NMR (CDCl$_3$) δ 1.00 (s, 3 H), 0.89–1.45 (m, 3 H), 1.89 (s, 1 H), 1.61–2.62 (m, 4 H), 4.54 (q, 1 H); ^{13}C NMR (CDCl$_3$) δ 7.31 (q, CH$_3$), 17.57 (d, C-6), 19.57 (d, C-1 and C-5), 32.76 (t, C-2 and C-4), 80.21 (d, C-3); IR (liquid film) 3320, 3055, 2965, 2890, 1445, 1350, 1265, 1010 cm^{-1}; mass spectrum, *m/e* (relative intensities) 112 (2), 94 (53), 79 (59), 68 (100), 67 (70), 57 (57), 55 (47), 53 (46), 41 (62). Anal. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78. Found: C, 74.75; H, 10.55.

***exo*-6-Methyl-*cis*-bicyclo[3.1.0]hexan-3-one (12ex).** To a slurry of zinc–copper couple, prepared from 30 g of zinc dust in the manner previously described, in 50 mL of anhydrous ether was added 3 mL (0.03 mol) of diethylzinc and 1.9 g (0.022 mol) of cyclopenten-4-ol. The dropwise addition of 8.2 g (0.044 mol) of 1,1-dibromoethane caused the reaction to self-reflux. After addition was complete, the reaction mixture was allowed to stand at room temperature overnight. Water was added cautiously and the reaction mixture suction filtered. The ether–water filtrate was continuously extracted with ether. The extract was dried (sodium sulfate) and the ether carefully removed by distillation. A vacuum short-path distillation yielded 2.1 g (85%) of only the exo bicyclic alcohol **12ex**.

***exo*-6-Methylbicyclo[3.1.0]hexan-3-one (6ex).** The oxidation of alcohol **12ex** was conducted by using the procedure of Winstein.[15] To 20 mL of ice-cold pyridine was added in several portions 2 g (0.02 mol) of chromium trioxide. The resulting yellow suspension was allowed to warm to room temperature and 510 mg (0.0046 mol) of alcohol **12ex**, dissolved in 10 mL of pyridine, was added in one portion. The mixture was stirred under nitrogen at room temperature for 20 h. Water was then added and the emulsion extracted with ether. The ethereal layer was washed successively with water, 1.8 N sulfuric acid, water, saturated sodium bicarbonate, and water. The ethereal layer was then dried (sodium sulfate). Distillation through a Snyder column was performed to remove the ether. The pot residue was purified by preparative GLC (10 ft × $^3/_8$ in., 28% SE-30, 60–70 mesh ABS Anakrom, 185 °C, inlet pressure of 6 psig), yielding 443 mg (89%) of the bicyclic ketone **6ex**. ^{1}H NMR[11] and IR spectra were identical with those previously reported; ^{13}C NMR (CDCl$_3$) δ 16.75 (q, CH$_3$), 20.32 (d, C-1 and C-5), 21.19 (d, C-6), 40.82 (t, C-2 and C-4), 187.35 (s, C-3); UV max (*n*-pentane) 288 nm (ϵ 17.1); UV max (gas phase) 280 nm (27).

***endo*-6-Methylbicyclo[3.1.0]hexan-3-one (6en).** The oxidation of alcohol **12en** was carried out by the same procedure described for oxidation of alcohol **12ex**. Purification was performed by preparative GLC (17 ft × $^3/_8$ in., 6% SE-30, 60–70 mesh ABS Anakrow, 145 °C, inlet pressure of 17 psig), yielding 412 mg (88%) of the bicyclic ketone **6en** from 480 mg (0.0043 mol) of the starting alcohol: ^{1}H NMR (CDCl$_3$) δ 0.84 (d, 3 H), 1.18 (m, 1 H), 2.21 (m, 2 H), 2.40–2.90 (m, 4 H); ^{13}C NMR (CDCl$_3$) δ 6.31 (q, CH$_3$), 13.94 (d, C-6), 14.88 (d, C-1 and C-5), 36.82 (t, C-2 and C-4), 219.36 (s, C-3); UV max (*n*-pentane) 287 nm (ϵ 14.4); UV max (gas phase) 280 nm (25); IR (liquid film) 3045, 3010, 2940, 1790, 1724, 1457, 1260, 1100, 810 cm^{-1}. Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.14; H, 9.11.

4-Methyl-1,3-pentadiene (19). To a slurry of 67.5 g (0.19 mol) of methyltriphenylphosphonium bromide and 100 mL of anhydrous ether was added 125 mL (0.18 mol) of 1.4 N *n*-butyllithium in pentane solution. After the resulting red solution was stirred for 1 h, 10 g (0.12 mol) of β,β-dimethylacrolein[41] was added dropwise. The mixture was stirred at room temperature overnight. A bulb-to-bulb flash vacuum distillation was then carried out on the reaction mixture to separate the volatile and nonvolatile components. Careful distillation of this distillate through a Snyder column removed the ether and pentane. Separation by preparative GLC (20 ft × 0.25 in., 10% dinonyl phthalate, 60–80 mesh Chromosorb W, 55 °C, inlet pressure of 16 psig) yielded 5.6 g (57%) of the diene **19**.

***cis*-1-Methyl-2-vinylcyclopropane (14c).** The procedure employed was analogous to that used by von Doering and Roth.[42] Dry diazomethane, prepared by the addition of 0.5 g of *N*-methyl-*N*-nitrosourea to the generator flask containing 50% aqueous potassium hydroxide solution, in a stream of nitrogen was passed into a stirred suspension of 200 mg of cuprous chloride in 5 g of *cis*-1,3-pentadiene. The reaction solution was filtered to remove the cuprous chloride. Purification by preparative GLC (20 ft × 0.25 in., 10% dinonyl phthalate, 70–80 mesh silanized Chromosorb W, 60 °C, inlet pressure of 17 psig) gave *cis*-1-methyl-2-vinylcyclopropane (**14c**): ^{1}H NMR (CDCl$_3$) δ 0.17 (m, 1 H), 1.06 (d, 3 H, J = 2 Hz), 0.82–1.65 (m, 3 H), 3.80–5.94 (m, 3 H); mass spectrum, *m/e* (relative intensities) 82 (53), 67 (100), 54 (25), 41 (49), 39 (43).

***trans*-1-Methyl-2-vinylcyclopropane (14t).** Diazomethane was added to *trans*-1,3-pentadiene in the manner described for the production of *cis*-1-methyl-2-vinylcyclopropane to produce *trans*-1-methyl-2-vinylcyclopropane (**14t**): ^{1}H NMR (CDCl$_3$) δ 1.09 (d, 3 H, J = 3.5 Hz), 0.33–1.49 (m, 4 H), 4.65–5.78 (m, 3 H); mass spectrum, *m/e* (relative intensities) 82 (69), 67 (100), 54 (29), 41 (59), 39 (47).

1-(2-Methyl-1-propenyl)cyclopropane (20). Diazomethane was added to 4-methyl-1,3-pentadiene (**19**) in the manner described for the production of *cis*-1-methyl-2-vinylcyclopropane to generate 1-(2-methyl-1-propenyl)cyclopropane (**20**): ^{1}H NMR (CDCl$_3$) δ 0.0–0.76 (m, 4 H), 1.06 (d, 1 H, J = 6 Hz), 1.67 (d, 3 H, J = 2 Hz), 1.75 (d, 3 H, J = 2 Hz), 4.55 (dq, 1 H, J = 6 and 2 Hz); mass spectrum, *m/e* (relative intensities) 96 (54), 81 (100), 67 (51), 53 (43), 41 (76).

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