

Solution-Phase Photodecarbonylation of the Bicyclo[3.1.0]hexan-3-one System^{1,2}

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Abstract: Direct irradiation of solutions containing (-)-thujone (6) or (+)-isothujone (7) affords *trans*- and *cis*-5-methylene-6-methylhept-2-ene (8 and 9) in quantitative yield. The epimeric ketones give identical product mixtures, which are somewhat temperature dependent. The product ratio remains constant throughout irradiation, and appropriate control experiments indicate that the observed diene mixture does not represent a rapidly established photostationary state. Limited epimerization of the ketones is observed although this process is much less efficient than extrusion of carbon monoxide. Quenching studies employing piperylene indicate that the majority of the decarbonylation products originate from a short-lived triplet state. Direct irradiation of solutions containing *exo*- or *endo*-2-methylbicyclo[3.1.0]hexan-3-one (10 or 11) yields *trans*- and *cis*-hexa-1,4-diene (12 and 13) in high yield. Again the epimeric ketones give identical product mixtures, which are slightly temperature dependent. Direct irradiation of solutions containing *exo,exo*-, *exo,endo*-, or *endo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (16, 15, or 14) affords similar, but not identical, mixtures of *trans,trans*-, *trans,cis*-, and *cis,cis*-hepta-2,5-diene (17, 18, and 19) in high yield. Each of these product ratios is somewhat temperature dependent. These data are explained in terms of a mechanism involving biradical intermediates. Excitation followed by intersystem crossing leads to a short-lived triplet state which undergoes Norrish I cleavage toward the more substituted α position. The diene products are formed upon synchronous cleavage of the cyclopropane bond and loss of carbon monoxide. If internal rotation in the intermediate is rapid with respect to decay, the observed product ratios may be rationalized. Inefficient reclosure of the biradical species leads to limited epimerization of the bicyclo[3.1.0]hexan-3-ones.

In the condensed phase⁴⁻⁹ or the vapor^{10,11} bicyclo[3.1.0]hexan-3-one systems undergo facile photodecarbonylation. Corresponding 1,4-dienes are formed with high quantum efficiency during photolyses performed in solution or with undiluted, liquid ketones. In the vapor phase these products are accompanied by lesser amounts of vinylcyclopropanes and 1,3-dienes, which presumably result from loss of ketene.

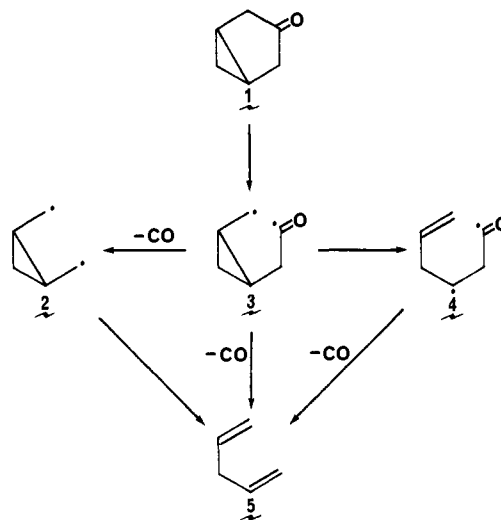
A satisfactory mechanistic description of these transformations has not been established by experiment. There remains uncertainty concerning the timing of bond making and breaking during extrusion of carbon monoxide from bicyclo[3.1.0]hexan-3-one and the formation of 1,4-pentadiene. Formally this conversion may be viewed as a linear or nonlinear cheletropic reaction occurring in a concerted fashion with conservation of orbital symmetry.¹² The lack of stereospecificity exhibited in photodecarbonylation product mixtures has prompted all authors to eschew this description and to invoke one or more routes encompassed by the biradical formalism depicted in Scheme I.

The present research examines the photolyses of bicyclo[3.1.0]hexan-3-one systems bearing stereochemical markers on the C₂ and C₄ positions. The distribution of 1,4-diene products produced during photodecarbonylation of this series of ketones permits further speculation about the intermediates possible within the biradical formalism.

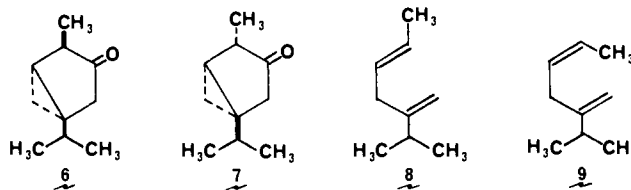
Results

Thujone. Samples of (-)-thujone (6) were most readily obtained from oil of white cedar (*Thuja occidentalis* L.) while (+)-isothujone (7) was isolated from oil of wormwood (*Artemisia ab-*

Scheme I. Plausible Biradical Intermediates Involved in Photodecarbonylation of Bicyclo[3.1.0]hexan-3-one



sinthum L.). Both of these essential oils were carefully distilled under vacuum to isolate the fraction of molecular formula C₁₀H₁₆O. Preparative gas-liquid chromatography (GLC) provided pure samples of each of the epimeric ketones. Spectral and physical data measured for these compounds were consistent with literature reports.¹³⁻¹⁹



(1) This article is dedicated to George S. Hammond on the occasion of his 60th birthday.

(2) This research has been described in the doctoral dissertation of Gregory D. Lyon, University of Oregon, Eugene, OR, 1975.

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Table I. Mole Percentage *cis*-5-Methylene-6-methylhept-2-ene (9) from (-)-Thujone (6) and (+)-Isothujone (7)

<i>t</i> , °C	(-)-thujone	(+)-isothujone
89.0	16.4 ± 0.3	16.9 ± 0.4
61.2 ^a	16.0 ± 0.2	16.1 ± 0.2
49.8	14.7 ± 0.1	15.4 ± 0.5
41.9 ^a	15.2 ± 0.2	15.2 ± 0.2
20.1 ^a	13.3 ± 0.2	13.3 ± 0.2
10.8	11.6 ± 0.1	11.7 ± 0.2
-26.5	7.8 ± 0.1	7.7 ± 0.1
-74.5	4.4 ± 0.2	4.8 ± 0.1

^a These experiments were performed in cyclohexane. The other entries represent photolyses carried out in isooctane.

Dilute pentane solutions containing a mixture of the thujones and internal standard were degassed and irradiated, employing a Pyrex-filtered 450-W medium-pressure mercury source. Analytical GLC demonstrated that two products were formed in 100.1 ± 0.8% yield.²⁰ Separation by preparative GLC afforded pure samples of each of these compounds, which were identified on the basis of their IR and ¹H NMR spectra. The major product, which showed strong IR absorptions at 969 and 894 cm⁻¹, proved to be *trans*-5-methylene-6-methylhept-2-ene (8).^{4,21} The minor product, which exhibited IR absorptions at 893 and 685 cm⁻¹ and none near 965 cm⁻¹, was assigned as *cis*-5-methylene-6-methylhept-2-ene (9).⁶ The ¹H NMR spectra were consistent with the structures suggested for these isomeric dienes.

Dilute solutions of each pure thujone isomer in either isooctane or cyclohexane were degassed and irradiated at 305 nm, employing an Ultraviolet Products source. The lamps encircled a Pyrex bath which permitted irradiation at constant temperature. Analytical GLC conducted at intervals demonstrated that the photoproduct ratios were time independent in all of the experiments. The mole percentages of *cis*-5-methylene-6-methylhept-2-ene formed from both (-)-thujone and (+)-isothujone at various temperatures are given in Table I. Statistical analysis employing a Student's *t* test indicated that the differences between the product ratios from the two ketones were not significant at the 0.85 confidence level in any of the experiments.

As a control experiment, a dilute isooctane solution of cyclopentanone and a mixture of the photoproducts was degassed and irradiated at 305 nm. Before photolysis, the mixture of dienes contained 42.0 mol % *cis*-5-methylene-6-methylhept-2-ene, and GLC analysis following a 30-min irradiation period indicated no detectable change in the photoproduct ratio.

In a second control experiment, dilute isooctane solutions of (-)-thujone were degassed and irradiated at 305 nm so that the appearance of (+)-isothujone could be followed by analytical GLC. In one experiment, (+)-isothujone existed as a 0.6 mol % impurity prior to photolysis. When the photodecarbonylation reaction was 30.6% complete, this epimer constituted 1.3 mol % of the total reaction mixture. In a companion study, (-)-thujone was present as a 0.3 mol % impurity prior to irradiation of (+)-isothujone. After 30.9% of the extrusion process was effected, the amount of (-)-thujone had increased to 4.0 mol % of the total photolysate. No detailed examinations which measured the quantum efficiencies of photoepimerization were undertaken.

Pentane solutions were prepared containing varying amounts of mixed *cis*- and *trans*-piperylene, the isomeric ketones (approximately 40 mol % (-)-thujone), and an internal standard. The thujone concentration was adjusted so that greater than 99% of the incident radiation would be absorbed throughout the course of the proposed experiments. Samples were degassed, sealed, and irradiated in a "merry-go-round" apparatus designed to isolate the 313-nm line of a 450-W medium-pressure mercury source.²²

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Table II. Quenching of Thujone Photodecarbonylation by Piperylene

piperylene, M	rel quantum yield, Φ_0/Φ	
	exptl	calcd ^a
0.49	2.27	2.14
0.98	3.08	3.10
	3.16	
1.90	4.40	4.52
	4.52	
2.86	5.76	5.65
3.75	6.46	6.48

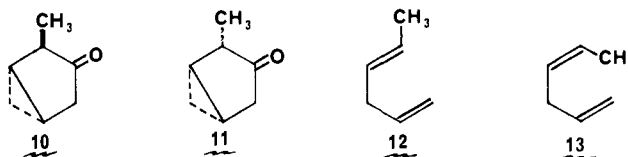
^a Assuming photodecarbonylation occurs from two states, only one of which is quenched by piperylene.

The relative quantum yields of photoproduct formation for samples containing varying amounts of piperylene were determined by analytical GLC. These data are shown in Table II.

Ampules charged with pentane solutions containing each of the pure thujone isomers and internal standard were prepared and irradiated as described above. During the course of the experiments, light intensity was measured, employing potassium ferrioxalate actinometry.^{23,24} Absolute yields of the photoproducts were determined by analytical GLC. The quantum yield for photodecarbonylation of (-)-thujone was calculated to be 0.908 ± 0.006, and the value for (+)-isothujone was 0.819 ± 0.002.

2-Methylbicyclo[3.1.0]hexan-3-one. Cyclopenten-4-ol was prepared from cyclopentadiene by using the hydroboration method described by Allred, Sonnenberg, and Winstein.²⁵ The Simmons-Smith procedure of Winstein and Sonnenberg²⁶ employing the zinc-copper couple described by LeGoff²⁷ was modified by the use of methylene bromide instead of the iodide to prepare *endo*-bicyclo[3.1.0]hexan-3-ol. Oxidation of the alcohol with dichromate in acetic acid²⁸ or Jones reagent²⁹ gave comparable yields of bicyclo[3.1.0]hexan-3-one. The overall sequence of reactions was effected in 14-15% yield.

The parent ketone was converted to 2-(hydroxymethylene)-bicyclo[3.1.0]hexan-3-one by using a modification of the method described by Ainsworth³⁰ for condensation with ethyl formate. Thiol condensation employing the procedure of Ireland and Marshall³¹ gave 2-((*n*-butylthio)methylene)bicyclo[3.1.0]hexan-3-one, which was then subjected to Raney nickel desulfurization. This sequence afforded mixtures of *exo*- and *endo*-2-methylbicyclo[3.1.0]hexan-3-one (10 and 11) in 60-63% overall yield. Pure samples of each of the ketones could be obtained by preparative GLC.



The epimeric products were characterized by comparison of ¹H NMR spectra with data for (-)-thujone and (+)-isothujone.¹⁵ Resonances for methyl groups in the *exo*-C₂₍₄₎ positions are found at lower field than the signals for those in the *endo* positions. A similar relationship holds for the resonances due to the methine proton at these centers. In addition, the signals for the methine

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Table III. Mole Percentage of *cis*-Hexa-1,4-diene (13) from *endo*-11 and *exo*-2-Methylbicyclo[3.1.0]hexan-3-one (10)

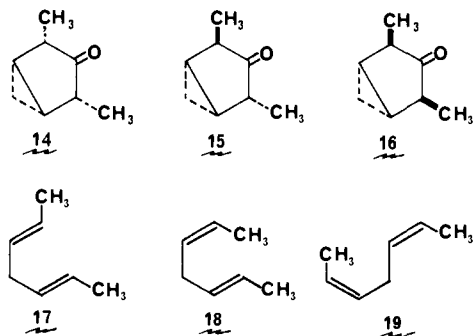
<i>t</i> , °C	exo isomer	endo isomer
20.0	16.3 ± 0.1	16.2 ± 0.1
35.0	17.1 ± 0.1	17.1 ± 0.2
50.0	18.3 ± 0.1	18.4 ± 0.1

protons in the *endo*-C₂₍₄₎ positions appear as quartets, whereas more complex patterns are found for those in the *exo* position, which are further coupled to the C₁₍₅₎ and C₆ hydrogens. This correlation firmly establishes the stereochemistry of the 2-methylbicyclo[3.1.0]hexan-3-one isomers since the structures of (-)-thujone and (+)-isothujone, including the stereochemistry at the C₄ position, are anchored in chemical correlation studies.^{32,33}

Dilute pentane solutions of *endo*-2-methylbicyclo[3.1.0]hexan-3-one and internal standard were degassed and irradiated, employing a Pyrex-filtered 450-W medium-pressure mercury source. Analytical GLC indicated that two volatile products were formed in 90.4 ± 1.4% yield. Separation by preparative GLC afforded pure samples of each of these compounds, which were identified by comparison of IR and ¹H NMR spectra with literature data.^{34,35} The major and minor photoproducts were assigned as *trans*- and *cis*-hexa-1,4-diene (12 and 13).

Dilute 3-methylpentane solutions of each pure 2-methylbicyclo[3.1.0]hexan-3-one isomer were degassed and irradiated at 305 nm, employing an Ultraviolet Products source. Analytical GLC conducted at intervals demonstrated that the photoproduct ratios were time independent in all of the experiments. The mole percentages of *cis*-hexa-1,4-diene formed from both ketones at various temperatures are given in Table III. Statistical analysis employing a Student's *t* test indicated that the differences in the product ratios from *endo*- and *exo*-2-methylbicyclo[3.1.0]hexan-3-one were not significant at the 0.90 confidence level in any of the experiments.

2,4-Dimethylbicyclo[3.1.0]hexan-3-one. Procedures effective in preparing 2-methylbicyclo[3.1.0]hexan-3-one were employed to convert that intermediate into 2,4-dimethylbicyclo[3.1.0]hexan-3-one in 60–63% overall yield. Analytical GLC employing a variety of liquid phases resolved the ketone mixture into only two fractions. Material comprising the major fraction (60–70 mol %) of longer retention time was isolated by preparative GLC. Analysis of the ¹H NMR spectrum of this compound in light of correlations demonstrated with the thujone isomers established that it was *endo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (14). Similar isolation and analysis of the minor fraction revealed that *exo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (15) was the main constituent. Careful examination of the ¹H NMR spectrum measured for this fraction showed a small doublet centered at δ 1.23 in the methyl region which could be attributed to *exo,exo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (16).



Samples of the synthetic 2,4-dimethylbicyclo[3.1.0]hexan-3-one mixture were equilibrated at 140 °C by passing through a short

Table IV. Mole Percentages of Hepta-2,5-diene Isomers (17–19) from *exo,exo*-2,4-Dimethylbicyclo[3.1.0]hexan-3-one (16)

<i>t</i> , °C	<i>trans,trans</i>	<i>trans,cis</i>	<i>cis,cis</i>
20.1	75.9 ± 0.2	22.9 ± 0.2	1.25 ± 0.01
41.9	71.6 ± 0.2	26.6 ± 0.2	1.79 ± 0.03
61.1	68.5 ± 0.1	29.2 ± 0.1	2.32 ± 0.02

Table V. Mole Percentages of Hepta-2,5-diene Isomers (17–19) from *exo,endo*-2,4-Dimethylbicyclo[3.1.0]hexan-3-one (15)

<i>t</i> , °C	<i>trans,trans</i>	<i>trans,cis</i>	<i>cis,cis</i>
20.1	79.5 ± 0.1	19.6 ± 0.1	0.93 ± 0.02
41.9	74.4 ± 0.3	24.1 ± 0.2	1.52 ± 0.03
61.1	70.8 ± 0.2	27.0 ± 0.2	2.16 ± 0.03

Table VI. Mole Percentages of Hepta-2,5-diene Isomers (17–19) from *endo,endo*-2,4-Dimethylbicyclo[3.1.0]hexan-3-one (14)

<i>t</i> , °C	<i>trans,trans</i>	<i>trans,cis</i>	<i>cis,cis</i>
20.1	81.3 ± 0.2	18.0 ± 0.1	0.72 ± 0.04
41.9	76.8 ± 0.2	21.9 ± 0.2	1.29 ± 0.02
61.1	73.0 ± 0.1	25.0 ± 0.1	2.03 ± 0.01

section of tubing charged with basic alumina and inserted between the injection port and the usual preparative GLC column. The fraction of shorter retention time, which comprised *exo,endo*- and *exo,exo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one, was reduced with lithium tri-*tert*-butoxyaluminum hydride.³⁶ The alcohol mixture was separated into three fractions by preparative GLC. The component of shortest retention time (approximately 50 mol %) was converted to *exo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one by Jones oxidation,²⁹ and the elusive *exo,exo* isomer was obtained by similar treatment of the fraction with longest retention time (approximately 15 mol %).

Dilute pentane solutions of 2,4-dimethylbicyclo[3.1.0]hexan-3-one and internal standard were degassed and irradiated, employing a Pyrex-filtered 450-W medium-pressure mercury source. Analytical GLC of volatile materials indicated that two major products and a minor component were formed in 93.9 ± 0.2% yield. Separation by preparative GLC afforded pure samples of each of the major products, which were identified on the basis of IR and ¹H NMR data.³⁷ The product of shortest retention time was found to be *trans,trans*-hepta-2,5-diene (17) and the other major product was assigned as the *trans,cis* isomer (18). The minor component was not isolated; however, it had a GLC retention time identical with that of an authentic sample of *cis,cis*-hepta-2,5-diene (19) prepared by Wittig reaction of 1,3-bis-(triphenylphosphonium)propane dibromide with acetaldehyde.

Dilute cyclohexane solutions of each pure 2,4-dimethylbicyclo[3.1.0]hexan-3-one isomer were degassed and irradiated at 305 nm, employing an Ultraviolet Products source. Analytical GLC conducted at intervals demonstrated that the photoproduct ratios were time independent in all of the experiments. The mole percentages of products from each of the ketones are given in Tables IV–VI. The product distributions from *exo,exo*- and *endo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one are noticeably different. Analysis employing a Student's *t* test shows that at all of the temperatures studied this difference for each of the products is significant above the 0.995 confidence level.

Discussion

Biradical Intermediates. Photolyses of (-)-thujone and (+)-isothujone yield indistinguishable mixtures of *cis*- and *trans*-5-methylene-6-methylhept-2-ene, and control experiments demonstrate that this ratio does not represent a rapidly established photostationary state. Although the limited epimerization observed is of mechanistic significance, the inefficiency of this process

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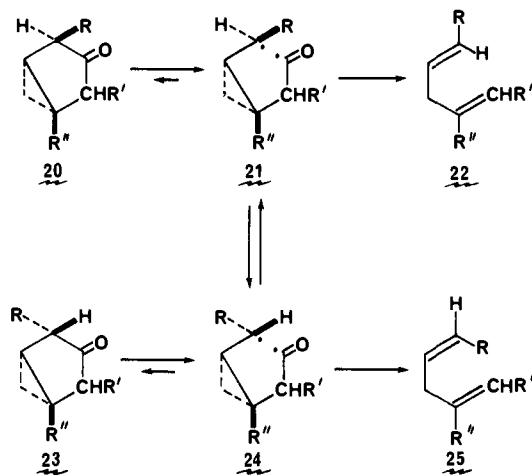
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Scheme II. Proposed Mechanism for Photodecarbonylation of Substituted Bicyclo[3.1.0]hexan-3-ones



precludes a trivial explanation of the common product mixture.

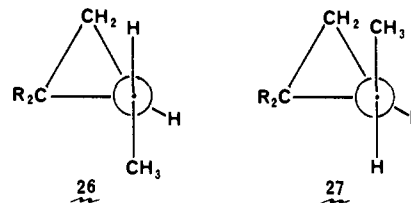
A simple mechanism which is consistent with these results and the data obtained in the variable-temperature photolyses of *exo*- and *endo*-2-methylbicyclo[3.1.0]hexan-3-one is shown in Scheme II. The excited states of the ketones undergo Norrish I cleavage toward the more substituted α center³⁸⁻⁴¹ with initial formation of biradicals which are conformational isomers. Production of a common product mixture in the thujone photolyses requires that internal rotation about the single bond terminating at the $-\text{CHCH}_3$ center must be rapid with respect to the decay modes of the biradical. Product formation occurs upon synchronous loss of carbon monoxide and cleavage of the internal cyclopropane bond. This process must be more facile than reclosure of the equilibrated biradical pair since high quantum yields of photodecarbonylation are observed.

Internal rotation about the single bond terminating at the $-\text{CHR}'\text{CO}$ center also occurs although it is not depicted in Scheme II. Since the product distributions from photolyses of thujone and 2-methylbicyclo[3.1.0]hexan-3-one provide no information about the process, a discussion of this degree of freedom is postponed. In addition, a number of stepwise pathways for conversion of the biradicals to products may be envisaged. A brief discussion of these possibilities is likewise postponed, and in the present description, a unit process is preferred since this is the simplest mode of decay consistent with the experimental results.

The biradicals formed upon α cleavage (21 and 24) are almost certainly involved in the epimerization of the thujones.⁴²⁻⁴⁴ The lifetimes of these intermediates may be intimated from results of studies on related systems in which the kinetics of the cyclopropylcarbinyl to allylcarbinyl radical rearrangement have been measured.⁴⁵⁻⁴⁸ The rate of internal rotation about the single bond terminating at the $-\text{CHCH}_3$ center is a matter for conjecture. If the torsional barrier is 2-3 kcal mol⁻¹, as suggested by relevant experimental measurements^{49,50} and by certain theoretical cal-

culations,⁵¹⁻⁵³ then estimated rates of internal rotation^{54,55} are consistent with equilibration of the biradical intermediates prior to formation of 1,4-diene products.

The data measured during photolyses of thujone at various temperatures may be plotted ($r = 0.985$) as the function $\ln(8/9) = \Delta\Delta S^*/R + \Delta\Delta H^*/RT$. If internal rotation is rapid with respect to other reactions of the intermediate, the apparent activation parameter differences measured in this study represent entropy and enthalpy differences between the transition states associated with decay of the biradical to isomeric 1,4-diene products.⁵⁶ Structures 26 and 27 are adequate representations of the stereoelectronic requirements^{48,52,57-65} for conversion of the cyclopropylcarbinyl to allylcarbinyl radical. Experimental values⁶⁶ of $\Delta\Delta S^* = -0.82 \pm 0.11$ cal mol⁻¹ K and $\Delta\Delta H^* = 1.37 \pm 0.03$ kcal mol⁻¹ are consistent with unremarkable differences between the proposed transition states.



Photolyses of epimeric 2,4-dimethylbicyclo[3.1.0]hexan-3-ones afford similar, but not identical, mixtures of hepta-2,5-diene isomers. These results are consistent with the mechanism and intermediates suggested in Scheme II if internal rotation about the single bond terminating at the $-\text{CHR}'\text{CO}$ center is considered. Structures 28 and 29 are partial representations of transition states for product formation during photolysis of *exo,exo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one. If internal rotation is rapid with respect to other reactions of the intermediates, then entropy and enthalpy differences between these proposed transition states govern the ratio of double-bond isomers formed at this terminus upon loss of carbon monoxide. In the likely event that moderately large torsional barriers^{68,69} dictate rates of internal rotation which are not much faster than rates of double-bond formation, the isomer ratio determined at this center also depends on activation parameters for interconversion and reclosure of the proposed rotamers.

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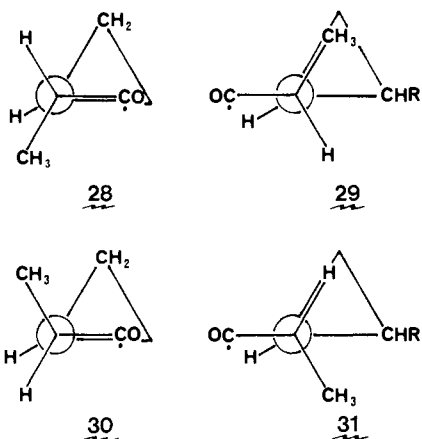
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The mixture of hepta-2,5-diene isomers obtained during photolysis of *endo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one may be discussed with reference to structures **30** and **31**. Since these



representations bear a diastereomeric relationship to structures **28** and **29**, nonidentical mixtures of 1,4-diene isomers are expected from the two epimeric ketones. The product distribution from photolysis of *exo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one depends on the extent to which each nonequivalent mode of α cleavage occurs.

Predictions based only on entropy and enthalpy differences between structures **28** and **29** provide a lower limit for the experimentally observed fraction of trans olefin attributable to reaction at the $-\text{CHCH}_3\text{CO}$ terminus during photolysis of *exo,exo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one. This mode of elimination is favored if torsional barriers are moderately high and rates of internal rotation correspondingly slow. An analogous argument may be advanced for photolysis of the *endo,endo* ketone. Throughout this discussion formation of the double bond at the $-\text{CHCH}_3$ terminus has been ignored. To a first approximation the ratio of isomeric olefins attributable to reaction at this center is expected to be identical in the photolyses of all 2,4-dimethylbicyclo[3.1.0]hexan-3-one epimers.

Species such as those represented by structures **2** and **4** could also be included as intermediates in a discussion of the mechanism for photodecarbonylation. If these proposed biradicals had lifetimes which were long with respect to the predicted rapid rates of internal rotation,⁵⁰ then identical mixtures of hepta-2,5-diene isomers would be expected from photolyses of all 2,4-dimethylbicyclo[3.1.0]hexan-3-one epimers. The fleeting existence of such transients is not ruled out by the experimental data; however, the simpler mechanistic description already advanced is preferred by us.

Excited States. All of the bicyclo[3.1.0]hexan-3-one systems studied show absorption maxima near 300 nm with molar extinction coefficients of $10\text{--}30 \text{ M}^{-1} \text{ cm}^{-1}$. A transition at this wavelength corresponds to a singlet state energy of approximately 95 kcal mol^{-1} and is certainly due to $n \rightarrow \pi^*$ excitation of the carbonyl group.

The photodecarbonylation of the thujone epimers can be quenched by the addition of high concentrations of piperylene. A normal Stern-Volmer plot shows some downward curvature suggesting that products are formed from more than one excited state. Participation of excited singlet and triplet states in Norrish I processes is not uncommon.^{70,71} The relative photodecarbonylation quantum yields as a function of piperylene concentration were fitted with the assumption that a singlet state component of the reaction was not quenched.⁷²⁻⁷⁴ Analyses based

on more complex schemes in which both excited states are deactivated by added quencher^{71,75-77} are unwarranted because of an unfortunate flaw in experimental design (*vide infra*). Shown in Table II is the best fit to experimental data calculated from the parameters $\Phi_0^S/(\Phi_0^S + \Phi_0^T) = 0.073$ and $k_Q^T \tau^T = 2.8 \text{ M}^{-1}$. If the diffusion-controlled bimolecular rate constant in pentane is assumed to be $k_Q^T = 2.7 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, a triplet lifetime of $\tau^T = 1.0 \times 10^{-10} \text{ s}$ may be extracted from the analysis. The short triplet lifetime is unremarkable for an excited state which undergoes Norrish I cleavage with such high quantum efficiency.^{78,79}

The triplet state quenching study was undertaken employing a mixture of (-)-thujone and (+)-isothujone. The nonlinear Stern-Volmer plot is conceivably the consequence of substantially different triplet state lifetimes of the epimeric ketones. Alternatively, curvature could be the result of changes in the medium upon addition of sizable amounts of quencher. We believe that neither of these explanations is as likely as the analysis in which photodecarbonylation occurs from both excited singlet and triplet states.

Summary

A mechanism involving biradical intermediates is proposed to account for efficient photodecarbonylation of the bicyclo[3.1.0]hexan-3-one system. Initial $n \rightarrow \pi^*$ excitation followed by intersystem crossing to a short-lived triplet state results in efficient Norrish I cleavage toward the more substituted α position. It is probable that some reaction occurs directly from the excited singlet state. Synchronous cleavage of the cyclopropane bond and loss of carbon monoxide leads to formation of 1,4-diene products.

The photolyses of epimeric, bicyclic ketones bearing a single methyl group in the $\text{C}_{2(4)}$ position results in identical 1,4-diene isomer mixtures. Initial cleavage leads to biradical species which are conformational isomers, and these intermediates equilibrate upon rapid internal rotation prior to subsequent reaction. Photolyses of epimeric 2,4-dimethylbicyclo[3.1.0]hexan-3-ones afford biradical intermediates which are configurational isomers. Although these species may undergo rapid internal rotation, the proposed diastereomeric relationship accounts for observed differences in the mixtures of hepta-2,5-diene isomers subsequently formed.

Experimental Section

General Considerations. Infrared spectra were recorded with a Beckman IR-5A or IR-7 spectrometer. Proton magnetic resonance spectra were recorded on a Varian Model HA-100 or XL-100 spectrometer. Deuteriochloroform was employed as solvent, and chemical shifts are reported as δ values in parts per million relative to tetramethylsilane. Ultraviolet spectra were measured on a Cary Model 15 recording spectrometer. Mass spectral data was measured by Susan Rottschaefer with a Consolidated Electrodynamic Corp. Model 21-110 double-focus mass spectrometer equipped with a direct inlet system. Gas-liquid chromatography was performed on a Varian Aerograph A-90P or a Hewlett-Packard 5771A laboratory chromatograph. Relative peak areas were determined by the "cut-and-weigh" method.

2-Methylbicyclo[3.1.0]hexan-3-one (10 and 11). To a 1000-mL Morton flask fitted with a mechanical stirrer, addition funnel, and reflux condenser topped with a gas inlet/outlet system were added 600 mL of dry ether and 5.00 g (0.12 mol) of 57% sodium hydride in oil. After slow addition of 10 mL (0.17 mol) of absolute ethanol, the mixture was allowed to stir several hours. A 60-mL portion (0.74 mol) of dry ethyl formate was added followed by addition after several hours of a mixture of 9.61 g (0.10 mol) of bicyclo[3.1.0]hexan-3-one in 80 mL (0.99 mol) of ethyl formate. The mixture was allowed to stir overnight during which time a thick, tan precipitate formed. To this mixture was added 60 mL of water, and stirring was continued until the precipitate had dissolved. The ether layer was washed with water, and the combined water layers were then backwashed with ether. The water layer was acidified with

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20 mL of 6 N hydrochloric acid and extracted with three 50-mL portions of ether. The ether extracts were dried over anhydrous sodium sulfate, filtered, and evaporated under vacuum to give a yellow solid which was used directly in the next step.

A sample for analysis and spectral data was purified by several vacuum sublimations: mp 89–91 °C; IR (CHCl₃) 1748, 1714, 1679, 1599 cm⁻¹; mass spectrum, *m/e* 124.051 (calcd for C₇H₈O₂, 124.052).

The entire sample of 2-(hydroxymethylene)bicyclo[3.1.0]hexan-3-one from above was dissolved in 200 mL of benzene and placed in a 300-mL round-bottom flask fitted with a Dean–Stark trap topped with a reflux condenser. After addition of 0.10 g (0.58 mmol) of *p*-toluenesulfonic acid and 10.00 g (1.1 mol) of butanethiol, the solution was heated at reflux overnight. The reaction mixture was cooled, extracted with aqueous sodium bicarbonate solution, dried over anhydrous magnesium sulfate, filtered, and evaporated. Vacuum transfer of the residue gave 14.30 g (73% yield from bicyclo[3.1.0]hexan-3-one) of 2-((*n*-butylthio)methylene)bicyclo[3.1.0]hexan-3-one as a yellow, viscous oil: IR (film) 1705, 1595, 830 cm⁻¹; mass spectrum, *m/e* 196.092 (calcd for C₁₁H₁₆OS, 196.092).

A 1000-mL round-bottom flask fitted with a mechanical stirrer, thermometer, and addition funnel was charged with a mixture comprising 100 mL of a settled suspension of Raney nickel⁸⁰ and 300 mL of absolute ethanol. The mixture was heated to 65 °C and stirred vigorously as a 14.30-g portion of 2-((*n*-butylthio)methylene)bicyclo[3.1.0]hexan-3-one was added over a 15-min period. Stirring was continued an additional 30 min. Approximately 100 mL of Florisil was added to the mixture, and the entire slurry was poured into a large chromatography column containing a 5-cm plug of Florisil. The initial eluant was collected, and the nickel was then washed with three additional volumes of absolute ethanol. The ethanol was removed followed by distillation of the residual material at 46–48 °C (16mmHg) to give 9.00 g of 2-methylbicyclo[3.1.0]hexan-3-one (69% of theory). Subsequent experiments provided 85–90% yields of mixtures containing 5–40 mol% *exo* isomer depending on the age of the catalyst. The individual ketones were isolated by preparative GLC on a 9.1 m × 6.4 mm 7.5% Carbowax 20M on 30/60 mesh Chromosorb W column.

exo-2-Methylbicyclo[3.1.0]hexan-3-one (10): IR (film) 2960, 1745, 1454, 1410, 1371, 1264, 1162, 1078, 1042, 1026, 1009, 908 cm⁻¹; UV max (cyclohexane) 291 nm (ϵ 21.3), 300 (23.0), 311 (19.4), 321 (8.9); NMR δ -0.05 (m, 1, *endo*-C₆), 0.90 (m, 1, *exo*-C₆), 1.17 (d, 3, *J* = 7 Hz, *exo*-CH₃), 1.2–1.5 (m, 2, C₁ and C₅), 2.14 (d, 1, *J* = 19 Hz, *endo*-C₄), 2.16 (q, 1, *J* = 7 Hz, *endo*-C₂), 2.60 (m, 1, *exo*-C₄); mass spectrum, *m/e* 110.073 (calcd for C₇H₁₀O, 110.073). A 2,4-dinitrophenylhydrazone derivative prepared in the usual fashion⁸¹ had a melting point of 124–125 °C.

endo-2-Methylbicyclo[3.1.0]hexan-3-one (11): IR (film) 2960, 1745, 1454, 1409, 1370, 1264, 1146, 1078, 1036, 1016, 992 cm⁻¹; UV max (cyclohexane) 287 nm (ϵ 13.2), 296 (13.3), 306 (10.5); NMR δ -0.22 (m, 1, *endo*-C₆), 0.68 (m, 1, *exo*-C₆), 1.00 (d, 3, *J* = 7 Hz, *endo*-CH₃), 1.3–1.7 (m, 2, C₁ and C₅), 2.17 (d, 1, *J* = 19 Hz, *endo*-C₄), 2.5–2.8 (m, 2, *exo*-C₂ and -C₄); mass spectrum, *m/e* 110.074 (calcd for C₇H₁₀O, 110.073). A 2,4-dinitrophenylhydrazone derivative had a melting point of 140–141 °C.

2,4-Dimethylbicyclo[3.1.0]hexan-3-one (14–16). A procedure identical with that described above was employed to convert 2-methylbicyclo-

[3.1.0]hexan-3-one to the hydroxymethylene derivative: IR (CHCl₃) 1681, 1705, 1605 cm⁻¹; mass spectrum, *m/e* 138.068 (calcd for C₈H₁₀O₂, 138.069). This intermediate was condensed with butanethiol as detailed above to provide 2-((*n*-butylthio)methylene)-4-methylbicyclo[3.1.0]hexan-3-one in 70% overall yield: IR (CHCl₃) 1705, 1595 cm⁻¹; mass spectrum, *m/e* 210.106 (calcd for C₁₂H₁₈OS, 210.108). Raney nickel reduction was performed as previously described to give 85–90% yields of 2,4-dimethylbicyclo[3.1.0]hexan-3-one. Preparative GLC employing a 6.4 m × 6.4 mm 7.5% Carbowax 20M on 30/60 mesh Chromosorb W column separated the mixture into two fractions. The material of longer retention time was collected and characterized as *endo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (14): IR (film) 1747, 1457, 1377, 1271, 1152, 1051, 1024, 968, 826 cm⁻¹; UV max (cyclohexane) 293 nm (ϵ 14.6); NMR δ -0.37 (m, 1, *endo*-C₆), 0.32 (m, 1, *exo*-C₆), 0.99 (d, 6, *J* = 7 Hz, *endo*-CH₃), 1.36 (m, 2, C₁ and C₅), 2.69 (m, 2, *exo*-C₂ and -C₄); mass spectrum, *m/e* 124.088 (calcd for C₈H₁₂O, 124.089). A 2,4-dinitrophenylhydrazone derivative had a melting point of 146–147 °C.

A 30.5 cm × 6.4 mm section of tubing was charged with five 2-cm plugs of a mixture comprising 10% Woelm basic alumina with 90% 60/80 mesh AW-DMCS Chromosorb W. The intervening space was filled with Chromosorb W. This unit was fitted between the injection port and the usual preparative GLC column and activated before use by a 0.04-mL injection of water. The mixture of ketones was equilibrated at 140 °C by using this equipment, and the fraction of shorter retention time (about 50 mol %) was collected. Examination of the ¹H NMR spectrum revealed that the material was a mixture of *exo,endo*- and *exo,exo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one containing approximately 20 mol % of the latter isomer. Direct separation of these materials proved impossible.

A 50-mL round-bottom flask fitted with a magnetic spinbar, thermometer, addition funnel, and a gas inlet/outlet tube was charged with 25 mL of dry ether and 0.22 g (6.9 mmol) of lithium aluminum hydride. A 1.53-g (20.6 mmol) portion of *tert*-butyl alcohol was added slowly. The mixture was stirred at room for 3 h and then cooled to 0 °C. A 0.43-g (3.4 mmol) portion of the ketone fraction isolated by preparative GLC was added slowly. The mixture was stirred at room temperature overnight and worked up in the usual fashion by addition of water and aqueous sodium hydroxide solution. The organic layer was carefully concentrated and separated by preparative GLC on a 9.1 m × 6.4 mm 7.5% Carbowax 20M on 30/60 mesh Chromosorb W column. The fraction of shortest retention time was isolated, reoxidized by treatment with Jones reagent in acetone, and purified by preparative GLC to give *exo,endo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (15): IR (film) 1748, 1452, 1371, 1265, 1180, 1044, 1003, 956, 816, 776 cm⁻¹; UV max (cyclohexane) 300 nm (ϵ 25.4); NMR δ -0.18 (m, 1, *endo*-C₆), 0.72 (m, 1, *exo*-C₆), 1.04 (d, 3, *J* = 7 Hz, *endo*-CH₃), 1.19 (d, 3, *J* = 7 Hz, *exo*-CH₃), 1.2–1.7 (m, 2, C₁ and C₅), 2.20 (q, 1, *J* = 7 Hz, *endo*-C₂), 2.77 (m, 1, *exo*-C₄); mass spectrum, *m/e* 124.088 (calcd for C₈H₁₂O, 124.089). A 2,4-dinitrophenylhydrazone derivative had a melting point of 171–173 °C.

The alcohol fraction of longest retention time was isolated, oxidized, and purified as above to give *exo,exo*-2,4-dimethylbicyclo[3.1.0]hexan-3-one (16): IR (film) 1730, 1451, 1371, 1170, 1031, 960, 809 cm⁻¹; UV max (cyclohexane) 292 nm (ϵ 23.7), 302 (27.5), 313 (23.3); NMR δ -0.03 (m, 1, *endo*-C₆), 0.92 (m, 1, *exo*-C₆), 1.23 (d, 6, *J* = 7 Hz, *exo*-CH₃), 1.20 (m, 2, C₁ and C₅), 2.13 (q, 2, *endo*-C₂ and -C₄); mass spectrum, *m/e* 124.088 (calcd for C₈H₁₂O, 124.089). A 2,4-dinitrophenylhydrazone derivative had a melting point of 160–161 °C.

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