Table V. Neutral Product Distribution in the Reaction of **1** and **3** with Potassium Amide

	Run no. 1	2	3
Reactants			
1, g	0.093	0.2524	...
3, g	...	...	0.065
Potassium, g	0.174	0.413	0.196
Reaction time	1 week	24 hr	1 week
Total chromatographed neutral products,[a] g	0.0523	0.1344	0.0558
% **4** (3.75)[b]	100	...	100
% **3** (10.0)[b]	...	80	...
% unknown (12.4)[b]	...	20	...

[a] Analyzed by vpc using a 6 ft × 0.25 in. o.d. 10% Carbowax 20M on Chromosorb P column, helium flow rate 158 cc/min, column temperature 250°. [b] Retention times (minutes) in parentheses; authentic samples[3] of **3** and **4** gave the indicated retention times.

Mutarotation of 1. Optical rotations were measured in toluene at 435 mμ using a 2-dm semimicro jacketed polarimeter tube. The temperatures were kept constant at ±0.05° by using a circulating bath. The change of rotation with time was followed by conventional methods. The first reading was normally taken *ca.* 10 min after dissolution. The rate constants of mutarotation were obtained using the integrated first-order rate law expression for the process of unimolecular mutarotation. These rate constants were used to calculate the extrapolated rotation ($[\alpha_0]$), taken to be the rotation at the time of dissolution. The results are collected in Table I.

Nmr Spectroscopy. Temperature-dependent spectra were run on a Varian A-60A spectrometer equipped with a variable-temperature probe. Samples were prepared as 0.072–0.268 g/ml solutions of (−)-**1** in toluene-d_8. Within experimental limits, the relative peak heights of NMe_2^A and NMe_2^B (*i.e.*, *K*) of equilibrated **1** were found to be independent of the concentration. Temperatures were measured using Varian ethylene glycol, which was placed in the inner tube of a coaxial cell; the outer tube was filled with sample. The use of this cell allowed the simultaneous measurement of the ethylene glycol peak separation and the NMe_2 peak heights over the temperature range of 305–377°K. Probable accuracies are estimated to be ±3° with a stability at any one temperature of ±1.5°. The correlation coefficient for the plot ln *K* against $1/T$ was −0.9303.

Decoupling experiments were carried out in the frequency sweep mode of the HA-100 with the aid of a Hewlett-Packard 200 CD audio oscillator. Samples were prepared as $CDCl_3$ solutions. The root-mean-square error for fitting the observed spectra to the computed spectra[48] was somewhat high (for (−)-**1**, 0.16; for (+)-**1**, 0.09) due to uncertainties in the measurement caused largely by the use of peak positions as frequencies.[62] In order to ascertain the effect of these uncertainties on the results, seven spectra were computed of (−)-**1** taken under different conditions, *i.e.*, of field strength (60 and 100 MHz), solvent (deuteriochloroform, toluene-d_8, and benzene), and temperature (0, 25, and 35°). The computed coupling constants were in the following ranges: $J_{AB} = -15.04$ to -15.54 Hz, $J_{AC} = 3.3$–3.7 Hz, and $J_{BC} = 2.4$–2.6 Hz. Thus, even though the root-mean-square errors were relatively high, the results may be considered good.

Acknowledgment. We wish to thank Dr. G. H. Wahl for performing preliminary experiments in the synthesis of **1**, and Professor A. Moscowitz for helpful discussions concerning the WFK method.

---

[62] Peak positions do not always correspond to line positions, because of the overlap of lines of various widths.

The Stereochemistry and Mechanism of the Photochemical Interconversion of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-ones. Mechanistic Organic Photochemistry. XXXII[1]

Howard E. Zimmerman, Kenneth G. Hancock, and George C. Licke

Contribution from the Chemistry Department, University of Wisconsin, Madison, Wisconsin 53706. *Received January 17, 1968*

Abstract: Photochemical conversion of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one to the *cis* isomer **2** and 3,4- and 4,4-diphenylcyclohex-2-en-1-ones (**4** and **3**) was shown to involve the triplet excited state of reactant, but not of product. The stereochemical course of the *trans–cis* isomerization involved only cleavage of the C-1 to C-6 (external) bond, with retention of stereochemistry at C-5; overlap control appeared determining. A rate constant of 4.6×10^9 sec^{-1} was measured for rearrangement of the triplet. The photochemical isomerization of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one to the *trans* isomer **1** and to 3,4-diphenylcyclohexenone was also investigated. The *cis–trans* isomerization involved fission of both the external (86%) and internal (14%) bonds. Strikingly, no 4,4-diphenylcyclohexenone was found. Microscopic reversibility was shown to be inapplicable, and the *cis–trans* and *trans–cis* mechanisms must not have potential energy surfaces which cross efficiently. The reasons for the different stereochemical behavior of the *cis* and *trans* ketones **1** and **2** are discussed. A triplet state was shown to be the most likely species involved in the *cis–trans* stereoisomerization. Reductive degradation of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones with lithium–liquid ammonia and the relation of this reaction to the photochemistry are discussed in terms of stereoelectronic control. In the course of this research, a general method for resolution of ketones and oxidation of tertiary amines to ketones was developed.

The present problem began with the observation by Wilson and Zimmerman[2] that the photochemical *trans–cis* interconversion of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** and **2**) accounted for the increasing proportion of the *cis* isomer **2** formed with increasing time in irradiations of 4,4-diphenylcyclohex-

---

[1] For paper XXXI, note H. E. Zimmerman and K. G. Hancock, *J. Am. Chem. Soc.*, **90**, 3749 (1968).

[2] H. E. Zimmerman and J. W. Wilson, *ibid.*, **86**, 4036 (1964).

Table I. Quantum Yields in Direct and Sensitized Irradiations of *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run[a]	*trans* concn, *M*	Light, mE	Sensitizer concn, *M*[b]	Quantum yields, mmol/mE[c] *trans*[d]	*cis*[e]	3,4-Enone[f]	4,4-Enone[g]
1	0.0095	0.115	None	0.105 (±0.003)	0.094 (±0.003)	0.0102 (±0.0005)	0.0008 (±0.0003)
2	0.0096	0.124	None	0.103 (±0.003)	0.093 (±0.003)	0.0099 (±0.0005)	0.0005 (±0.0002)
3	0.0098	0.217	Propiophenone, 0.44	0.0027[h] (±0.0003)	0.0025 (±0.0003)	0.00012[j] (±0.00006)	0.0001[j] (±0.0001)
4	0.0117	0.234	Propiophenone, 0.28	0.0054[h] (±0.0005)	0.0052 (±0.0005)	0.00019[j] (±0.00009)	0.00002[j] (±0.0001)
5	0.0100	0.125	Chlorobenzene,[i] 9.82	0.040 (±0.002)	0.036 (±0.002)	0.0040 (±0.0004)	0.0003 (±0.0001)
6	0.0090	0.134	Chlorobenzene,[i] 9.82	0.040 (±0.002)	0.035 (±0.002)	0.0040 (±0.0004)	0.0006 (±0.0002)

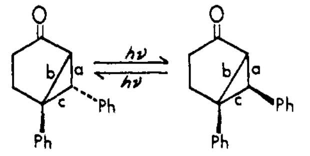
[a] In benzene at 313 mμ, 24.0°, monochromator B, liquid scintillation analysis. [b] Adjusted to absorb ≥95% of incident light. [c] Error estimated from data. [d] Disappearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [e] Appearance of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [f] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [g] Appearance of 4,4-diphenylcyclohex-2-en-1-one. [h] Quantum efficiencies approximately those anticipated for reaction only from direct light absorption by reactants. [i] 256-mμ irradiation. [j] Inaccurate due to extraordinarily small amounts of products formed.

Table II. Quantum Yields in Direct and Sensitized Irradiations of *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run[a]	*cis* concn, *M*	Light, mE	Sensitizer concn, *M*[b]	Quantum yields, mmol/mE[c] *cis*[d]	*trans*[e]	3,4-Enone[f]	4,4-Enone[g]
1	0.0089	0.099	None	0.097 (±0.003)	0.094 (±0.003)	0.0028 (±0.0002)	0.00000 (±0.00007)
2	0.0096	0.142	None	0.095 (±0.003)	0.092 (±0.003)	0.0027 (±0.0002)	0.00000 (±0.00007)
3	0.0099	0.222	Propiophenone, 0.275	0.0053[i] (±0.0005)	0.0052[i] (±0.0005)	0.00008 (±0.00005)	*j*
4	0.0094	0.140	Chlorobenzene,[h] 9.82	0.046 (±0.003)	0.045 (±0.003)	0.00081 (±0.00008)	0.00022 (±0.00007)

[a] In benzene at 313 mμ, 24.0°, monochromator B, liquid scintillation analysis. [b] Adjusted to absorb ≥95% of incident light. [c] Error estimated from data. [d] Disappearance of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [e] Appearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [f] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [g] Appearance of 4,4-diphenylcyclohex-2-en-1-one. [h] Chlorobenzene as solvent, 256-mμ irradiations. [i] Cannot fully account for product formation by the fraction of light absorbed directly by the bicyclic ketone. [j] Not determined.

2-en-1-one (**3**). Different mechanisms were considered. All three bonds of the cyclopropane ring—a, b, and c—seemed potentially capable of fission. Such cleavage of one of these bonds followed by free



1 **2** (1)

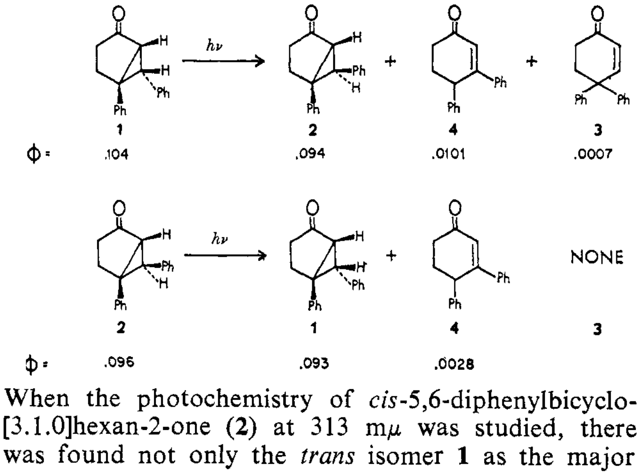
rotation and reclosure would account for the photochemical stereoisomerization. The present investigation had as its goals the determination of the gross reaction route and stereochemistry, the reaction efficiency, and elucidation of the electronic mechanism.

The Reaction Course and Quantum Yields. As demonstrated in the preceding investigation,[1] determination of product distributions and quantum yields on a semimicro scale and at low conversions by use of isotope dilution provides a general and powerful method of following the photochemistry of solid organic compounds, having particular advantages over classical methods in the analysis for minor reaction products.

Application of the isotopic dilution technique to this investigation required preparation of radioactive *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** and **2**). These were prepared by photolysis of 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C.[1] The experimental method and apparatus were those described by us earlier[1] (details in the Experimental Section).

Isotope dilution analysis of the photochemical reaction of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (**1**) in benzene at 313 mμ revealed that in addition to the expected conversion to *cis*-bicyclic isomer **2**, there were formed lesser quantities of 3,4- and 4,4-diphenylcyclohex-2-en-1-ones (**4** and **3**, respectively). These findings are summarized in Chart I and Table I.

Chart I. Quantum Yields for Direct Irradiation of *cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-ones



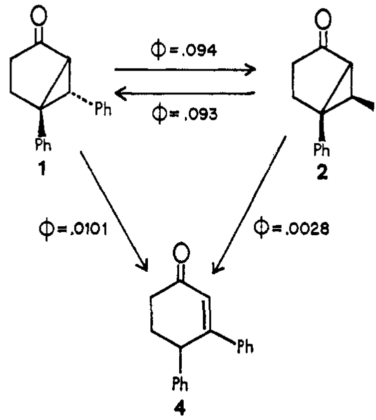
When the photochemistry of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) at 313 mμ was studied, there was found not only the *trans* isomer **1** as the major product, but also a small proportion of 3,4-diphenylcyclohexenone (**4**) as in the case of the *trans* to *cis* interconversion. In striking contrast to the *trans–cis* reaction, however, there was no detectable formation of 4,4-diphenylcyclohexenone (**3**) (Chart I, Table II).

In order to confirm the quantum yields obtained by the low conversion runs, a steady-state experiment was devised (Chart II). Neglect of the minor reactions in a kinetic analysis of the system led to the prediction that the ratio of the *trans*- to *cis*-bicyclic ketones **1** and **2** at the stationary state would be a simple function of the quantum yields for their formation and their extinction coefficients (eq 2). This was only an approxima-

$$[trans]/[cis] = (\Phi_{c\rightarrow t}\epsilon_c)/(\Phi_{t\rightarrow c}\epsilon_t) \qquad (2)$$

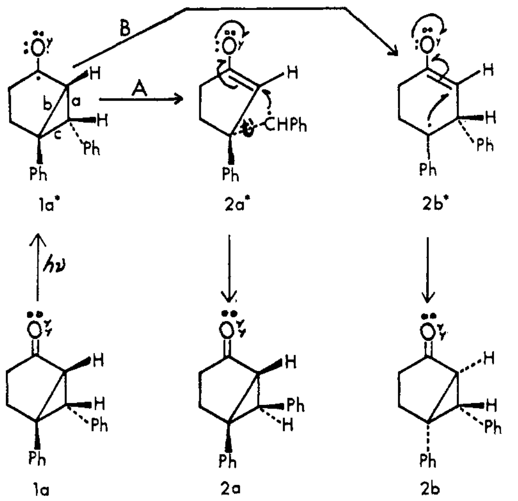
tion because of the photochemically irreversible drain to 3,4-diphenylcyclohexenone (**4**), which was a one-way exit from the two-compound system.[3] Substitution into this expression of the low-conversion quantum yields and extinction coefficients at 313 mμ predicted a *trans*:*cis* steady-state ratio of 43:57%. Experimentally, extended photolyses of mixtures of **1** and **2** bracketing the predicted value gave a 44:56 *trans*:*cis* ratio by chromatographic separation and a 43:57 ratio by isotope dilution analysis. The situation is summarized in Chart II.

Chart II. Steady-State Experiment



Approach to the Stereochemistry of the Reaction. Two mechanisms considered by Wilson and Zimmerman[2] for conversion of the *trans*-bicyclic ketone **1** to the *cis* isomer **2** are outlined in Chart III. Although, in principle, either bond a or b could cleave, the two routes for the *trans*–*cis* interconversion would have different stereochemical implications. In route A, n–π^* excitation of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (*e.g.*, **1a** in Chart III), subsequent fission of the external bond a, followed by free rotation about the bond c and reclosure gives *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2a**). Alternatively, n–π^* excitation of **1a** could be followed by cleavage of the internal bond b (route B). The hydrogen at C-1 and the phenyl group at C-5 of the reactant, which originally were above the five-ring molecular plane, now may bend below the five-ring plane to give *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2b**). This reclosure occurs by overlap of the back lobes (projecting below the five-ring plane) of the p orbitals at C-1 and C-5 (bicyclohexane numbering). However, the molecules obtained by these two routes are not identical but enantiomeric. Thus by starting with one enantiomer of the *trans*-ketone **1a** the stereochemical course of the photochemical rearrangement could be determined by determining which enantiomer of the *cis*-ketone product, **2a** or **2b**, was formed.

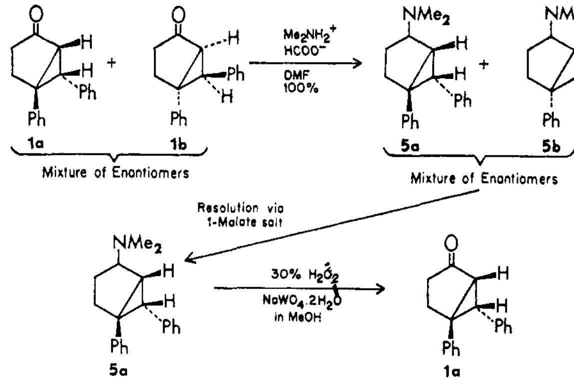
Chart III



Synthesis and Resolution of Bicyclic Ketones. Irradiation of 4,4-diphenylcyclohex-2-en-1-one (**3**) in benzene with a Pyrex filter[2] gave a mixture of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** and **2**) which was separated by chromatography on silica gel.

The *trans* isomer **1** was resolved by reductive amination, resolution by recrystallization of the *l*-malate salt, and oxidation of the regenerated amine to optically active *trans*-ketone **1a** (Chart IV).

Chart IV[4]



In using the general method of Wallach[5a] and Wagner,[5b] *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) was treated with dimethylammonium formate and dimethylformamide to yield 2-N,N-dimethylamino-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (**5**), mp 72.5–73.5°, in quantitative yields. The amine was treated with *l*-malic acid to afford the salt **6**, which was recrystallized to constant rotation ([α]D +54.5°, mp 80.8–82.8°). Recovery of optically active amine with base and recrystallization brought the resolved free amine to constant rotation ([α]D +53.6°, mp 79.2–79.7°).

2-N,N-Dimethylamino-*trans*-5,6-diphenylbicyclo[3.1.0]hexane (**5**) was oxidized under conditions similar to those used by Kahr and Berther[6] for conversion of primary amines to oximes. A solution of the amine **5** in anhydrous methanol was treated with 30% hydrogen

---

[3] H. E. Zimmerman and J. S. Swenton, unpublished observation, have noted that photolysis of 3,4-diphenylcyclohexenone gives mainly dimers.

[4] The absolute configurations are unknown; however, the stereochemical conclusions are dependent only on relative configurations.

[5] (a) O. Wallach, *Ann.*, **343**, 54 (1905); (b) E. Staple and E. C. Wagner, *J. Org. Chem.*, **14**, 559 (1949).

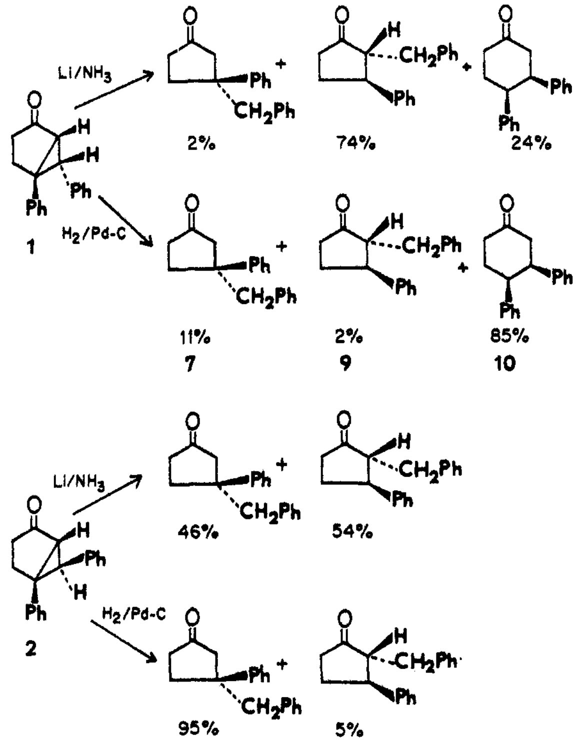
[6] K. Kahr and C. Berther, *Chem. Ber.*, **93**, 132 (1960).

peroxide and sodium tungstate catalyst at room temperature to afford *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in excellent yields. *trans*-Ketone **1a** was recrystallized to constant rotation ($[\alpha]_D$ +97.7°, $[\alpha]_{306}$ +6830°, mp 86–87°).

Optically active *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one was prepared by photolysis of the optically active *trans* isomer and recrystallization to constant rotation, $[\alpha]_{304}$ +2605°.

Correlation of Reactant and Product Configurations. In general, interrelating the configurations of the reactant and product can prove a formidable challenge. Hence, a simple approach was needed. One reaction which had seen earlier use in structure elucidation was the lithium–liquid ammonia reductive cleavage of cyclopropyl ketones.[7,8] Application of this procedure to *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) (Chart V) afforded 46% 3-benzyl-3-phenylcyclopentanone (**7**), synthesized independently by conjugate addition of benzylmagnesium chloride to 3-phenylcyclopent-2-en-1-one[9] (**8**). A second cyclopentanone formed in 54% yield in the reduction was tentatively identified as 2-benzyl-3-phenylcyclopentanone (**9**) on the basis of ir, nmr, and mass spectra and sodium deuterioxide exchange of three protons.

Chart V

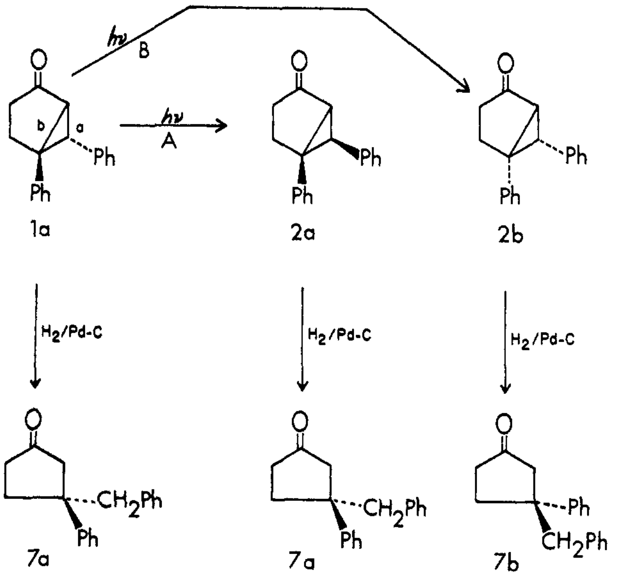


It may be noted that the lithium–liquid ammonia reaction succeeds in destroying all asymmetric centers except the one originally at C-5, which has become C-3 in **7**. Hence, 3-benzyl-3-phenylcyclopentanone (**7**) promised to be a degradation product common to both *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. Unfortunately, it was found that lithium–liquid ammonia reduction of *trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one (**1**) gave only 2% the desired 3-benzyl-3-phenylcyclopentanone (**7**), along with 74% 2-benzyl-3-phenylcyclopentanone (**9**) and 24% *cis*-3,4-diphenylcyclohexanone (**10**)[10] (note Chart V).

An equivalent degradation reaction which proved synthetically more useful in this instance was catalytic hydrogenation of the cyclopropane ring with palladium on carbon (Chart V). Catalytic hydrogenation of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) gave 11% 3-benzyl-3-phenylcyclopentanone (**7**), 85% *cis*-3,4-diphenylcyclohexanone (**10**), and 2% 2-benzyl-3-phenylcyclopentanone (**9**). Similarly, catalytic hydrogenation of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) gave 95% 3-benzyl-3-phenylcyclopentanone (**7**) and 5% 2-benzyl-3-phenylcyclopentanone (**9**) with no 3,4-diphenylcyclohexanone. A useful configurational correlation scheme was thus at hand (note Chart VI). All asymmetric centers in 3-benzyl-3-phenylcyclopentanone except C-3 have been destroyed in the rupture of the cyclopropane ring.

Thus, if route A was the correct mechanism, starting with enantiomer **1a** of *trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one, photolysis and hydrogenation of the *cis*-bicyclic ketone product obtained (*i.e.*, then **2a**) would lead to the same enantiomer of 3-benzyl-3-phenylcyclopentanone (**7a**) as hydrogenation of the reactant. On the other hand, if pathway B was followed, the other enantiomer of *cis*-bicyclic ketone (*i.e.*, **2b**) would be formed. This would be hydrogenated to **7b**, the enantiomer of 3-benzyl-3-phenylcyclopentanone opposite to that formed by hydrogenation of reactant **1a**. With admixtures of these two reaction mechanisms, the rotation of the product *cis*-ketone **2** would be intermediate between these extremes and linear with the fraction of the rearrangement that proceeded *via* route A.

Chart VI



The third alternative, scission of bond c, would afford the same stereochemical result as route A; this point is discussed below.

In order to verify that the ORD curves from the degradation products of optically active *cis*- and *trans*-

---

[7] (a) R. Volkenburgh, K. W. Greenlee, J. M. Derfer, and C. E. Boord, *J. Am. Chem. Soc.*, **71**, 3595 (1949); (b) T. Norin, *Acta Chim. Scand.*, **19**, 1289 (1965); (c) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. Digiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965); (d) W. G. Dauben and E. J. Deviny, *J. Org. Chem.*, **31**, 3794 (1966).

[8] H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *J. Am. Chem. Soc.*, **89**, 2033 (1967).

[9] W. Borsche and W. Menz, *Chem. Ber.*, **41**, 190 (1908).

[10] H. E. Zimmerman and R. G. Peterson, unpublished results.

bicyclic ketones **1** and **2** did not arise from impurities, the ORD curve of independently partially resolved 3-benzyl-3-phenylcyclopentanone (**7**) was obtained. Resolution was accomplished by the method described earlier for *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (see Experimental Section).

There was inherent in the approach a check on the optical purity of *cis*-ketone **2** used in runs beginning with *cis* isomers. Degradation of optically pure *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) must, of course, lead to optically pure 3-benzyl-3-phenylcyclopentanone (**7**) of the *same* configuration, since as noted the quaternary carbon (*i.e.*, C-5 of the *trans*-ketone **1** or C-3 of the degradation product **7**) is undisturbed in the reductive ring opening. Similarly, reductive ring opening of the *cis*-bicyclic ketone **2** will afford 3-benzyl-3-phenylcyclopentanone (**7**) of the same magnitude specific rotation if the *cis*-ketone **2** is optically pure; to the extent that it is not and gives 3-benzyl-3-phenylcyclopentanone (**7**) of a lower rotation, one can calculate the rotation of totally resolved *cis*-bicyclic ketone **2**. Finally, essentially optically pure *cis*-ketone **2** was crystallized to a constant melting point and rotation. The latter was identical with the calculated value.

Stereochemical Results. Because it was important to ascertain that the optical activity being measured (and hence mechanistic conclusions) derived only from the bicyclic products and was not in error due to contaminants, two chromatographic fractions of each compound of interest were used in each run. Additionally, ORD curves rather than mere rotations at a single wavelength were employed (see Experimental Section). This allowed use of the ORD intercepts as still another check on purity. It was observed that the ORD curves of the different chromatographic fractions of each bicyclic ketone agreed within experimental error. Finally, the chromatographic fractions of the *cis*- and *trans*-bicyclic ketones exhibited the same ORD curves as the corresponding authentic enantiomers described above.

It should be noted that it was not necessary to measure the activity of the 3-benzyl-3-phenylcyclopentanone (**7**) from degradation in each run, since the signs and magnitudes of the specific rotations of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** and **2**), both totally resolved and of the same configuration at C-5 (bicyclic numbering), were known from their degradation to the common 3-benzyl-3-phenylcyclopentanone (**7**) (*vide supra*).

The raw ORD data are summarized in the Experimental Section for photolyses of optically active *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones. In Tables III and IV are the amounts of racemization in these runs, given as a function of the per cent conversion. The degree of racemization was taken from ORD rotations at several wavelengths. The independence of the calculated amounts of racemization of the wavelength at which rotation was measured lent credence to the reliability of the results.

The findings of the experiments may be summarized as follows: (1) irradiation of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) proceeds with retention of C-5 configuration to give *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) with essentially no loss of optical activity; (2) recovered reactant *trans*-ketone **2** showed virtually no racemization (note Table III); (3) in runs beginning with *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**), the product *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) was formed with 28% racemization (Table IV; lowest conversion runs were used to determine this figure); (4) recovered *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) reactant, however, showed no apparent loss of optical activity.

Table III. Irradiation of Optically Active *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run	Convrsn, %	Racemization,[a] % (± standard error)[b]	
		cis product[c]	Recovd *trans* reactant[d]
1	6	+4.03 (±4.6)[e]	+0.40 (±2.2)[g]
2	8	+2.60 (±1.9)[f]	+1.11 (±1.8)[g]
3	12	+0.99 (±5.4)[e] 0.00[f,h]	+0.76 (±1.6)[g]
4	34	+4.44 (±5.5)[e] +1.29 (±4.5)[f]	+0.49 (±2.7)[g]
5	39	+1.85 (±4.2)[f]	+4.40 (±2.5)[g]
6	52	+4.60 (±3.4)[f]	+13.3 (±2.3)[g]
7	54	+11.6 (±4.2)[f,i]	+22.5 (±2.3)[g,i]

[a] Values given are based on ORD data listed in the Experimental Section, and are the average of measurements at at least five different wavelengths. [b] Estimated from data. [c] *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one. [d] *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one. [e] Based on ORD curves of 3-benzyl-3-phenylcyclopentanone degradation product. [f] Based on ORD curve of isolated *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one without degradation. [g] Based on ORD curve of isolated *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one without degradation. [h] 0.00% by definition since used as a standard for the higher conversion runs. [i] More racemization since nearly a steady-state percentage.

Table IV. Irradiation of Optically Active *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

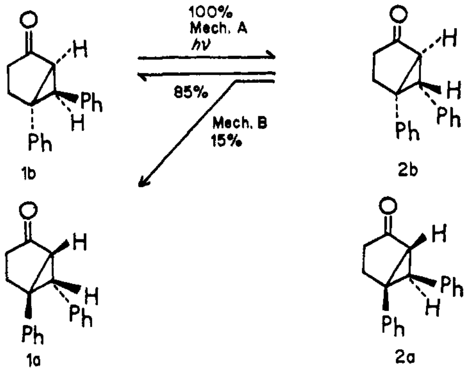
Run	Convrsn, %	Racemization,[a] % (± standard error)[b]	
		trans product[c]	Recovd *cis* reactant[d]
1	5	+27.7 (±3.4)	+0.37 (±1.5)
2	7	+29.3 (±5.5)	+0.84 (±2.6)
3	12	+35.5 (±2.5)	+2.20 (±1.9)
4	27	+34.8 (±2.9)	+3.66 (±3.6)
5	42[e]	+42.6 (±1.7)	+30.7 (±1.8)

[a] Values given are based on ORD data from curves on isolated *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones without degradation, and are the averages of rotation measurements at five different wavelengths. [b] Estimated from data. [c] *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one. [d] *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one. [e] Higher racemization since nearly a steady-state percentage.

Hence, the reaction proceeded in both directions predominantly with retention of configuration at C-5. While the *trans–cis* reaction appeared essentially stereospecific, in the *cis–trans* reaction predominant retention was accompanied by 14% inversion of stereochemistry at C-5. In both cases, recovered reactant had retained all optical activity at low conversion.

The stereochemical implications of these findings were intriguing. The complete retention of configuration at C-5 in formation of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2a**) from the optically active *trans* isomer **1a** (Chart VI) indicated that the photochemical interconversion occurred exclusively *via* fission of the peripheral bond a (route A, Charts III and VII). Contrastingly, the 28% racemization observed in *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) produced by irradiation of optically active *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2a**) meant that two reaction path-

Chart VII. Summary of Pathways Utilized in Bicyclic Ketone Interconversions



ways were superimposed (note Chart VII). While 86% of optically active *cis*-ketone **2a** was transformed into enantiomer **1a** of the *trans* isomer by cleavage of the external bond a in the excited state (Chart VII, reverse of path A in Chart III), 14% of the reaction occurred *via* fission of the internal bond b (reverse of path B in Chart III).

Quenching and Sensitization Experiments. It was thus of great interest to examine the electronic character of the excited states of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** and **2**) which were responsible for the intriguing differences in stereochemical reactivity.

Photosensitization with propiophenone at 313 mμ in benzene, under conditions in which over 95% of the incident light was absorbed by the sensitizer, resulted in very low quantum efficiency in either direction of the isomerization (Tables I and II). In fact, all product formation from the propiohenone-sensitized isomerization of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) could be accounted for by the small fraction of incident light absorbed directly by the *trans*-ketone **1** reactant. The quantum yield for the propiophenone-sensitized isomerization of the *cis*-bicyclic ketone **2**, while small, could not be fully accounted for by only the light absorbed directly by the *cis*-bicyclic ketone reactant, and the 2% triplet sensitization may be real.

When irradiation of either *trans*- or *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (**1** or **2**) was carried out at 256 mμ in chlorobenzene (E_T = *ca.* 82 kcal/mol),[11] with the solvent absorbing over 95% of the incident light, sensitization was much more efficient (Tables I and II). The ratio of products, whose utility as a "fingerprint" for the identity of an excited state has been pointed out earlier,[1] was the same for the direct photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) and for the chlorobenzene-sensitized isomerization. The low conversions in propiophenone-sensitized runs made the fingerprint ratio unreproducible and inaccurate. In reactions of the *cis*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**2**), the product ratios from direct irradiation and from the chlorobenzene-sensitized run were, for the most part, similar.[12]

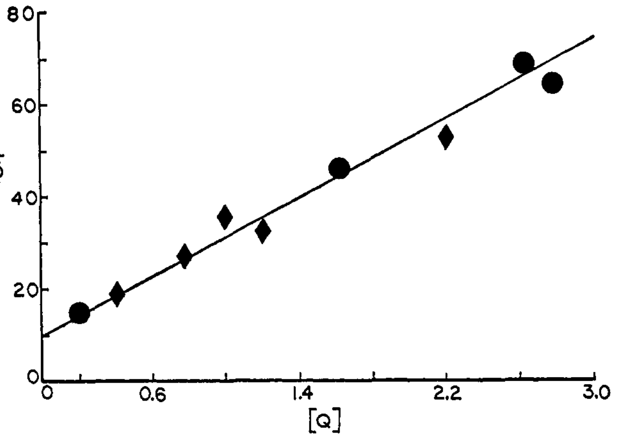


Figure 1. Stern–Volmer plot of the quenching of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one: ●, 1,3-cyclohexadiene; ◆, 2,5-dimethyl-2,4-hexadiene.

Attention was also directed to quenching. In both the *trans–cis* and *cis–trans* isomerizations, quenching studies were severely complicated by competition for light between the bicyclic ketone (**1** or **2**) and the high concentrations of quencher needed. One major difficulty was estimation of the fraction of incident light that was actually absorbed by the quencher instead of the ketone. A method of integrating the varying absorptivity of ketones and quenchers over the irradiation band width which also took into account varying lamp output with wavelength was required. Using the quantum yield light source (313 mμ, 22-mμ band width, and a short cell; see Experimental Section), light transmitted was measured both with pure benzene, with solutions of ketone, and with solutions of quencher in benzene. Integrated-effective extinction coefficients over the 22-mμ band width were calculated from Beer's law. These integrated-effective extinction coefficients were not in the same ratio as the monochromatic extinction coefficients of the same compounds at 313 mμ.[13]

The quenched quantum yields are summarized in Tables V and VI. Integrated-effective extinction coefficients were used in most runs to calculate the distribution of incident light between ketones and quenchers. As a check, the remaining runs were made with more truly monochromatic light (1.5-mμ band width) so that monochromatic extinction coefficients could be used. The two types of calculation agreed well.

Nearly 90% of the reaction of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) was quenched by addition of 2.8 *M* 1,3-cyclohexadiene. A linear Stern–Volmer plot of the reciprocal of the quantum yield *vs.* quencher concentration was obtained, with intercept at 9.6 and a slope of 21.6 l./mol. 1,3-Cyclohexadiene and 2,5-dimethyl-2,4-hexadiene appeared to quench at a common rate with irradiation over either a 1.5- or a 22-mμ band width (Figure 1). The product ratio of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) to 3,4-diphenyl-

---

(11) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

(12) The most noteworthy difference was the apparent formation of a very small amount of 4,4-diphenylcyclohex-2-en-1-one (3) in the chlorobenzene irradiation. This ketone had been conspicuously absent in direct irradiations (Table VII). Additionally, the ratio of the main product, *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, to the secondary product, 3,4-diphenylcyclohex-2-en-1-one, seemed slightly lower in both the propiophenone- and chlorobenzene-sensitized runs than in direct irradiations.

(13) The use of single-wavelength extinction coefficients to calculate relative light capture where reactant-sensitizer or reactant–quencher combinations are used is inaccurate. Occasionally one finds such an assumption of monochromaticity in the literature with mention of a solution filter designed to "isolate" a mercury band. However, medium- and high-pressure lamps have very heavy emission surrounding the mercury lines, and the filters seldom are sufficiently narrow to give a predominance of the mercury line wavelength or to justify the assumption of monochromaticity.

Table V. Quantum Yields in Quenched Irradiations of *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run[a]	*trans* concn, *M*	Light, mE	Quencher concn, *M*[b]	Quantum yields, mmol/mE[c] *trans*[d]	*cis*[e]	3,4-Enone[f]	4,4-Enone[g]
1[h]	0.0108	0.162	Cyclohexadiene, 0.198	0.068 (±0.007)	0.062 (±0.006)	0.0065 (±0.0007)	0.00009 (±0.0001)
2[h]	0.0109	0.203	Dimethylhexadiene, 0.410	0.053 (±0.005)	0.049 (±0.005)	0.0044 (±0.0005)	0.0002 (±0.0001)
3[h]	0.0107	0.281	Dimethylhexadiene, 0.777	0.037 (±0.004)	0.034 (±0.003)	0.0028 (±0.0003)	0.0002 (±0.0001)
4[i]	0.0120	0.0308	Dimethylhexadiene, 0.994	0.028 (±0.003)	0.025 (±0.003)	*j*	*j*
5[h]	0.0110	0.336	Dimethylhexadiene, 1.20	0.031 (±0.003)	0.028 (±0.003)	0.0029 (±0.0003)	0.00006 (±0.0001)
6[h]	0.0110	0.259	Cyclohexadiene, 1.61	0.022 (±0.002)	0.019 (±0.002)	0.0022 (±0.0003)	0.0003 (±0.0001)
7[h]	0.0158	0.762	Dimethylhexadiene, 2.20	0.019 (±0.002)	0.017 (±0.002)	0.0018 (±0.0002)	0.00002 (±0.0001)
8[i]	0.0103	0.0298	Cyclohexadiene, 2.62	0.015 (±0.001)	0.015 (±0.001)	*j*	*j*
9[h]	0.0112	0.251	Cyclohexadiene, 2.78	0.016 (±0.002)	0.013 (±0.001)	0.0015 (±0.0002)	0.0007 (±0.0005)

[a] In benzene, 313 mμ, 24.0°, liquid scintillation analysis. [b] Correction applied for light absorption by quencher. [c] Error estimated from data. [d] Disappearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [e] Appearance of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [f] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [g] Appearance of 4,4-diphenylcyclohex-2-en-1-one. [h] 22-mμ band width required use of integrated extinction coefficients to calculate percentage of light absorbed by quencher. [i] 1.5-mμ band width, monochromatic extinction coefficients used. [j] Not determined.

Table VI. Quantum Yields in Quenched Irradiations of *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run[a]	*cis* concn, *M*	Light, mE	Quencher concn, *M*[b]	Quantum yields, mmol/mE[c] *cis*[d]	*trans*[e]	3,4-Enone[f]
1[g]	0.0100	0.192	Cyclohexadiene, 0.120	0.084 (±0.009)	0.083 (±0.008)	0.0017 (±0.0004)
2[g]	0.0098	0.163	Dimethylhexadiene, 0.263	0.089 (±0.009)	0.086 (±0.009)	0.0020 (±0.0005)
3[g]	0.0102	0.122	Dimethylhexadiene, 0.502	0.083 (±0.008)	0.080 (±0.008)	0.0026 (±0.0006)
4[g]	0.0113	0.163	Dimethylhexadiene, 0.992	0.108 (±0.011)	0.105 (±0.011)	0.0023 (±0.0006)
5[g]	0.0106	0.114	Dimethylhexadiene, 1.001	0.069 (±0.018)	0.068 (±0.017)	0.0013 (±0.0010)
6[h]	0.0108	0.0039	Dimethylhexadiene, 1.003	0.089 (±0.009)	0.086 (±0.009)	*i*
7[g]	0.0234	0.194	Dimethylhexadiene, 1.399	0.099 (±0.010)	0.097 (±0.010)	0.0022 (±0.0005)
8[g]	0.0114	0.0754	Cyclohexadiene, 1.816	0.098 (±0.010)	0.094 (±0.010)	0.0035 (±0.0009)

[a] In benzene, 313 mμ, 24.0°, liquid scintillation analysis. [b] Correction applied for light absorption by quencher. [c] Error estimated from data. [d] Disappearance of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [e] Appearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [f] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [g] 22-mμ band width required use of integrated extinction coefficients to calculate percentage of light absorbed by quencher. [h] 1.5-mμ band width, monochromatic extinction coefficients used. [i] Not determined.

cyclohex-2-en-1-one (**4**) appeared to be the same within experimental error as the direct irradiation product ratio over the entire concentration range of quenchers used. The apparent ratio of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one to 4,4-diphenylcyclohex-2-en-1-one (**3**) was quite variable because of the small amounts of **3** formed; however, no trend was discernible.

On the other hand, attempts to quench the reaction of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) were in vain. Neither 1,3-cyclohexadiene nor 2,5-dimethyl-2,4-hexadiene significantly quenched the reaction even at 1.8 *M* concentrations (Figure 2, Table VI). The ratio of products, *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) to 3,4-diphenylcyclohex-2-en-1-one (**4**), varied somewhat from run to run due to experimental error, but no trend was noticed.

Interpretation of the Multiplicities of the Reactive States. Chlorobenzene sensitization is suggestive, but does not appear to be completely straightforward. It may be noted that triplet photosensitization with propiophenone (E_T = 74 kcal/mol)[14] failed for *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**). The question, then, is whether the successful sensitization by chlorobenzene (E_T = *ca.* 82 kcal/mol)[11] was indeed triplet transfer rather than singlet.

Although every bicyclic ketone molecule (**1** or **2**) in chlorobenzene solution will necessarily be surrounded by chlorobenzene molecules, very few (<1%) chlorobenzene excited singlet molecules will be adjacent to a bicyclic ketone molecule at the instant of excitation. A very low steady-state concentration of chlorobenzene singlets is assured by the rapid decay of the chlorobenzene singlet (maximum lifetime *ca.* 10^{-9} sec)[15]

---

(14) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Am. Chem. Soc.*, **86**, 4537 (1964).

(15) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin,

coupled with the modest lamp intensity (*ca.* 10^{15} quanta $\sec^{-1}$ ml^{-1}). If singlet energy transfer is diffusion controlled, then unimolecular decay of the chlorobenzene singlet (k_d = *ca.* 10^9–10^{10} $\sec^{-1}$) is too fast for diffusion-controlled collision with a molecule of bicyclic ketone (k_{diff} = *ca.* 5×10^9 l. mol^{-1} $\sec^{-1}$, or pseudounimolecular k = *ca.* 5×10^7 $\sec^{-1}$ at 0.01 *M* bicyclic ketone). However, the possibility of more rapid than diffusion-controlled singlet energy transfer cannot be totally discounted.[18]

Since the same products were formed in both direct irradiations and chlorobenzene-photosensitized reactions of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones, and in about the same proportions (*cf.* Tables I and II), then to the extent that chlorobenzene is accepted as a *bona fide* triplet sensitizer, it can be concluded that the triplets of **1** and **2** can give the observed rearrangements. This is a minimum conclusion. A likely but not necessary further deduction is that the products observed in the direct photolyses of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one arose from the triplet states as well.

In quenching of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**), it was noted that, in contrast to the case of 4,4-diphenylcyclohexenone (**3**),[1] 1,3-cyclohexadiene and 2,5-dimethyl-2,4-hexadiene quenched at identical rates in benzene (Table V, Figure 1). Assuming on this basis[19] that quenching was diffusion controlled, and using a bimolecular rate of diffusion in benzene[18,20] of 1.0×10^{10} l. mol^{-1} $\sec^{-1}$, the rate of triplet rearrangement, k_r, of *trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one was calculated to be $(4.6 \times 10^8)/f$ $\sec^{-1}$. Here f is the intersystem crossing efficiency which must be between 0.1 and 1.0 in view of the reaction quantum yield. Hence $4.6 \times 10^8 < k_r < 4.6 \times 10^9$ $\sec^{-1}$.

One might be concerned about the possibility of singlet quenching; this point has been discussed in connection with the 4,4-diphenylcyclohexenone (**3**) study.[1] Although, in general, quenching of singlets could be mistaken for triplet quenching, there is a circumstance in which linear Stern–Volmer behavior can be safely construed to provide evidence for a triplet. This involves an extension of the "fingerprint" technique, utilized previously in interpretation of photosensitization,[1] to quenching phenomena. Failure of a product distribution to change with the extent of quenching can be taken to mean that only one multiplicity species is involved in the quenched and unquenched photolyses. This deduction is based on the reasonable assumption that the singlet product distribution is appreciably different from that of the triplet. The method depends on having a very precise method of assay (*e.g.*, isotope dilution) in which minor products (*e.g.*, 2%) can be determined with some accuracy. In fact, the method is especially applicable to such situations. Alternatively, the mere linearity of a Stern–Volmer plot can be taken to provide evidence for homogeneity of multiplicity in the region of linearity. Unfortunately, it is often impossible to study that region approaching 100% quenching.

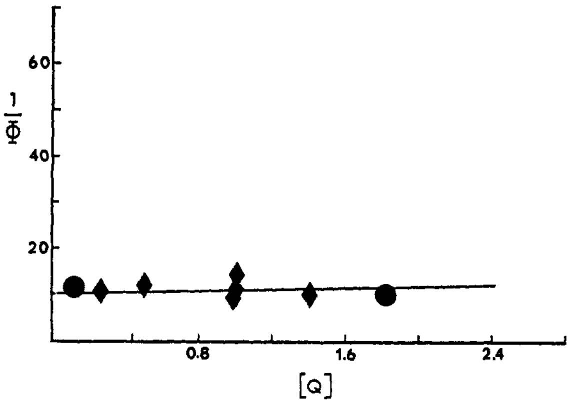


Figure 2. Stern–Volmer plot of the apparent nonquenching of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one: ●, 1,3-cyclohexadiene; ◆, 2,5-dimethyl-2,4-hexadiene.

From the sensitization and quenching studies, it can be concluded that the rearrangement of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) probably proceeds *via* a high-energy (above 75 kcal/mol) triplet state. Since *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one could not be significantly quenched (Table VI, Figure 2), nor efficiently sensitized with propiophenone, mechanistic conclusions must be limited to the chlorobenzene sensitization evidence. Such nonquenching of fast triplets has been encountered before,[21,22] but in those cases efficient sensitization with acetophenone clarified matters. Thus, while the evidence for the triplet nature of the *trans* to *cis* rearrangement is good, that for the *cis* to *trans* process is imperfect. Efforts employing still different approaches to provide further evidence are in progress.

Stereochemistry and Mechanism. The first important conclusion that can be drawn is that a different pathway is followed for the *cis–trans* than for the *trans–cis* isomerization. Hence the potential energy surfaces for the two reactions do not cross (at least in an efficient manner). This is discussed below. Microscopic reversibility, as ordinarily used, does not apply to photochemical reactions if one considers only ground-state reactant and product. Since it is the excited state of each stereoisomer in the isomerization which is the true reactant, and not necessarily the excited state of product which is formed, the two reactions—forward and reverse—do not necessarily have

---

Inc., New York, N. Y., 1965, p 75, has estimated the rate of intersystem crossing in chlorobenzene as over 10^{10} $\sec^{-1}$. This value is at least approximately correct in view of the chlorobenzene fluorescence and phosphorescence quantum yields of 0.00 and 0.06, respectively.[16] Additionally, the structurally similar *p*-chlorotoluene has been reported[17] to have a 1.0-nsec singlet decay time.

(16) E. K. Gilmore, G. E. Gibson, and D. S. McClure, *J. Chem. Phys.*, **20**, 829 (1952).

(17) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press Inc., New York, N. Y., 1965, p 51.

(18) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964), has discussed exciton and long-range energy transfer in solution. Ordinary long-range transfer seems unlikely in view of the weak extinction coefficient for the lowest energy singlet of the bicyclic ketones **8** and **9**. Long-range transfer is most commonly observed when both acceptor and donor transitions have large oscillator strengths. Exciton transfer through chlorobenzene may still not be rapid enough to compete with decay, but this is uncertain.

(19) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5715 (1967), has suggested that linear Stern–Volmer plots should result only when diffusion-controlled energy transfer has not been reached. This interesting suggestion needs experimental verification and study.

(20) H. L. J. Bäckström and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955).

(21) H. E. Zimmerman and J. S. Swenton, *J. Am. Chem. Soc.*, **89**, 906 (1967).

(22) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

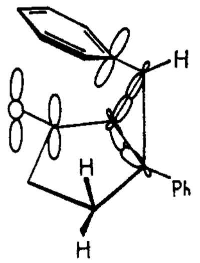


Figure 3. Overlap control of bond cleavage in *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**).

two species in equilibrium and microscopic reversibility does not apply here and must be cautiously used in general.

A second point is more specific, *viz.*, why there is a predominance of mechanism A with external bond fission. Reference to Figure 3 reveals that there is greater overlap between the orbital at the carbonyl carbon[23] and the orbitals comprising cyclopropane ring bond a than with the endocyclic orbitals of bond b. Therefore, of the two bonds expected to sever in the gradual expulsion of a group from the carbon α to the carbonyl carbon[24] of the $n-\pi^*$ excited state,[26] bond a is expected to be preferred in a smooth electron redistribution process.

Although the *cis–trans* and *trans–cis* interconversions proceed mainly by external bond cleavage, it should be noted that both *trans-* and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones *do* open the internal bond as well, as evidenced by the presence of 3,4-diphenylcyclohexenone (**4**) as a reaction product from both **1** and **2**. Since the quantum yield is only *ca.* 0.1 in either direction, there is the *a priori* possibility that this internal bond is broken and re-formed repetitively and stereospecifically. Similarly the external bond a may break reversibly to detract from the quantum yield. This complicates interpretation of the reasons for *trans-* and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones choosing differing amounts of the two reaction routes A and B.

Suggestive evidence, however, was found in the lithium–liquid ammonia reduction of *trans-* and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones. Reductive cleavage of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) led to 12 times as much internal b as external bond a cleavage (although bond c fission accounted for 74% of the reaction). Lithium–liquid ammonia treatment of *cis*-diphenylcyclo[3.1.0]hexan-2-one (**2**), however, resulted in nearly equal amounts of bonds a and c cleavage with no apparent products from fission of the internal bond b. Inspection of a model of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (Figure 3) revealed that in the *trans* isomer **1** fission of bond a might be hampered by steric interaction between an *o*-hydrogen on the C-6 phenyl ring and the *endo*-methylene proton on C-4 when the phenyl ring is rotated into a position favorable for overlap with the C-1 to C-6 cyclopropane bond a. No such steric hindrance was obvious for the conformation of **1** in which the phenyl group was oriented for best overlap with the internal bond b to facilitate cleavage between C-1 and C-5. The preference for external bond a (over bond b) fission in the *cis* isomer then probably derives from overlap control as noted by Norin[7b] and Dauben.[7d] Similar effects have been noted by Zimmerman, Rieke, and Scheffer[8] and by Zimmerman and Morse.[28]

Perhaps the steric factors affecting the bond opening in the lithium–liquid ammonia reduction had their effect in bond closure steps under photochemical conditions. According to this interpretation, the stereochemistry of the interconversion between **1** and **2** would have been controlled by the willingness of a reversibly formed species such as **2a*** (Chart III) or its demoted zwitterion counterpart to close to the *trans* isomer **1** rather than to the *cis*-ketone **2**.

A final aspect of the connection between stereochemistry and electronic mechanism which has not been discussed is the possibility that breakage of bond c (eq 1) might have been responsible for the observed stereochemistry. However, the intervention of appreciable mechanism B (which does not involve benzylic–benzylic fission) in the *cis* to *trans* conversion shows minmally that benzylic–benzylic fission of bond c is not a necessary route.[29]

Chronology. One of the more important aspects of mechanistic photochemistry which has drawn attention recently[31] has been chronology. Of special interest is how and at what stage electronically excited reactant has proceeded along the reaction coordinate to the point where electronic excitation has been lost. Excluding reactions of vibrationally "hot" ground states, there are two basic reaction pathways possible for a photochemical reaction. These are: (1) excitation, rearrangement of the reactant excited state to product excited state, and demotion to product; and (2) excitation, followed by rearrangement to product, but bypassing the excited state of the product.

In addition to their importance *per se*, the quantum yields for reaction of *trans-* and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones permitted some important conclusions about the reaction chronology followed in both the *cis–trans* and *trans–cis* isomerizations of **1** and **2** and in the photochemical reaction of 4,4-diphenylcyclohex-2-en-1-one (**3**).[1] The potential energy

---

(23) For ease of presentation the orbital at the carbonyl carbon has been pictured as p and the hybridization as sp^2. In fact, a pyramidal configuration is more likely (*cf.* J. C. D. Brand and D. G. Williamson, *Advan. Phys. Org. Chem.*, **1**, 365 (1963), who have discussed the formaldehyde case). Although such deformation at the carbonyl carbon does allow appreciable overlap with the internal bond orbitals, overlap with bond a is still better.

(24) This is another of the general α-expulsion reactions of $n-\pi^*$ species, wherein a group α to the carbonyl carbon of such an excited state is homolytically or heterolytically expelled. The phenomenon was first discussed by H. E. Zimmerman, Abstracts, 17th National Organic Chemistry Symposium, Bloomington, Ind., 1961, p 38. Note also H. E. Zimmerman, *Tetrahedron Suppl.*, **2**, 396 (1963), and H. E. Zimmerman, *Advan. Photochem.*, **1**, 199 (1963). The application in a cyclopropyl ketone was first discussed by Zimmerman and Schuster.[25]

(25) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).

(26) Whether the lowest excited state is termed $n-\pi^*$ or $n-\sigma^*$ is a matter of semantics. Three-dimensional Hückel calculations on similar molecules[27] indicate that in the lowest excited state promotion is from the nonbonding p orbital to an antibonding orbital comprising both the carbonyl π system and the cyclopropane ring orbitals. Whether this antibonding orbital is termed π^* or σ^* is arbitrary.

(27) H. E. Zimmerman and R. W. Binkley, unpublished results.

(28) H. E. Zimmerman and R. L. Morse, *J. Am. Chem. Soc.*, **90**, 954 (1968).

(29) In not too dissimilar systems independent evidence is available[30] that such benzylic–benzylic fission is much less efficient than fission α to carbonyl groups.

(30) Unpublished results of H. E. Zimmerman with C. Moore and S. Hixson.

(31) H. E. Zimmerman and J. O. Grunewald, *J. Am. Chem. Soc.*, **89**, 5163 (1967).

surfaces interconnecting the four ketones studied (**1**, **2**, **3**, and **4**) and their excited states are illustrated schematically in Figure 4. This representation is an oversimplification, but it serves to illustrate several general features.

Firstly, the triplet excited state of 4,4-diphenylcyclohex-2-en-1-one (**3**) reacts to give *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**1**) relatively efficiently, but gives the *cis* isomer **2** and 3,4-diphenylcyclohexenone (**4**) only very inefficiently. Thus there may be larger kinetic barriers for these processes.

Secondly, the question of whether or not the conversion of 4,4-diphenylcyclohexenone (**3**) to the *trans*-bicyclic ketone **1** passes through the excited state of the product (dotted-line route in Figure 4) can now be answered. When the triplet excited state of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one was generated by direct irradiation, it gave the *cis* isomer **2** one-tenth of the time (*i.e.*, $\Phi = 0.093$). Hence, if a significant fraction of the 4,4-diphenylcyclohexenone reaction had proceeded through the excited state **1*** of the *trans*-product **1**, we would expect **1*** to proceed onward to *cis*-ketone with this usual efficiency. We would therefore observe a larger proportion of the *cis* isomer in the reaction mixture, and a *trans*:*cis* product ratio approaching 10:1 instead of the 140:1 ratio actually found.[1] Demotion to ground-state chemistry must, therefore, have occurred somewhere along the reaction coordinate before the excited state of the product was reached (solid line, Figure 4).

Similar reasoning can be applied to the photochemical *cis–trans* isomerization. The *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one excited state reverted to 4,4-diphenylcyclohexenone (**3**) about 1% of the time when generated directly (Chart I, Table I). If the *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one reaction had reached the excited state of *trans*-isomer product, we would have expected to find, as before, the usual products of this excited state. With the sensitivity of isotopic dilution, detectable amounts of 4,4-diphenylcyclohexenone (**3**) in the reaction mixture would be found but were not. Ergo, once again demotion to ground-state chemistry must have happened before the excited state of the product could be reached.

The quantum yield studies alone did not give sufficient information to allow a definite conclusion about the chronology of events in the *trans–cis* isomerization. The stereochemical observations, however, indicated that the excited state of the product, *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one could not have been an intermediate en route to the *cis*-ketone **2** from the *trans* isomer **1**, since this excited state isomerized to the *trans*-ketone **1** with loss of optical activity when generated directly. Thus, had the excited state of **2** been an intermediate, recovered reactant **1** should not have been optically pure, but it was. Hence, in this direction of isomerization as well, demotion to ground-state chemistry must have occurred during the reaction, before product geometry was fully attained. Furthermore, the *cis–trans* and *trans–cis* conversions could not have a species common to both processes, since different stereochemical results were observed starting with *cis*- than with *trans*-ketone.

There was not sufficient information about the other reaction pathways to warrant definite conclusions, but similar processes seem reasonable.

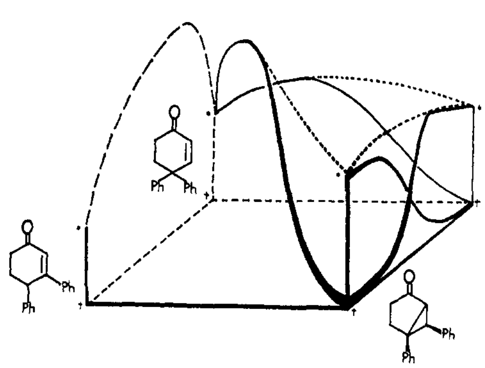


Figure 4. Potential energy pathways: ——, pathways utilized; ----, pathways not utilized; — —, unknown; *, excited states; †, ground states.

Experimental Section[32]

4,4-Diphenylcyclohex-2-en-1-one was prepared by an improved version of the method of Zimmerman and Nasielski.[22] To a cooled, stirred solution of 46.2 g (0.236 mol) of diphenylacetaldehyde and 18.0 g (0.257 mol) of methyl vinyl ketone in 315 ml of anhydrous ether under nitrogen was added 23.7 ml of a 2.97 *N* alcoholic potassium hydroxide solution during 1 hr. The yellow orange solution was stirred for 2 hr at 0° and an additional 2 hr at room temperature during which time a yellow solid separated. The reaction mixture was transferred to a separatory funnel containing 125 ml of water and the solid redissolved by the addition of 50 ml of benzene; the two-phase mixture was neutralized with 10% hydrochloric acid. The organic layer was washed with water, dried over sodium sulfate, and concentrated to yield 63.0 g (105%) of crude product which was recrystallized from ethanol to afford 56.4 g (96%) of 4,4-diphenylcyclohex-2-en-1-one, mp 93.5–94.5° (lit.[22] mp 91–94°); ir (CS_2): 5.95 (C=O), 7.24, 8.42, 11.31, 12.86, 13.34, and 14.35 μ. More typical yields of 4,4-diphenylcyclohexenone, mp 93.5–94.5°, were 75–90%.

***cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-ones** were prepared by photolysis of 4,4-diphenylcyclohexenone in benzene according to Wilson and Zimmerman.[2]

2-N,N-Dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0[hexane was prepared using conditions patterned after the methods of Wallach[5a] and Staple and Wagner.[5b] In a typical run a solution of 10.028 g (40.4 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 25 ml of dimethylformamide was added to a suspension of dimethylammonium formate, prepared by the cautious addition of 3.50 ml (86.2 mmol) of 91% formic acid to 20 ml (0.302 mol) of dimethylamine which had been cooled to −10°. The resulting mixture was refluxed for 5 hr using a reflux condenser equipped with an Ascarite–potassium hydroxide drying tube. The cooled reaction mixture was taken up in ether and extracted with 10% hydrochloric acid, 10% sodium hydroxide, and water. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to yield 44.9 mg of oily material whose ir revealed no carbonyl or aromatic absorption.

The acid extracts were made basic with 20% sodium hydroxide and ether extracted; the ether extract was dried over sodium sulfate and concentrated *in vacuo* to yield 12.022 g (108%) of a light-colored solid, mp 69–71°. Crystallization from ether–ethanol afforded 10.964 g (98%) of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane, mp 72.5–73.5°.

Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.59; H, 8.30; N, 4.96.

Spectral properties were: ir (CCl_4): 3.23, 3.27, 3.36, 3.46, 3.52, 3.58, 6.24, 6.68, 6.90, 7.36, 7.54, 7.91, 8.56, 9.46, 11.44, 11.67, 13.89, and 14.31 μ; nmr ($CDCl_3$): τ 2.35–3.00, multiplet (10 H, aromatic); 6.90–7.33, multiplet (1 H, CHN); 7.43–8.13, multiplet, with a singlet at 7.72 (10 H, NCH_3 and CH_2CH_2); 8.42, doublet (1 H, CH, $J = 3.5$ cps); 9.43, triplet (1 H, CH, $J = 11$ cps).

Oxidation of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane was carried out under conditions similar to those

---

[32] All melting points were run on a calibrated Fisher–Johns hot-stage apparatus, and are corrected. All optical rotatory dispersion curves were run in ethanol at 24° on a Cary Model 60 ORD spectrophotometer.

described by Kahr and Berther[6] for the oxidation of cyclohexylamine to cyclohexanone oxime. In a typical run, 2.00 ml (25.9 mmol) of a 30% hydrogen peroxide solution was added by syringe to a stirred solution of 2.00 g (7.22 mmol) of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane and 61.1 mg (0.186 mmol) of sodium tungstate dihydrate in 72.0 ml of anhydrous methanol. The mixture was shielded from light and stirred 40 hr at room temperature. The reaction was quenched by the addition of a solution of 1.091 g (105.0 mmol) of sodium bisulfite in 10.0 ml of water; an additional 10.0 ml of water was added and the methanol removed *in vacuo*. The resulting suspension was taken up in ether and extracted with 10% hydrochloric acid, 10% sodium hydroxide, and water. The organic layer was dried over sodium sulfate and concentrated to yield 0.751 g (42%) of neutral material, mp 74–75°, whose ir and nmr spectra were identical with that of authentic 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one; the mixture melting point was undepressed, 73–74°.

The acid extracts were combined, made basic with 20% sodium hydroxide, and ether extracted. The ether extracts were combined, dried over sodium sulfate, and concentrated to yield 1.073 g (54%) of basic material, mp 68–70°, whose ir spectrum was identical with that of starting material. Crystallization from ether–ethanol gave 646 mg, mp 72–73°. The total mass balance was 96%.

A second run beginning with 2.00 g (7.22 mmol) of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane, 56.2 mg (0.170 mmol) of sodium tungstate dihydrate, 1.95 ml (25.3 mmol) of 30% hydrogen peroxide, and 72 ml of anhydrous methanol was run as described above for 27.5 hr to give 0.471 g (26%) of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one and 1.239 g (61%) of unreacted starting material.

A third run beginning with 2.00 g (7.22 mmol) of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane, 238.7 mg (0.753 mmol) of sodium tungstate dihydrate, 3.10 ml (40.2 mmol) of 30% hydrogen peroxide, and 30 ml of anhydrous methanol was run as described above for 22.5 hr to give 0.971 g (54%) of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one and 0.340 g (17%) of unreacted starting material.

Resolution of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane was carried out several times; a typical run is described. A solution of 5.881 g (21.2 mmol) of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane in 33.0 ml of anhydrous ether was added to a solution of 1.440 g (10.7 mmol) of *l*-malic acid, $[\alpha]^{23.7}\mathrm{D}$ −5.86° (*c* 0.0115 g/ml, EtOH), in 25.0 ml of anhydrous ether and 3.60 ml of anhydrous methanol; the reaction flask was tightly stoppered and allowed to stand at room temperature for 17 hr. The resulting oil was scratched to effect solidification and the mixture allowed to stand for an additional 5 hr before collecting a yield of 4.074 g (93% based on *l*-malic acid) of malate salt, $[\alpha]^{22.6}\mathrm{D}$ +5.56° (*c* 0.0076 g/ml, EtOH), mp 129–131°, recrystallized from ethyl acetate–ethanol. This material was essentially unresolved.

Anal. Calcd for $C_{24}H_{29}NO_5$: C, 70.05; H, 7.10; N, 3.40. Found: C, 70.25; H, 7.20; N, 3.41.

Spectral properties were: ir ($CHCl_3$) 2.80, 3.14–4.54 (broad), 5.84, 9.28, 12.04, 14.34, and 15.16 μ.

The methanol mother liquor was concentrated to dryness and ether extracted to afford 3.765 g (64%) of unreacted amine, mp 69–71°. This was recrystallized from ether–ethanol and was available for reuse.

The crude malate salt was dissolved in a mixture of 70.0 ml of ethyl acetate and 9.9 ml of anhydrous methanol and set aside in an unstoppered flask to crystallize at room temperature. After 12–17 hr a small crystal formed which was then crushed to a fine powder to induce rapid crystallization; a finely divided solid separated and was collected after an additional 12–14 hr; this weighed 1.592 g, $[\alpha]^{22.5}\mathrm{D}$ +5.35° (*c* 0.006 g/ml, EtOH).

A second crop of 0.817 g was collected from the methanol mother liquor after an additional 24–36 hr when the same technique of of crystal crushing described above was followed, $[\alpha]^{23.8}\mathrm{D}$ +51.5° (*c* 0.0047 g/ml, EtOH). This material was combined with crops from other runs with similar specific rotations and subjected to further recrystallization as described below.

A third crop was collected from the methanol–ethyl acetate mother liquor of the above after an additional 36–48 hr. This was semisolid and weighed 0.6634 g, $[\alpha]^{23.8}\mathrm{D}$, −0.974° (*c* 0.0046 g/ml, EtOH). Only oils resulted on further standing.

Crops 1 and 3 from above proved unresolved; these were treated with 10% sodium hydroxide and ether extracted. The ether extract was dried over sodium sulfate and concentrated to yield racemic amine which was recrystallized to mp 72–73° and used in other runs. In general, crop 2 proved heavily resolved.

Crop 2 from above was combined with the same crop from other runs whose specific rotations ranged from +51.5 to +53.4° to give a total of 4.293 g of malate salt. This was crystallized from a mixture of 75.0 ml of ethyl acetate and 10.3 ml of anhydrous methanol using the crystal-crushing technique described above to give 2.846 g of malate salt after 20–24 hr, $[\alpha]^{22.8}\mathrm{D}$ +53.8° (*c* 0.004 g/ml, EtOH), mp 80.8–82.8°. The ir was identical with that of the racemic malate salt described above.

Anal. Calcd for $C_{24}H_{29}NO_5$: C, 70.05; H, 7.10; N, 3.40. Found: C, 70.16; H, 7.24; N, 3.42.

A second crop was collected after an additional 24–36 hr following crystal crushing. This weighed 0.997 g, $[\alpha]^{22.8}\mathrm{D}$ +55.2° (*c* 0.0025 g/ml, EtOH).

Crops 1 and 2 of the resolved malate were combined with resolved malate from other runs to give a total of 26.220 g, treated with 300 ml of 10% sodium hydroxide, and ether extracted. The ether extract was dried over sodium sulfate and concentrated to yield 16.580 g of optically active 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane, $[\alpha]^{25.8}\mathrm{D}$ +51.0° (*c* 0.0024 g/ml, EtOH), which was crystallized from ether–ethanol to yield 13.947 g, $[\alpha]^{24.1}\mathrm{D}$ +52.3° (*c* 0.0013 g/ml, EtOH), of optically active amine. A second crystallization of this material afforded 12.919 g of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane whose ir and nmr spectra were identical with those of racemic material, $[\alpha]^{24.7}\mathrm{D}$ +52.6° (*c* 0.00095 g/ml, EtOH), mp 79.2–79.7°.

Anal. Calcd for $C_{20}H_{23}N$: C, 86.59; H, 8.36; N, 5.05. Found: C, 86.75; H, 8.36; N, 5.10.

Oxidation of optically active 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane was repeated several times using the conditions described previously for the racemic 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane; the yields ranged from 39 to 59% conversion to 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one with mass balances ranging from 95 to 99%; the remainder of the material was unreacted starting material. In a typical run, 2.00 ml (25.9 mmol) of a 30% hydrogen peroxide solution was added to a stirred solution of 1.999 g (7.21 mmol) of optically active 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane and 57.0 mg (0.172 mmol) of sodium tungstate dihydrate in 75.0 ml of anhydrous methanol. After 41 hr at room temperature, the reaction was quenched by the addition of a solution of 0.952 g (83.5 mmol) of sodium bisulfite in 10.0 ml of water; an additional 10.0 ml of water was added and the methanol removed *in vacuo*. The resulting suspension was taken up in ether and extracted with 10% hydrochloric acid, 10% sodium hydroxide, and water. The organic layer was dried over sodium sulfate and concentrated to yield 0.873 g (49%) of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one as an oil, $[\alpha]^{23.1}\mathrm{D}$ +89.4° (*c* 0.0048 g/ml, EtOH). This material was combined with the crude ketone from other runs and recrystallized as described below. The ir and nmr spectra of this material were identical with those of racemic 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one.

The acid extracts from above were made basic and ether extracted to yield 0.964 g (48%) of a light tan oil which was crystallized from ether–ethanol to yield 329 mg of unreacted amine, mp 78–79°, $[\alpha]^{26.0}\mathrm{D}$ +57.7° (*c* 0.0078 g/ml, EtOH); this material was reusable. The ir and nmr spectra of the recovered amine were identical with those of starting material.

Further Purification of Optically Active 5,6-*trans*-Diphenylbicyclo[3.1.0]hexan-2-one. The crude optically active 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one obtained from a number of oxidations as described above was combined to give a total of 13.792 g. These were of comparable rotation. This material was crystallized from ethanol to yield a first crop of 7.942 g, $[\alpha]^{23.8}\mathrm{D}$ +96.6° (*c* 0.0011 g/ml, EtOH), and a second crop of 4.355 g, $[\alpha]^{23.8}\mathrm{D}$ +99.7° (EtOH).

Crops 1 and 2, weighing 12.297 g combined, were recrystallized from ethanol to yield a first crop of 9.835 g, $[\alpha]^{21.7}\mathrm{D}$ +95.1° (*c* 0.0082 g/ml, EtOH), and a second crop of 1.061 g, $[\alpha]^{21.7}\mathrm{D}$ +97.7° (*c* 0.00082 g/ml, EtOH); the first crop was recrystallized from ethanol to yield 9.180 g of ketone, $[\alpha]^{21.7}\mathrm{D}$ +97.6° (*c* 0.00096 g/ml, EtOH).

The total amount of optically active 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one was 10.241 g, with an average specific rotation $[\alpha]\mathrm{D}$ +97.7° (EtOH). The ir and nmr spectra of this material were identical with those of the racemic 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one; the material melted at 86–87°.

A portion of the resolved 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one (111 mg, $[\alpha]\mathrm{D}$ +97.7° (EtOH)) was crystallized from ethanol and yielded 68 mg of ketone, $[\alpha]^{24}\mathrm{D}$ +97.2° (*c* 0.0012 g/ml, EtOH).

The ORD curve of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one exhibited a positive Cotton effect with a peak at 306 mμ, $[\alpha]^{24}$ +6830° (*c* 6×10^{-5} g/ml, EtOH), and an intercept at 291.2 mμ.

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.97; H, 6.63.

Lithium–Liquid Ammonia Reduction of 5,6-*cis*-Diphenylbicyclo[3.1.0]hexan-2-one. The general method of Zimmerman, Rieke and Scheffer[8] was used. In a typical run, 90 ml of anhydrous liquid ammonia was distilled into an apparatus equipped with a Dry Ice condenser and potassium hydroxide–Ascarite drying tube and containing a solution of 300.3 mg (1.21 mmol) of 5,6-*cis*-diphenylbicyclo[3.1.0]hexan-2-one in 15.0 ml of anhydrous ether; 24.4 mg (3.52 g-atom) of freshly cut lithium was added with stirring. While the metal was dissolving the solution turned to a deep violet color which remained until the reaction was quenched after 50 min by the addition of 349.6 mg of ammonium chloride; then the solution became colorless. The liquid ammonia was allowed to evaporate at room temperature. The resulting residue was ether extracted, dried over sodium sulfate, and concentrated *in vacuo* to yield 306.2 mg of colorless oil. This was chromatographed on a 2.4 × 59.2 cm silica gel column slurry packed in 5% ether in hexane; elution in 250-ml fractions gave: fractions 1–4, 5% ether–hexane, and 5–6, 8%, nil; 7–12, 168 mg (54%) of colorless oil, assumed to be 2-benzyl-3-phenylcyclopentanone; 13, 10%, a mixture of 2-benzyl-3-phenylcyclopentanone and 3-benzyl-3-phenylcyclopentanone by inspection of the ir spectrum; 14–20, 140 mg (46%) of a colorless oil which solidified on standing, mp 67–68°, identified as 3-benzyl-3-phenylcyclopentanone. No other products were isolated.

The material in fractions 5–10 exchanged three hydrogens upon deuterium exchange as described below and was not investigated further; ir (CS_2): 5.73, 7.12, 7.80, 8.80, 9.70, 12.72, 13.24, and 14.32 μ; nmr (CCl_4): τ 2.57–3.22, multiplet (10 H, aromatic); 6.72–8.5, multiplet (8 H, aliphatic).

The material in fractions 12–18 was shown to be 3-benzyl-3-phenylcyclopentanone by comparison of ir and nmr spectra and undepressed mixture melting point with independently synthesized material.

The ir and nmr were identical with those of the independently synthesized 3-benzyl-3-phenylcyclopentanone. This material also exchanged four hydrogens upon deuterium exchange as described below.

Deuterium Exchange of 3-Benzyl-3-phenylcyclopentanone. The 3-benzyl-3-phenylcyclopentanone obtained from the above chromatography (111.5 mg, 0.446 mmol) in 2.0 ml of anhydrous dioxane was added to 1.0 ml of deuterium oxide and 0.10 ml of 5% sodium deuterioxide in deuterium oxide. The reaction mixture was stirred for 1.0 hr at room temperature in a serum-capped flask and ether extracted and the ether dried over sodium sulfate and concentrated *in vacuo* to yield 117.9 mg of solid whose nmr indicated the exchange of four hydrogens; nmr (CCl_4): τ 2.67–3.58, multiplet (10 H, aromatic); 7.13, singlet (2 H, CH_2); 7.78, singlet (2 H, CH_2). The ir spectrum was similar to that of starting material and the melting point and the mixture melting point were undepressed. The above treatment was repeated on the recovered deuterated 3-benzyl-3-phenylcyclopentanone, and the nmr and ir spectra were unchanged after the second deuterium exchange; 110.6 mg of deuterated 3-benzyl-3-phenylcyclopentanone was recovered.

Deuterium Exchange of 2-Benzyl-3-phenylcyclopentanone. The material from fractions 7–12 (139.2 mg) of the above chromatography of the lithium–liquid ammonia reduction of 5,6-*cis*-diphenylbicyclo[3.1.0]hexan-2-one was dissolved in 2.0 ml of anhydrous dioxane and treated with 1.0 ml of deuterium oxide and 0.10 ml of 5% deuterioxide for 65 min as described above. This afforded 129.1 mg of colorless oil after work-up whose ir was very similar to that of starting material but whose nmr revealed the exchange of three hydrogens; nmr (CCl_4): τ 2.57–3.22, multiplet (10 H, aromatic); 6.75–7.54, multiplet (3 H, CH, CH_2); an AB quartet could be discerned in this (191, 177.5, 164.5, 151 cps); 7.58–8.33, multiplet (2 H, CH_2). Upon repeating the above treatment on the recovered material, the ir and nmr spectra remained unchanged and 121.8 mg was recovered.

Lithium–Liquid Ammonia Reduction of 5,6-*trans*-Diphenylbicyclo[3.1.0]hexan-2-one. The reaction was run using the same procedure as described above for 5,6-*cis*-diphenylbicyclo[3.1.0]hexan-2-one. In a typical run 716.8 mg (2.89 mmol) of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one was dissolved in 15.0 ml of anhydrous ether, and 90 ml of anhydrous liquid ammonia was distilled into the apparatus. Then 63.0 mg (9.08 g-atoms) of freshly cut lithium was added. After 1.0 hr, 719.3 mg of ammonium chloride was added; the liquid ammonia was allowed to evaporate at room temperature and the residue ether extracted. The ether extract was dried over sodium sulfate and concentrated *in vacuo* to yield 750 mg of colorless oil which was chromatographed on a 3.3 × 89.1 cm silica gel column slurry packed in 5% ether–hexane; 250-ml fractions were collected: fractions 1–4, 5% ether–hexane, and 5–12, 8%, nil; 13–33, 8%, 456 mg (74% based on weight of material eluted from the column) of a colorless oil identified as 2-benzyl-3-phenylcyclopentanone by inspection of the ir and nmr spectra; 34–41, 9%, nil; 42–49, 9%, 9.2 mg (2%) of 3-benzyl-3-phenylcyclopentanone as a colorless oil, identified by inspection of the ir and nmr spectra; 50, 9%, nil; 51–79, 10%, 144 mg (24%) of 3,4-*cis*-diphenylcyclohexanone, mp 68.5–70°, as identified by ir and an undepressed mixture melting point with an authentic sample,[33] 69–70° (reported[33] 3,4-*cis*-diphenylcyclohexanone mp 71°, 3,4-*trans*-diphenylcyclohexanone mp 107°).

Catalytic hydrogenation of 5,6-*cis*-diphenylbicyclo[3.1.0]hexan-2-one was carried out volumetrically at atmospheric pressure. To a suspension of 84.8 mg of palladium on carbon in 10.0 ml of ethanol, which had been preequilibrated with hydrogen, was added 365 mg (1.47 mmol) of 5,6-*cis*-diphenylbicyclo[3.1.0]hexan-2-one in 15.0 ml of ethanol. The reaction was allowed to continue for 50 min until no further uptake of hydrogen was observed; 32.2 cc (corrected to STP, 1.44 mmol) of hydrogen was absorbed. The catalyst was filtered and the solvent removed *in vacuo* to yield 371 mg of solid, mp 57.5–60.5°; ir (CS_2): 5.73, 12.82, 13.01, 13.22, 13.36, 13.65, 13.81, and 14.30 μ. This was almost identical with that of the independently synthesized 3-benzyl-3-phenylcyclopentanone, as was the nmr. The crude product was chromatographed on a 2.7 × 95.8 cm silica gel column slurry packed with 2% ether–hexane and eluted with 7% ether–hexane; 500-ml fractions were collected, giving: fraction 1, nil; 2–3, 7.8 mg of an oil whose ir exhibited no carbonyl or hydroxyl bands; 4, nil; 5–9, 20 mg of 2-benzyl-3-phenylcyclopentanone, identified by ir and nmr spectra; 10, nil; 11–18, 345 mg (95%) of 3-benzyl-3-phenylcyclopentanone, mp 66–67.5°, mixture melting point undepressed, ir and nmr spectra identical with those of an authentic sample. There was no trace of any 3,4-diphenylcyclohexanone formed.

Catalytic hydrogenation of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one was carried out volumetrically at atmospheric pressure. To a suspension of 104.4 mg of palladium on carbon in 10.0 ml of ethanol, which had been preequilibrated with hydrogen, was added a solution of 400 mg (1.61 mmol) of 5,6-*trans*-diphenylbicyclo[3.1.0]hexan-2-one in 15.0 ml of ethanol. The reaction was allowed to continue for 1 hr until no further uptake of hydrogen was observed; 35.4 cc of hydrogen (corrected to STP, 1.58 mmol) was absorbed. The catalyst was filtered and the solvent removed *in vacuo* to yield 450 mg of colorless oil which was chromatographed on a 2.7 × 101.2 cm silica gel column slurry packed in 2% ether in hexane; 250-ml fractions were collected: fractions 1–2, 2% ether–hexane, nil; 3–10, 6%, 23.5 mg of an oil whose ir contained no hydroxyl or carbonyl bands; 11–14, 6%, nil; 15–20, 6%, 7 mg (2%) of 2-benzyl-3-phenylcyclopentanone identified by inspection of the ir; 21–34, 6%, nil; 35–42, 7%, 48 mg (12%) of 3-benzyl-3-phenylcyclopentanone, mp 64.5–66.0°, mmp 66–67°, ir and nmr identical with those of independently synthesized material; 43, 7%, 4 mg of a mixture of 3-benzyl-3-phenylcyclopentanone and 3,4-diphenylcyclohexanone by inspection of the ir spectrum; 44–50, 10%, 339 mg (85%) of 3,4-*cis*-diphenylcyclohexanone, mp 67–69°, identified by ir comparison.

3-Phenylcyclopent-2-en-1-one was prepared by the method of Borsche and Menz.[34] There was obtained 17.7 g (63%) of 3-phenylcyclopent-2-en-1-one, mp 83–84°, after recrystallization from ether (lit.[34] mp 82.5–83.5°).

3-Benzyl-3-phenylcyclopentanone. Benzylmagnesium chloride was prepared as follows. Magnesium (4.62 g, 0.19 g-atom) was placed in a dry flask under nitrogen, and 0.50 g (4.0 mmol) of benzyl chloride in 50.0 ml of anhydrous ether was added. A small crystal of iodine was added to initiate the reaction, and the remaining 23.58 g (0.186 mol) of benzyl chloride (total of 24.08 g, 0.190 mol) in 50.0 ml of anhydrous ether was added dropwise with rapid stirring during 35 min; the mixture was then refluxed for an additional 1 hr under nitrogen. The solution of benzylmagnesium chloride was cooled in an ice bath and 0.832 g (5.8 mmol) of cuprous bromide added. The resulting suspension was stirred 30 min under nitrogen. A solution of 15.0 g (92.0 mmol) of 3-phenylcyclopent-2-en-1-one[34] in 150.0 ml of anhydrous tetrahydrofuran was added dropwise

---

[33] H. E. Zimmerman and R. Peterson, unpublished results; we wish to thank Dr. Peterson for a sample of this compound.

[34] W. Borsche and W. Menz, *Chem. Ber.*, **41**, 190 (1908).

during 1 hr and 40 min to the cooled, stirred reaction mixture under nitrogen. The reaction was allowed to continue for an additional 17 hr at room temperature and then poured into a separatory funnel containing 15.0 ml of concentrated hydrochloric acid and 50.0 g of ice. The organic layer was washed with water, combined with the ether extracts of the aqueous layers, dried over sodium sulfate, and concentrated *in vacuo* to yield 32.0 g of dark brown oil which was chromatographed on a 3.3 × 83.9 cm silica gel column slurry packed with 8% ether–hexane. Elution in 500-ml fractions gave: fractions 1–3, 8% ether–hexane, 5.92 g of solid, mp 196–198°, whose ir contained no carbonyl or hydroxyl absorption; 4–9, 15%, 12.0 g (52% based on weight of 3-phenylcyclopent-2 en-1-one) of crude 3-benzyl-3-phenylcyclopentanone as an orange oil identified by inspection of the ir spectrum; 10–20, 75%, 12.7 g of reddish oil, whose ir exhibited hydroxyl and aromatic absorption but no carbonyl band, and which was not studied further.

Fractions 4–9 were chromatographed on a 4.7 × 11.6 cm column of 20% Norit–silica gel, slurry packed in 20% ether–hexane. Elution with 6 l. of 20% ether–hexane gave 9.5 g (42%) of colorless oil which solidified on standing, mp 67–68°, after crystallization from ether–hexane. Recrystallization did not raise the melting point.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.25. Found: C, 86.35; H, 7.26.

Spectral properties were: ir (CS_2): 5.73, 12.80, 13.01, 13.22, 13.35, 13.65, 13.81, 13.97, and 14.30 μ; nmr (CCl_4): τ 2.67–3.58, multiplet (10 H, aromatic); 7.13, singlet (2 H, $ArCH_2$); 7.52, singlet (2 H, α-CH_2); 7.78, singlet (4 H, α'- and β-CH_2).

N,N-Dimethylamino-3-benzyl-3-phenylcyclopentane was prepared using the method as described above for 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane. A solution of 5.003 g (20.0 mmol) of 3-benzyl-3-phenylcyclopentanone in 40.0 ml of dimethylformamide was added to a suspension of dimethylammonium formate, prepared by the cautious addition of 1.75 ml (43.1 mmol) of 91% formic acid to 8.0 ml (0.177 mol) of dimethylamine which had been cooled to −10°. The resulting mixture was refluxed for 4 hr using a reflux condenser equipped with an Ascarite–potassium hydroxide drying tube. The cooled reaction mixture was taken up in ether and extracted with 10% hydrochloric acid, 10% sodium hydroxide, and water. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to yield 5.608 g (99%) of an orange oil whose ir spectrum (CS_2) revealed no carbonyl absorption but typical N,N-dimethylamino peaks[35] at 3.46, 3.51, and 3.57 μ as well as aromatic absorption at 13.01, 13.36, 13.90, and 14.30 μ. One portion of the crude product (2.460 g) was chromatographed on a 2.4 × 51.4 cm column of Woelm alumina (neutral, activity grade 1) packed in 10% ether–hexane; 250-ml fractions were collected: fractions 1, 10% ether–hexane, and 2–3, 20%, nil; 4–14, 20%, 1.513 g of N,N-dimethylamino-3-benzyl-3-phenylcyclopentane as a colorless oil; 15–22, 35%, 0.318 g of colorless oil; 23–27, 100% ether, 0.184 g of yellow oil whose ir (CS_2) exhibited absorption at 2.36, 5.74, and 5.90 μ as well as the aromatic and N,N-dimethylamino peaks. This material was not studied further.

Material in fractions 4–14 exhibited the following spectral properties: ir (CS_2): 3.22, 3.24, 3.28, 3.37, 3.48, 3.53, 3.59, 6.24, 7.36, 7.87, 8.71, 8.95, 9.09, 9.30, 9.60, 9.68, 10.05, 11.02, 13.05, 13.35, 13.90, and 14.33 μ; nmr (CCl_4): τ 2.75–3.65, multiplet (10 H, aromatic); 7.03–7.28, doublet (2 H, $ArCH_2$, $J = 7.5$ cps); 7.62–8.55, multiplet with a singlet discernible at 7.85 (13 H, NCH_3, CH, CH_2).

The ir spectrum (CS_2) of the material in fractions 15–22 was almost identical with that described above except for the lack of a band at 8.95 μ and a slight difference in intensity of the two bands at 9.60 and 9.68 μ.

The remainder of the crude product (3.148 g) afforded, by a similar chromatography, 2.808 g of N,N-dimethylamino-3-benzyl-3-phenylcyclopentane as a colorless oil with an ir spectrum (CS_2) identical with that obtained above. Also, 212 mg of colorless oil whose ir spectrum (CS_2) was identical with that of the material contained in fractions 15–22 above was obtained.

The two chromatograms afforded a total of 4.321 g (78%) of the major stereoisomer of N,N-dimethylamino-3-benzyl-3-phenylcyclopentane.

Anal. Calcd for $C_{20}H_{25}N$: C, 85.97; H, 9.02; N, 5.01. Found: C, 85.82; H, 9.18; N, 5.20.

Partial resolution of N,N-dimethylamino-3-benzyl-3-phenylcyclopentane was obtained using the method described for the resolution of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane. A solution of 1.471 g (5.26 mmol) of N,N-dimethylamino-3-benzyl-3-phenylcyclopentane in 50.0 ml of anhydrous ether was added to a solution of 0.700 g (5.21 mmol) of *l*-malic acid ($[\alpha]^{23.7}\mathrm{D}$ −5.86° (EtOH)) in 25.0 ml of anhydrous ether and 3.0 ml of anhydrous methanol; the reaction flask was tightly stoppered and allowed to stand at room temperature for 48 hr. The resulting solid was collected to yield 1.992 g of solid (93% based on *l*-malic acid), $[\alpha]^{21}\mathrm{D}$ +7.03° (*c* 0.0091 g/ml, EtOH). This material melted at 193.5–194.5° with evaluation of gas after recrystallization from ethanol–ethyl acetate and was essentially unresolved.

The crude malate salt was dissolved in a mixture of 55.0 ml of ethyl acetate and 13.0 ml of anhydrous methanol and set aside in an unstoppered flask to crystallize at room temperature. After 20 hr, 335 mg of finely divided solid was collected, $[\alpha]\mathrm{D}^{21.3}$ +12.4° (*c* 0.0030 g/ml, EtOH); a second crop of 390 mg was collected from the mother liquor after an additional 48 hr, $[\alpha]^{21.3}\mathrm{D}$ +18.9° (*c* 0.0031 g/ml, EtOH). A third crop of 452 mg was collected from the mother liquor after an additional 48 hr, $[\alpha]^{22.4}\mathrm{D}$ +14.8° (*c* 0.0031 g/ml, EtOH), and a fourth crop was collected after an additional 72 hr giving 299 mg, $[\alpha]^{21.7}\mathrm{D}$ +2.46° (*c*, 0.0032 g/ml, EtOH). Only oils resulted on further standing.

Crops 2 and 3 were combined with material from the run described below, having similar rotations.

A second run beginning with 2.748 g (9.85 mmol) of N,N-dimethylamino-3-benzyl-3-phenylcyclopentane and 1.317 g (9.82 mmol) of *l*-malic acid yielded 3.596 g (89%) of malate salt, $[\alpha]^{22.4}\mathrm{D}$ +4.46° (*c* 0.0084 g/ml, EtOH), which was crystallized from a mixture of ethyl acetate and methanol as described above to yield a first crop of 512 mg after 24 hr, $[\alpha]^{22.4}\mathrm{D}$ +2.95° (*c* 0.0046 g/ml, EtOH); a second crop of 151 mg, $[\alpha]^{21.7}\mathrm{D}$ +12.20° (*c* 0.0030 g/ml, EtOH), after an additional 36 hr; a third crop of 423 mg, $[\alpha]\mathrm{D}^{21.7}$ +22.2° (*c* 0.0030 g/ml, EtOH), after an additional 48 hr; a fourth crop of 360 mg, $[\alpha]^{21.7}\mathrm{D}$ +18.0° (*c* 0.0032 g/ml, EtOH), after an additional 36 hr; a fifth crop of 240 mg, $[\alpha]^{21.7}\mathrm{D}$ +17.7° (*c* 0.0030 g/ml, EtOH), after an additional 18 hr; a sixth crop of 546 mg, $[\alpha]^{22.2}\mathrm{D}$ + 4.87° (*c* 0.0033 g/ml, EtOH), after an additional 72 hr. Only oils resulted in further standing.

Crops 2 and 3 from run 1 were combined with crops 3–5 from run 2 to give 1.865 g of malate salt (specific rotations +14.8–22.2°), dissolved in 75.0 ml of ethyl acetate and 13.0 ml of anhydrous methanol, and set aside in an unstoppered flask to crystallize at room temperature. After 5 days the fluffy solid which separated was collected, 374 mg, $[\alpha]^{22.2}\mathrm{D}$ +24.5° (*c* 0.0026 g/ml, EtOH); a second crop was collected after an additional 24 hr, 538 mg, $[\alpha]^{22.6}\mathrm{D}$ +23.2° (*c* 0.0029 g/ml, EtOH), mp 134.5–135.5°.

Anal. Calcd for $C_{24}H_{31}NO_5$: C, 69.71; H, 7.56; N, 3.39. Found: C, 69.72; H, 7.70; N, 3.50.

The two crops from above were combined to give 912 mg of partially resolved malate salt which was treated with 10% sodium hydroxide and ether extracted. The ether extract was dried over sodium sulfate and concentrated *in vacuo* to yield 676 mg of colorless oil whose ir and nmr spectra were identical with those for racemic N,N-dimethylamino-3-benzyl-3-phenylcyclopentane, $[\alpha]^{25.7}\mathrm{D}$ +17.0° (*c* 0.0030 g/ml, EtOH).

Oxidation of racemic N,N-dimethylamino-3-benzyl-3-phenylcyclopentane was run using the conditions described for the oxidation of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane. To a stirred solution of 500 mg (1.79 mmol) of racemic N,N-dimethylamino-3-benzyl-3-phenylcyclopentane and 40.9 mg (0.124 mmol) of sodium tungstate dihydrate in 50.0 ml of anhydrous methanol was added 0.75 ml (9.70 mmol) of a 30% hydrogen peroxide solution. After 43.0 hr at room temperature, the reaction was quenched by the addition of a solution of 735 mg (70.6 mmol) of sodium bisulfite in 20.0 ml of water and the methanol removed *in vacuo*. The resulting suspension was taken up in ether and extracted with 10% hydrochloric acid, 10% sodium hydroxide, and water. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to give 241 mg (53%) of 3-benzyl-3-phenylcyclopentanone, the ir spectrum of which was identical with that of authentic 3-benzyl-3-phenylcyclopentanone.

The acid extracts from above were made basic and ether extracted, and the ether extract was dried over sodium sulfate and concentrated *in vacuo* to give 178 mg (36%) of unreacted amine. The ir spectrum of the recovered amine was identical with that of starting material.

Oxidation of Optically Active N,N-Dimethylamino-3-benzyl-3-phenylcyclopentane. Using the conditions described earlier for the oxidation of 2-N,N-dimethylamino-5,6-*trans*-diphenylbicyclo[3.1.0]hexane, 0.900 ml (11.6 mmol) of 30% hydrogen peroxide solution was added to a stirred solution of 645 mg (2.31 mmol) of

---

(35) K. Nakanishi, "Infrared Absorption Spectroscopy, Practical," Holden-Day, Inc., San Francisco, Calif., 1962, p 40.

optically active N,N-dimethylamino-3-benzyl-3-phenylcyclopentane, $[\alpha]^{25.7}_{D}$ +17.0° (EtOH), and 48.1 mg (0.146 mmol) of sodium tungstate dihydrate in 60 ml of anhydrous methanol. The reaction was allowed to continue for 48 hr at room temperature in a stoppered flask; then 819 mg (78.6 mmol) of sodium bisulfite in 20 ml of water was added. The methanol was removed *in vacuo* and the resulting suspension taken up in ether and extracted with 10% hydrochloric acid, 10% sodium hydroxide, and water. The organic layer was dried over sodium sulfate and concentrated *in vacuo* to yield 134 mg (23%) of a colorless oil identified as 3-benzyl-3-phenylcyclopentanone by inspection of the ir spectrum.

The acid extracts were made basic and ether extracted; the ether extracts were dried over sodium sulfate and concentrated *in vacuo* and gave 462.4 mg (72%) of unreacted N,N-dimethylamino-3-benzyl-3-phenylcyclopentane by inspection of the ir spectrum.

The crude 3-benzyl-3-phenylcyclopentanone from above was chromatographed on a 2.4 × 59.4 cm silica gel column slurry packed in 3% ether–hexane and eluted with 8% ether–hexane; 250-ml fractions were collected: fractions 1–6, nil; 7–13, 91 mg (16%) of 3-benzyl-3-phenylcyclopentanone as a colorless oil identified by ir spectrum and its characteristic ORD curve.

The ORD curve of the independently resolved 3-benzyl-3-phenylcyclopentanone was identical in all respects with that of the 3-benzyl-3-phenylcyclopentanone obtained by degradation of the *cis*- or *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones, exhibiting a multiple negative Cotton effect with intercepts at 311.2 and 287.2 mμ and maxima or minima at 324 mμ, $[\alpha]^{25.7}_{D}$ −78° (EtOH); 319 mμ, −33°; 317 mμ, −36°; 308 mμ, +69°; 306 mμ, +60°, 298 mμ, +107°.

Photolysis of Racemic *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one. Using the apparatus and procedure described earlier[2] for the preparation of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones, 1.001 g (4.04 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one in 700 ml of freshly distilled benzene was photolyzed for 30 min under nitrogen through Pyrex; the solvent was removed *in vacuo* to yield 1.013 g of light yellow oil. This was chromatographed on a 3.3 × 87.2 cm silica gel column slurry packed in 10% ether–hexane and eluted with 15% ether–hexane; 250-ml fractions were collected: fractions 1–10, nil; 11–24, 947 mg (95%) of recovered *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 73–74°; 25–26, nil; 27–39, 39 mg (4%) of pure *cis*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one, mp 114–116°; 40–48, 19 mg (2%) of a mixture of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one identified by ir spectra; in all of the latter fractions the carbonyl band in the ir at 6.00 μ was only of minor intensity. The total conversion to product was 58 mg (6%).

In a second run, 1.006 (4.05 mmol) of *trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one in 250 ml of freshly distilled benzene was photolyzed for 1.5 hr under nitrogen through Pyrex; the solvent was removed *in vacuo* to yield 1.033 g of oil. This was chromatographed on a 3.3 × 87.2 cm silica gel column as described above to yield 883 mg (86%) of recovered *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, 123 mg (12%) of pure *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, and 20 mg (2%) of a mixture of *cis*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one. The total conversion to product was 143 mg (14%).

Similarly, irradiations of 1.002 and 1.005 g in 700 ml for 1 hr and 1.5 hr, respectively, gave conversions of 11 and 10%.

Photolysis of Optically Active *trans*-5,6-Diphenylbicyclo[3.1.0]-hexan-2-one. Using the procedure described above, 1.001 g (4.04 mmol) of optically active *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, $[\alpha]_{D}$ +97.7° (EtOH), $[\alpha]_{306}$ +6830° (EtOH), in 700 ml of freshly distilled benzene was photolyzed for 1.0 hr under nitrogen through Pyrex. The solvent was removed *in vacuo* to yield 1.013 g of oil which was chromatographed on a 3.3 × 81.0 cm silica gel column slurry packed in 5% ether–hexane and eluted with 15% ether–hexane; 500-ml fractions were collected: fractions 1–2, nil; 3–8, 948 mg (95%) of unreacted starting material, mp 85–86°, $[\alpha]^{21}_{D}$ +101° (*c* 0.0009 g/ml, EtOH); 9–10, nil; 11–17, 49 mg (5%) of pure *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 148–149°, $[\alpha]^{21}_{D}$ +139° (*c* 0.0008 g/ml, EtOH); 18–20, 9 mg (1%) of a mixture of 5,6-*cis*-diphenylbicyclo[3.1.0] hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one by inspection of the ir spectra. The total conversion to products was 6%.

The ORD of the recovered *trans*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one was obtained without further purification but the *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one was degraded by catalytic hydrogenation (*vide infra*) and the product analyzed.

The ORD of the recovered starting material showed the characteristic positive Cotton effect and the typical intercept at 291.2 mμ, $[\alpha]^{24}_{306}$ +6910° (EtOH). Except for the very long runs, the recovered *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one had a specific rotation unchanged within experimental error of the original starting material.

In a second run 1.035 g (4.17 mmol) of optically active *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 700 ml of freshly distilled benzene was photolyzed 8.5 hr under nitrogen through Pyrex. The solvent was removed *in vacuo* to yield 1.138 g of oil which was chromatographed on a 3.3 × 89.0 cm silica gel column as described above to yield 651 mg (61%) of recovered starting material, $[\alpha]_{306}$ +6625° (EtOH); 393 mg (38%) of pure *cis*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one, $[\alpha]_{304}$ +2605° (EtOH), and 18 mg (1%) of a mixture of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one by inspection of ir spectra. The total conversion to products was 39%.

Anal. Calcd for $C_{18}H_{16}O$ (*cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one): C, 87.06; H, 6.50. Found: C, 86.98; H, 6.38.

The results of the above and further runs are summarized in Tables VII and VIII.

Table VII. Photolysis of Optically Active *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run	Wt, g	mmol	$[\alpha]_{306}$, deg	Vol, ml	Time, hr	Convrsn to prodt, %
1	1.001	4.04	+6830	700	1	6
2	1.642	6.63	+7660[a]	700	$1^{3}/_{4}$	8
3	0.640	2.58	+6830	700	$1^{1}/_{6}$	12
4	0.410	1.65	+6830	700	$5^{1}/_{6}$	34
5	1.035	4.17	+6830	700	$8^{1}/_{2}$	39
6	0.312	1.26	+6830	250	20	52
7	0.311	1.25	+6830	250	$17^{1}/_{4}$	54

[a] The material used for this run was recovered and recrystallized *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one from earlier runs.

Photolysis of Optically Active *cis*-5,6-Diphenylbicyclo[3.1.0]-hexan-2-one. Using the procedure described above, 144 mg (0.58 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, obtained from the second photolysis of optically active *trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one described above ($[\alpha]_{304}$ +2605° (EtOH)), was dissolved in 250 ml of freshly distilled benzene and photolyzed under nitrogen through Pyrex for 4.5 hr. The solvent was removed *in vacuo* to yield 132 mg of oil which was chromatographed on a 3.3 × 80.8 cm silica gel column slurry packed in 5% ether–benzene and eluted with 15% ether–hexane; 250-ml fractions were collected: fractions 1–6, nil; 7–14, 34 mg (27%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a colorless oil, identified by ir and nmr spectra comparison; 18–26, 85 mg (69%) of recovered pure *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, identified by ir and nmr spectra comparison; 27–28, 5 mg (4%) of a mixture of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one by inspection of ir spectra.

The ORD curve for the recovered *cis*-5,6-diphenylbicyclo[3.1.0]-hexan-2-one showed the characteristic positive Cotton effect with a peak at 304 mμ, $[\alpha]_{304}$ +2485° (*c* 2 × 10^{-4} g/ml, EtOH), and a trough at 287.5 mμ.

The ORD curve for the *trans*-5,6-diphenylbicyclo[3.1.0]hex-2-one showed the characteristic positive Cotton effect with an intercept at 291.2 mμ, $[\alpha]_{306}$ +4320° (*c* 8 × 10^{-5} g/ml, EtOH).

In a second run 212 mg (0.86 mmol) of *cis*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one, obtained from the second photolysis of optically active *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one described, was dissolved in 250 ml of freshly distilled benzene and photolyzed for 1.25 hr under nitrogen through Pyrex. The solvent was removed *in vacuo* to yield 206 mg of oil which was chromatographed on a 3.3 × 77.1 cm silica gel column slurry packed in 5% ether–hexane and eluted with 15% ether–hexane to yield 15 mg (7%) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one as a colorless oil, identified by ir and nmr spectra comparison, $[\alpha]_{306}$ +4690° (EtOH); 182 mg (88%) of pure recovered *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, $[\alpha]_{304}$ +2585° (EtOH); and 9 mg (4%) of a mixture of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one by inspection of ir spectra. The results of the above and further runs are summarized in Tables IX and X.

Table VIII. ORD Data; Photolysis of *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run	Convrsn, %	Specific rotation, [α], deg (error)[a]					Intercept, mμ
		300.0 mμ	302.5 mμ	306.0 mμ	312.5 mμ	317.5 mμ	
		a. Recovered *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one					
...	Starting material[b]	+5100 (±51)	+6205 (±59)	+6830 (+64)	+6150 (+58)	+4915 (+50)	291.2
...	Starting material[c]	+5315 (±51)	+6270 (±58)	+7060 (±64)	+6145 (±56)	+4980 (±48)	291.0
1	6	+5080 (±63)	+6105 (±72)	+6910 (±80)	+6048 (±72)	+4940 (±62)	291.2
2	8	+5340 (±48)	+6280 (±55)	+6930 (±59)	+6020 (±52)	+4860 (±45)	291.2
3	12	+4820 (±55)	+5780 (±64)	+6750 (±72)	+5915 (±65)	+4780 (±55)	291.2
4	34	+4880 (±86)	+5980 (±105)	+6930 (±121)	+6135 (±108)	+5030 (±89)	291.2
5	39	+4980 (±79)	+5820 (±91)	+6625 (±103)	+5795 (±91)	+4690 (±75)	291.2
6	52	+4475 (±39)	+5305 (±44)	+6000 (±48)	+5295 (±44)	+4295 (±27)	291.2
7	54	+3970 (±69)	+4680 (±81)	+5333 (±91)	+4680 (±80)	+3815 (±66)	291.2
		300.0 mμ	304.0 mμ	307.5 mμ	312.5 mμ	320.0 mμ	
		b. Product *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one					
2	8	+2560 (±22)	+2725 (±22)	+2675 (±22)	+2370 (±20)	+1845 (±18)	
3	12	+2500 (±70)	+2640 (±72)	+2550 (±71)	+2275 (±65)	+1810 (±54)	
4	34	+2465 (±37)	+2600 (±38)	+2535 (±38)	+2285 (±35)	+1765 (±29)	
5	39	+2465 (±35)	+2605 (±37)	+2520 (±36)	+2260 (±35)	+1725 (±26)	
6	52	+2360 (±13)	+2510 (±13)	+2460 (±13)	+2210 (±12)	+1700 (±10)	
7	54	+2205 (±31)	+2335 (±33)	+2280 (±32)	+2030 (±30)	+1568 (±25)	

[a] Errors estimated on the basis of ±0.1 mg weighing, ±0.0006° readability on ORD curves, and 1.5 mg column residue per fraction. [b] Resolved *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one used as starting material for runs 1 and 3–7. [c] Recovered and recrystallized *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one from earlier runs used as starting material for run 2.

Table IX. Photolysis of Optically Active *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run	Wt, mg	mmol	$[\alpha]_{304}$, deg	Vol, ml	Time, hr	Convrsn to prodt, %
1	318	1.29	+2735	250	1¼	5
2	212	0.86	+2605	250	1¼	7
3	182	0.73	+2800	110	3½	12
4	144	0.58	+2605	250	4½	27
5	101	0.41	+2720	250	25½	42

Catalytic hydrogenation of optically active *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one was carried out volumetrically at atmospheric pressure. To a suspension of 260.4 mg of palladium on carbon in 15.0 ml of ethanol which had been preequilibrated with hydrogen was added a solution of 1.024 g (4.14 mmol) of unphotolyzed resolved *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, $[\alpha]_D$ +97.7° (EtOH), $[\alpha]_{306}$ +6830° (EtOH), in 20.0 ml of ethanol. The reaction was allowed to continue for 1 hr. When no further uptake of hydrogen was observed (93.2 cc cor to STP, 4.16 mmol), the catalyst was filtered and the solvent removed *in vacuo* to yield 1.089 g of colorless oil which was chromatographed on a 3.3 × 84.0 cm silica gel column slurry packed in 2% ether–hexane. Elution in 250-ml fractions gave: fractions 1–2, 2% ether–hexane, nil; 3–10, 6%, 40 mg of oil whose ir spectrum indicated it to be a hydrocarbon; 11–14, 7%, nil; 15–26, 7%, 15 mg (1%) of 2-benzyl-3-phenylcyclopentanone, identified by inspection of the ir spectrum, as a colorless oil; 27–37, 7%, 113 mg (11%) of 3-benzyl-3-phenylcyclopentanone identified by ir, nmr spectra, and ORD curves, as a colorless oil; 38, 7%, 13 mg of a mixture of *3-benzyl-3-phenylcyclopentanone and 3,4-diphenylcyclohexanone*, determined by inspection of the ir spectrum; 39–61, 10%, 920 mg (87%) of 3,4-*cis*-diphenylcyclohexanone, mp 67–68.5°.

The ir and nmr spectra of the 3-benzyl-3-phenylcyclopentanone were identical with those of the independently synthesized material. The ORD curves of four consecutive column fractions were superimposable, exhibiting a multiple negative Cotton effect with maxima or minima at: 324 mμ, [α] −114° (EtOH); 319 mμ, [α] −55°; 317 mμ, [α] −60°; 308 mμ, [α] +75°; 306 mμ, [α] +61°; 298 mμ, [α] +121°; and intercepts at 311.2 and 287.2 mμ. The above results are summarized in Table XI.

Catalytic hydrogenation of optically active 5,6-*cis*-diphenylbicyclo[3.1.0]hexan-2-one was carried out volumetrically at atmospheric pressure. To a suspension of 58.6 mg of palladium on carbon, preequilibrated with hydrogen, was added 49.3 mg (0.20 mmol) of optically active *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, from the photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one described earlier, in 15.0 ml of ethanol. The reaction was allowed to continue for 45 min, when no further uptake of hydrogen was observed (5.65 cc cor to STP, 0.25 mmol); the catalyst was filtered and the solvent removed *in vacuo* to yield 47.5 mg of colorless oil which was chromatographed on a 1.9 × 87.9 cm silica gel column slurry packed in 2% ether–hexane and eluted with 7% ether–hexane. Collection in 250-ml fractions gave: fraction 1, nil; 2–5, 5.9 mg of colorless oil whose ir spectrum indicated it to be a hydrocarbon; 6, nil; 7–8, 5.1 mg (11%) of 2-benzyl-3-phenylcyclopentanone identified by its ir spectrum; 9, nil; 10–16, 41.6 mg (89%) of 3-benzyl-3-phenylcyclopentanone as a colorless oil whose ir and nmr spectra were identical with those of the independently synthesized material. There was no trace of any *cis*- or *trans*-3,4-diphenylcyclohexanone.

The ORD curves of fractions 12 and 13 were recorded without further purification and are presented in Table XII. The ORD curve of the 3-benzyl-3-phenylcyclopentanone exhibited the characteristic multiple negative Cotton effect with maxima or minima at: 324 mμ, [α] −114°; 319 mμ, [α] −55°; 317 mμ, [α] −59°; 308 mμ, [α] +68°; 306 mμ, [α] +55°; 298 mμ, [α] +115°; and intercepts at 311.2 and 287.2 mμ.

In a second run 65.7 mg (0.265 mmol) of optically active *cis*-5,6-

Table X. ORD Data; Photolysis of *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Run	Convrsn, %	Specific rotation, [α], deg (error[a]) 300.0 mμ	304.0 mμ	307.5 mμ	312.5 mμ	320.0 mμ	
		a. Recovered *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one					
...	Starting material[b]	+2640	+2800	+2720	+2455	+1898	
		(±29)	(±31)	(±30)	(±27)	(±21)	
1	5	+2565	+2720	+2660	+2400	+1845	
		(±17)	(±18)	(±17)	(±16)	(±13)	
2	7	+2485	+2585	+2475	+2215	+1717	
		(±28)	(±29)	(±28)	(±25)	(±21)	
3	12	+2560	+2745	+2665	+2410	+1862	
		(+21)	(±22)	(±22)	(±20)	(±16)	
4	27	+2345	+2485	+2415	+2175	±1712	
		(±53)	(±56)	(±54)	(±49)	(±39)	
5	42	+1790	+1890	+1840	+1650	+1276	
		(±29)	(±31)	(±30)	(±27)	(±21)	
		300.0 mμ	302.5 mμ	306.0 mμ	312.5 mμ	317.5 mμ	Intercept, mμ
		b. Product *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one					
1	5	+3850	+4535	+5075	+4450	+3615	291.1
		(±128)	(±150)	(±167)	(±151)	(±121)	
2	7	+3530	+4140	+4690	+4070	+3305	291.2
		(±193)	(±226)	(±256)	(±222)	(±180)	
3	12	+3380	+3980	+4465	+3885	+3110)	291.2
		(±89)	(±105)	(±107)	(±102)	(±80)	
4	27	+3230	+3790	+4320	+3790	+3085	291.2
		(±53)	(±56)	(±54)	(±49)	(±39)	
5	42	+3035	+3580	+4040	+3535	+2885	291.2
		(±41)	(±48)	(±54)	(±47)	(±39)	

[a] Errors estimated on the basis of ±0.1 mg weighing, ±0.0006° readability on ORD curves, and 1.5 mg column residue per fraction. [b] Recovered and recrystallized from earlier runs; used in run 3.

Table XI. ORD Data; Hydrogenation of *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Chromatography fraction	Specific rotation, [α], deg 324 mμ	319 mμ	317 mμ	308 mμ	306 mμ	298 mμ	Intercept, mμ
17	−116.5	−57.3	−61.5	+73.2	+59.9	+122.6	287.2, 311.2
18	−111.0	−52.5	−58.0	+76.4	+61.7	+120.2	287.2, 311.2
Average	−113.8	−54.9	−59.8	+74.8	+60.8	+121.4	
error[a]	±2.6	±1.5	±1.6	±1.9	±1.9	±2.3	

[a] Errors estimated on the basis of ±0.1 mg weighing, 0.0006° readability on ORD curves, and 1.5 mg column residue per fraction.

Table XII. ORD Data; Hydrogenation of *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one

Fraction	Convn, %	Specific rotation, [α], deg 324 mμ	319 mμ	317 mμ	308 mμ	306 mμ	298 mμ	Intercept, mμ
12	6	−116.0	−52.6	−57.2	+68.8	+55.4	+117.0	311.2 287.2
13		−112.0	−57.1	−60.3	+67.5	+55.2	+113.5	311.2 287.2
Average		−114.0	−54.9	−58.8	+68.2	+55.3	+115.3	
error[a]		±4.5	±2.6	±2.8	±3.1	±2.7	±4.5	
11	12	−113.8	−53.6	−61.0	+74.0	+61.8	+122.0	311.2 287.2
12		−106.4	−49.4	−63.5	+75.6	+60.9	+116.8	311.2 287.2
Average		−110.1	−51.5	−62.3	+74.8	+61.4	+119.4	
error[a]		±5.8	±3.2	±3.6	±4.1	±3.6	±5.9	
11	34	−107.8	−53.4	−58.5	+70.9	+58.2	+113.0	311.2 287.2
12		−108.2	−53.7	−59.0	+70.9	+59.7	+116.4	311.2 287.2
Average		−108.0	−53.6	−58.8	+70.9	+59.0	+114.7	
error[a]		±3.0	±1.8	±1.9	±2.2	±1.9	±3.1	

[a] Errors estimated on the basis of ±0.1 mg weighing, ±0.0006° readability on ORD curves, and 1.5 mg column residue per fraction.

diphenylbicyclo[3.1.0]hexan-2-one obtained from a photolysis of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one to 34% conversion in 15.0 ml of ethanol was added to a preequilibrated suspension of 105.2 mg of palladium on carbon in 10.0 ml of ethanol. The reaction was allowed to continue for 65 min, when no further uptake of hydrogen was noted (8.5 cc cor to STP, 0.35 mmol). The catalyst was filtered and the solvent removed *in vacuo* to yield 63.3 mg of oil which was chromatographed on a 1.9 × 91.6 cm silica gel column slurry packed in 3% ether–hexane and eluted with 8% ether–hexane to afford 3.6 mg (6%) of 2-benzyl-3-phenylcyclopentanone and 58.3 mg (94%) of 3-benzyl-3-phenylcyclopentanone.

The ORD curves of consecutive column fractions were superimposable and possessed the characteristic multiple negative Cotton effect with intercepts at 311.2 and 287.2 mμ with specific rotations at the maxima or minima of: −108 (324), −54 (319), −59 (317), +71 (308), +71 (308), +59 (306), and +115° (298 mμ). The results of these and further runs are summarized in Table XII.

Anal. Calcd for $C_{18}H_{18}O$ (3-benzyl-3-phenylcyclopentanone): C, 86.36; H, 7.25. Found: C, 86.19; H, 7.33.

***cis*- and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C.** In a typical preparatory photolysis, 2.98 g (0.0120 mol) of 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C, activity 12.12 μCi/mmol, in 500 ml of dry benzene was irradiated 40 hr under deoxygenated nitrogen through a Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. When the ir spectrum indicated nearly total conversion of starting material, solvent was removed *in vacuo*, and the residue was chromatographed on a 2.5 × 110 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 5% ether in hexane. Elution in 250-ml fractions gave: fraction 1–4, 5% ether in hexane, nil; 5–8, 10%, nil; 9, 15%, 3 mg; 10–16, 15%, 1.820 g of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C; 17–24, 15%, 1.105 g of crude *cis*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one-5-^{14}C; 25–28, 15%, 84 mg of a mixture of *cis*-bicyclic ketone and 3,4-diphenylcyclohex-2-en-1-one-4-^{14}C. Three recrystallizations from ethanol of material in fractions 10–16 gave 923 mg of pure *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C, mp 76.0–77.0°, constant specific activity 12.27 μCi/mmol. Five recrystallizations from ethanol of material in fractions 17–24 gave 654 mg of pure *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C, mp 116–118°, constant specific activity 11.97 μCi/mmol. Each ketone was shown to be free of contamination by the other or by 3,4- or 4,4-diphenylcyclohex-2-en-1-one-^{14}C by the isotopic dilution technique (zero-light control runs).

Quantum Yield Irradiations. All quantum yield photolyses were carried out using a Bausch and Lomb high-intensity monochromator and the optical bench assembly and procedure previously described.[1] Unless otherwise stated, all runs were done in benzene in 10.0-cm (38.0 ml) quartz-faced cells, at 24.0°, 313 mμ, with a 22-mμ band width.[1] All radioactivity analyses were done on a Nuclear-Chicago Mark I liquid scintillation system, also as previously outlined.[1] Specific radioactivities of the starting materials were 12.27 μCi/mmol for *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 11.97 μCi/mmol for *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Quenchers and Sensitizers. Propiophenone was distilled twice, bp 41° (0.15 mm), before use and was removed by short-path distillation at 40° (0.01 mm). 2,5-Dimethyl-2,4-hexadiene was distilled, bp 134°, before use through a spinning-band column and was removed by short-path distillation at 35° (0.1 mm). 1,3-Cyclohexadiene was distilled from hydroquinone at room temperature under nitrogen immediately before use and was removed *in vacuo* with solvent. Chlorobenzene was distilled through a spinning-band column, bp 131°, before use and was removed by short-path distillation at 35° (0.1 mm).

Integrated-Effective Extinction Coefficients. In quenched irradiations of *cis*- and *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones, there was appreciable direct absorption by quencher over the 22-mμ band width generally employed. Wavelength dependence of the extinction coefficients and lamp output made calculated ketone:quencher absorbance ratios based on the monochromatic extinction coefficients at 313 mμ unreliable. Integrated extinction coefficients which took varying absorption and light intensity over the band width into account automatically were determined. Light from the Bausch and Lomb high-intensity monochromator (band width 22 mμ) at 313 mμ transmitted through a 2.3-cm cell filled alternately with pure benzene and with solutions of quenchers or ketones in benzene was monitored. Assuming linearity of energy and intensity over the 22-mμ band width, calculation of the integrated extinction coefficients from Beer's law was repeated for different concentrations of materials. Average values were: *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, 34 ± 2; *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, 14 ± 1; 2,5-dimethyl-2,4-hexadiene, 0.32 ± 0.02; 1,3-cyclohexadiene, 0.16 ± 0.015.

Steady-State Experiments. A mixture of 48.0 mg (0.194 mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one and 52.0 mg (0.210 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one in 38.0 ml of benzene was irradiated at 313 mμ, 4-mμ band width, 1.14 mE,[36] with a Bausch and Lomb high-intensity monochromator. After concentration *in vacuo*, the residue was chromatographed on a 1.6 × 60 cm column of silica gel (Davison 950, 60–200 mesh) slurry packed in 5% ether–hexane; 70-ml fractions were taken: fractions 1–10, 5% ether–hexane, nil; 11–20, 10%, nil; 21–24, 15%, nil; 25–27, 16%, 43.5 mg of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 75–76°, (43.8%); 28–29, 16%, nil; 30–33, 16%, 55.9 mg of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 115–117° (56.2%); 34, 16%, nil; 35–36, 17%, 0.7 mg of material, mainly 3,4-diphenylcyclohex-2-en-1-one by ir.

Similarly, 40.0 mg (0.161 mmol) of *trans*- and 60.0 mg (0.225 mmol) of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one were irradiated, 1.12 mE, and chromatographed to give: fractions 1–10, 5% ether–hexane, nil; 11–20, 10%, nil; 21–24, 15%, nil; 25–28, 16%, 43.5 mg of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 75.5–77.0° (44.0%); 29–30, 16%, nil; 31–33, 16%, 55.5 mg of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 115–117.5° (56.0%); 34, 16%, nil; 35–36, 17%, 0.9 mg of material, mainly 3,4-diphenylcyclohex-2-en-1-one by ir.

A third mixture of 28.9 mg (0.116 mmol, 11.97 μCi/mmol) of *cis*- and 22.0 mg (0.0886 mmol, 12.27 μCi/mmol) of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C in 38.0 ml of benzene was irradiated as above, 0.175 mE, and analyzed by isotope dilution. The photolysate was concentrated, then diluted to 25.0 ml. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (476.1 mg, 1.917 mmol) added to 15.0 ml of ^{14}C photolysate (30.5 mg, 0.123 mmol) had, after four recrystallizations from 10% benzene in hexane, constant radioactivity, 329.0 nCi/mmol, mp 76–77°. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (369.5 mg, 1.488 mmol) added to 10.0 ml of ^{14}C photolysate (20.4 mg, 0.082 mmol) had, after four recrystallizations, activity 364.0 nCi/mmol, mp 116.0–118.0°. These activities correspond to 0.0880 and 0.116 mmol or 43.1 and 56.9%, respectively, of *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Quantum Yields. Data for each determination are listed as follows: first, amounts of starting material, additive, and light used, plus any deviations from the general conditions cited above; secondly, isotope dilution data for each compound whose analysis was sought. Following the amounts of ^{12}C material and ^{14}C mixture which were used in dilution are listed in order: the number of recrystallizations (from 10% benzene–hexane or 5% methanol–hexane) required to bring a compound to constant activity, the recovered weight (mg), melting point, asymptotic specific activity (nCi/mmol) with standard error; calculated μmoles of reactant recovered or product produced; and quantum yield for formation of product. The quantum yield for disappearance of reactant has been obtained only as the sum of quantum yields for appearance of products since the low conversions employed made the absolute errors in amounts of reactant employed and recovered comparable in magnitude to the amount converted.

Control Run. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (90.0 mg, 362.5 μmol) in 25.0 ml of benzene stored 168 hr in the dark.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (262.2 mg, 1056 μmol) plus ^{14}C mixture (10.8 mg, 43.5 μmol): 4, 70 mg, 76.0–77.0°, 491.2 ± 1.5; 366.2 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (441.5 mg, 1778 μmol) plus ^{14}C mixture (10.8 mg, 43.5 μmol): 5, 184 mg, 116.0–118.0°, 0.000 ± 0.001; no product formed.

3,4-Diphenylcyclohex-2-en-1-one (421.2 mg, 1696 μmol) plus ^{14}C mixture (25.2 mg, 101.5 μmol): 3, 139 mg, 99.0–100.0°, 0.000 ± 0.001; no product formed.

4,4-Diphenylcyclohex-2-en-1-one (464.4 mg, 1870 μmol) plus ^{14}C mixture (43.2 mg, 174.0 μmol): 4, 185 mg, 94.0–95.0°, 0.000 ± 0.001; no product formed.

Run I-1. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (89.9 mg, 362.1 μmol), 115 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (391.6 mg, 1577 μmol) plus ^{14}C mixture (14.4 mg, 57.9 μmol): 4, 36 mg, 76.0–77.0°, 430.5 ± 1.5; 357.8 μmole recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (280.2 mg, 1128 μmol) plus ^{14}C mixture (25.2 mg, 101.4 μmol): 6, 75 mg, 116.0–118.0°, 32.87 ± 0.14; 10.79 μmol produced; ϕ = 0.0941 ± 0.003.

3,4-Diphenylcyclohex-2-en-1-one (389.1 mg, 1567 μmol) plus ^{14}C mixture (25.2 mg, 101.4 μmol): 5, 138 mg, 99.0–100.0°, 2.570 ± 0.021; 1.17 μmol produced; $\phi = 10.2 (\pm 0.5) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (356.2 mg, 1435 μmol) plus ^{14}C mixture (25.2 mg, 101.4 μmol): 5, 36 mg, 94.0–95.0°, 0.226 ± 0.009; 0.094 μmol produced; $\phi = 8.2 (\pm 2.5) \times 10^{-4}$.

Run I-2. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (90.6 mg, 364.9 μmol), 124 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (462.4 mg, 1862 μmol) plus ^{14}C mixture (10.9 mg, 43.8 μmol): 4, 229 mg, 76.0–77.0°, 277.2 ± 0.9; 359.2 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (369.9 mg, 1490 μmol) plus ^{14}C mixture (14.5 mg, 58.4 μmol): 6, 85 mg, 116.0–118.0°, 15.13 ± 0.05; 11.51 μmol produced; ϕ = 0.0931 ± 0.003.

---

[36] mE = millieinstein.

3,4-Diphenylcyclohex-2-en-1-one (344.1 mg, 1386 μmol) plus ^{14}C mixture (25.4 mg, 102.2 μmol): 6, 78 mg, 99.0–100.0°, 3.019 ± 0.015; 1.22 μmol produced; $\phi = 9.9 (\pm 0.5) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (401.6 mg, 1617 μmol) plus ^{14}C mixture (39.9 mg, 160.5 μmol): 6, 50 mg, 94.0–95.0°, 0.207 ± 0.004; 0.062 μmol produced; $\phi = 5.0 (\pm 1.5) \times 10^{-4}$.

Run I-3. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (92.6 mg, 372.9 μmol) and 2.250 g of propiophenone (0.0168 mol, 0.441 *M*), 217 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (397.7 mg, 1602 μmol) plus ^{14}C mixture (14.8 mg, 59.7 μmol): 4, 80 mg, 76.0–77.0°, 450.3 ± 1.5; 380.6 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (291.9 mg, 1176 μmol) plus ^{14}C mixture (25.9 mg, 104.4 μmol): 6, 64 mg, 116.0–118.0°, 1.564 ± 0.023; 0.534 μmol produced; $\phi = 2.5 (\pm 0.3) \pm 10^{-3}$.

3,4-Diphenylcyclohex-2-en-1-one (328.4 mg, 1323 μmol) plus ^{14}C mixture (25.9 mg, 104.4 μmol): 6, 79 mg, 99.0–100.0°, 0.0693 ± 0.0065; 0.027 μmol produced; $\phi = 1.2 (\pm 0.6) \times 10^{-4}$.

4,4-Diphenylcyclohex-2-en-1-one (368.4 mg, 1484 μmol) plus ^{14}C mixture (25.9 mg, 104.4 μmol): 6, 73 mg, 94.0–95.0°, 0.0536 ± 0.0065; 0.023 μmol produced; $\phi = 1.1 (\pm 1.0) \times 10^{-4}$.

Run I-4. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (109.9 mg, 442.6 μmol) and 1.417 g of propiophenone (0.0106 mol, 0.278 *M*), 234 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (447.9 mg, 1804 μmol) plus ^{14}C mixture (13.2 mg, 53.1 μmol): 4, 78 mg, 76.0–77.0°, 351.8 ± 1.1; 443.2 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (405.0 mg, 1631 μmol) plus ^{14}C mixture (13.2 mg, 53.1 μmol): 5, 71 mg, 116.0–118.0°, 1.097 ± 0.014; 1.22 μmol produced; $\phi = 5.2 (\pm 0.5) \times 10^{-3}$.

3,4-Diphenylcyclohex-2-en-1-one (413.1 mg, 1664 μmol) plus ^{14}C mixture (35.2 mg, 141.6 μmol): 5, 48 mg, 99.0–100.0°, 0.105 ± 0.005; 0.045 μmol produced; $\phi = 1.9 (\pm 0.9) \times 10^{-4}$.

4,4-Diphenylcyclohex-2-en-1-one (470.9 mg, 1.897 μmol) plus ^{14}C mixture (48.4 mg, 194.8 μmol): 5, 87 mg, 94.0–95.0°, 0.0107 ± 0.0033; 0.0038 μmol produced; $\phi = 0.16 (\pm 1.0) \times 10^{-4}$.

Run I-5. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (94.2 mg, 379.4 μmol) in 38.0 ml of chlorobenzene (9.82 *M*) irradiated at 256 mμ (20-mμ band width), 125 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (601.1 mg, 2421 μmol) plus ^{14}C mixture (11.3 mg, 45.5 μmol): 4, 277 mg, 76.0–77.0°, 227.1 ± 0.8; 380.7 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (468.5 mg, 1887 μmol) plus ^{14}C mixture (11.3 mg, 45.5 μmol): 7, 73 mg, 116.0–118.0°, 3.521 ± 0.013; 4.52 μmol produced; $\phi = 0.0361 \pm 0.002$.

3,4-Diphenylcyclohex-2-en-1-one (502.8 mg, 2025 μmol) plus ^{14}C mixture (30.1 mg, 121.4 μmol): 6, 93 mg, 99.0–100.0°, 0.974 ± 0.008; 0.502 μmol produced; $\phi = 4.0 (\pm 0.4) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (539.0 mg, 2171 μmol) plus ^{14}C mixture (41.5 mg, 166.9 μmol): 6, 110 mg, 94.0–95.0°, 0.106 ± 0.005; 0.043 μmol produced; $\phi = 3.4 (\pm 1.0) \times 10^{-4}$.

Run I-6. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (84.5 mg, 340.3 μmol) in 38.0 ml of chlorobenzene (9.82 *M*) irradiated at 256 mμ (15-mμ band width), 134 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (512.0 mg, 2062 μmol) plus ^{14}C mixture (10.1 mg, 40.8 μmol): 4, 113 mg, 76.0–77.0°, 238.2 ± 0.8; 340.7 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (431.3 mg, 1737 μmol) plus ^{14}C mixture (10.1 mg, 40.8 μmol): 6, 69 mg, 116.0–118.0°, 4.025 ± 0.018; 4.75 μmol produced; $\phi = 0.0354 \pm 0.002$.

3,4-Diphenylcyclohex-2-en-1-one (437.2 mg, 1761 μmol) plus ^{14}C photolysate (23.7 mg, 95.3 μmol): 6, 47 mg, 99.0–100.0°, 1.060 ± 0.010; 0.543 μmol produced; $\phi = 4.0 (\pm 0.4) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (414.9 mg, 1671 μmol) plus ^{14}C mixture (40.6 mg, 163.4 μmol): 6, 70 mg, 94.0–95.0°, 0.287 ± 0.005; 0.081 μmol produced; $\phi = 6.1 (\pm 1.8) \times 10^{-4}$.

Control Run. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (92.1 mg, 370.9 μmol) in 25.0 ml of benzene stored 168 hr in the dark.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (548.7 mg, 2210 μmol) plus ^{14}C mixture (11.1 mg, 44.5 μmol): 4, 157 mg, 116.0–118.0°, 235.9 ± 0.8; 370.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (486.3 mg, 1959 μmol) plus ^{14}C mixture (11.1 mg, 44.5 μmol): 3, 106 mg, 76.0–77.0°, 0.000 ± 0.001; no product formed.

3,4-Diphenylcyclohex-2-en-1-one (494.6 mg, 1992 μmol) plus ^{14}C mixture (25.8 mg, 103.9 μmol): 4, 174 mg, 99.0–100.0°, 0.000 ± 0.001; no product formed.

4,4-Diphenylcyclohex-2-en-1-one (480.0 mg, 1933 μmol) plus ^{14}C mixture (44.2 mg, 178.0 μmol): 4, 117 mg, 94.0–95.0°, 0.000 ± 0.001; no product formed.

Run II-1. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (83.7 mg, 337.1 μmol), 99.0 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (373.3 mg, 1503 μmol) plus ^{14}C mixture (13.4 mg, 53.9 μmol): 5, 114 mg, 116.0–118.0°, 411.1 ± 1.4; 333.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (413.8 mg, 1667 μmol) plus ^{14}C mixture (23.4 mg, 94.4 μmol): 4, 46 mg, 76.0–77.0°, 18.67 ± 0.10; 9.30 μmol produced; $\phi = 0.0940 \pm 0.003$.

3,4-Diphenylcyclohex-2-en-1-one (398.0 mg, 1603 μmol) plus ^{14}C mixture (23.4 mg, 94.4 μmol): 6, 20 mg, 99.0–100.0°, 0.581 ± 0.011; 0.278 μmol produced; $\phi = 2.8 (\pm 0.2) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (396.6 mg, 1597 μmol) plus ^{14}C mixture (23.4 mg, 94.4 μmol): 5, 92 mg, 94.0–95.0°, 0.000 ± 0.001; no product formed.

Run II-2. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (90.3 mg, 363.7 μmol), 142 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (378.0 mg, 1522 μmol) plus ^{14}C mixture (14.5 mg, 58.2 μmol): 5, 59 mg, 116.0–118.0°, 428.8 ± 1.4, 353.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (93.0 mg, 1542 μmol) plus ^{14}C mixture (25.3 mg, 101.8 μmol): 5, 78 mg, 76.0–77.0°, 28.26 ± 0.13; 13.03 μmol produced; $\phi = 0.0918 + 0.003$.

3,4-Diphenylcyclohex-2-en-1-one (368.7 mg, 1485 μmol) plus ^{14}C mixture (25.3 mg, 101.8 μmol): 6, 84 mg, 99.0–100.0°, 0.872 ± 0.012; 0.386 μmol produced; $\phi = 2.7 (\pm 0.2) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (339.4 mg, 1367 μmol) plus ^{14}C mixture (25.3 mg, 101.8 μmol): 5, 50 mg, 94.0–95.0°, 0.000 ± 0.001; no product formed.

Run II-3. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (93.3 mg, 375.8 μmol) and 1.403 g of propiophenone (0.0105 mol, 0.275 *M*), 222 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (372.2 mg, 1499 μmol) plus ^{14}C mixture (18.7 mg, 75.2 μmol): 4, 116 mg, 116.0–118.0°, 579.8 ± 1.9; 381.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (530.1 mg, 2135 μmol) plus ^{14}C mixture (18.7 mg, 75.2 μmol): 4, 169 mg, 76.0–77.0°, 1.296 ± 0.008; 1.16 μmol produced; $\phi = 0.0052 \pm 0.0005$.

3,4-Diphenylcyclohex-2-en-1-one (514.7 mg, 2073 μmol) plus ^{14}C mixture (56.0 mg, 225.5 μmol): 5, 115 mg, 99.0–100.0°, 0.060 ± 0.005; 0.017 μmol produced; $\phi = 0.08 (\pm 0.05) \times 10^{-3}$.

Run II-4. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (88.7 mg, 357.2 μmol) in 38.0 ml of chlorobenzene (9.82 *M*) irradiated at 256 mμ (15-mμ band width), 140 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (457.9 mg, 1844 μmol) plus ^{14}C mixture (10.6 mg, 42.9 μmol): 4, 175 mg, 116.0–118.0°, 266.9 ± 0.9; 350.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (548.8 mg, 2210 μmol) plus ^{14}C mixture (10.6 mg, 42.9 μmol): 4, 66 mg, 76.0–77.0°, 4.099 ± 0.032; 6.31 μmol produced; $\phi = 0.0451 \pm 0.003$.

3,4-Diphenylcyclohex-2-en-1-one (503.4 mg, 2207 μmol) plus ^{14}C mixture (31.9 mg, 128.6 μmol): 5, 68 mg, 99.0–100.0°, 0.241 ± 0.006; 0.113 μmol produced; $\phi = 0.81 (\pm 0.08) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (525.7 mg, 2117 μmol) plus ^{14}C mixture (35.5 mg, 142.9 μmol): 5, 81 mg, 94.0–95.0°, 0.071 ± 0.005; 0.031 μmol produced; $\phi = 2.2 (\pm 0.7) \times 10^{-4}$.

Run V-1. *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (102.2 mg, 411.6 μmol) and 0.602 g of 1,3-cyclohexadiene (0.0075 mol, 0.198 *M*), 162 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (443.0 mg, 1784 μmol) plus ^{14}C mixture (12.3 mg, 494 μmol): 4, 76 mg, 76.0–77.0°, 330.7 ± 1.1; 411.5 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (418.2 mg, 1684 μmol) plus ^{14}C mixture (12.3 mg, 49.4 μmol): 8, 70 mg, 116.0–118.0°, 8.683 ± 0.037; 9.94 μmol produced; $\phi = 0.0615 \pm 0.0061$.

3,4-Diphenylcyclohex-2-en-1-one (449.4 mg, 1810 μmol) plus ^{14}C mixture (32.7 mg, 131.7 μmol): 6, 112 mg, 99.0–100.0°, 2.271 ± 0.011; 1.05 μmol produced; $\phi = 6.5 (\pm 0.7) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (449.6 mg, 1811 μmol) plus ^{14}C mixture (45.0 mg, 181.1 μmol): 6, 144 mg, 94.0–95.0°, 0.042 ± 0.005; 0.014 μmol produced; $\phi = 0.88 (\pm 1.0) \times 10^{-4}$.

Run V-2. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (102.8 mg, 414.0 μmol) and 1.718 g of 2,5-dimethyl-2,4-hexadiene (0.0156 mol, 0.410 *M*), 203 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (483.9 mg, 1949 μmol) plus ^{14}C mixture (12.3 mg, 49.7 μmol): 4, 76 mg, 76.0–77.0°, 298.2 ± 1.0; 404.8 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (420.3 mg, 1693 μmol) plus ^{14}C mixture (12.3 mg, 49.7 μmol): 5, 137 mg, 116.0–118.0°, 8.623 ± 0.036; 9.92 μmol produced; $\phi = 0.0488 \pm 0.0049$.

3,4-Diphenylcyclohex-2-en-1-one (391.6 mg, 1577 μmol) plus

^{14}C mixture (32.9 mg, 132.5 μmol): 5, 85 mg, 99.0–100.0°, 2.208 $\pm$ 0.013; 0.886 μmol produced; $\phi = 4.4\,(\pm 0.5) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (386.0 mg, 1555 μmol) plus ^{14}C mixture (45.2 mg, 182.2 μmol): 5, 67 mg, 94.0–95.0°, 0.169 $\pm$ 0.002; 0.049 μmol produced; $\phi = 2.4\,(\pm 1.2) \times 10^{-4}$.

Run V-3. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (101.2 mg, 407.6 μmol) and 3.256 g of 2,5-dimethyl-2,4-hexadiene (0.0295 mol, 0.777 *M*), 281 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (512.9 mg, 2066 μmol) plus ^{14}C mixture (12.1 mg, 48.9 μmol): 5, 60 mg, 76.0–77.0°, 265.8 $\pm$ 0.8; 381.2 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (399.3 mg, 1608 μmol) plus ^{14}C mixture (16.2 mg, 65.2 μmol): 7, 54 mg, 116.0–118.0°, 11.68 $\pm$ 0.03; 9.58 μmol produced; $\phi = 0.0341 \pm 0.0034$.

3,4-Diphenylcyclohex-2-en-1-one (401.7 mg, 1618 μmol) plus ^{14}C mixture (28.3 mg, 114.1 μmol): 6, 58 mg, 99.0–100.0°, 1.682 $\pm$ 0.009; 0.792 μmol produced; $\phi = 2.8\,(\pm 0.3) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (424.1 mg, 1708 μmol) plus ^{14}C mixture (44.5 mg, 179.3 μmol): 5, 97 mg, 94.0–95.0°, 0.171 $\pm$ 0.002; 0.054 μmol produced; $\phi = 1.9\,(\pm 1.0) \times 10^{-4}$.

Run V-4. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}-C (113.3 mg, 456.3 μmol) and 4.159 g of 2,5-dimethyl-2,4-hexadiene (0.0377 mol, 0.994 *M*) irradiated at 313 mμ, 1.5-mμ band width, 30.8 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (545.7 mg, 2198 μmol) plus ^{14}C mixture (22.7 mg, 91.3 μmol): 4, 139 mg, 76.0–77.0°, 491.5 $\pm$ 1.6; 458.0 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (438.4 mg, 1766 μmol) plus ^{14}C mixture (90.6 mg, 365.0 μmol): 6, 107 mg, 116.0–118.0°, 4.489 $\pm$ 0.019; 0.808 μmol produced; $\phi = 0.0254 \pm 0.0025$.

Run V-5. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (104.0 mg, 418.8 μmol) and 5.024 g of 2,5-dimethyl-2,4-hexadiene (0.0456 mol, 1.20 *M*), 336 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (440.4 mg, 1774 μmol) plus ^{14}C mixture (12.5 mg, 50.3 μmol): 4, 88 mg, 76.0–77.0°, 338.9 $\pm$ 1.1; 419.8 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (429.0 mg, 1728 μmol) plus ^{14}C mixture (12.5 mg, 50.3 μmol): 5, 121 mg, 116.0–118.0°, 8.070 $\pm$ 0.036; 9.48 μmol produced; $\phi = 0.0283 \pm 0.0028$.

3,4-Diphenylcyclohex-2-en-1-one (480.0 mg, 1933 μmol) plus ^{14}C mixture (33.3 mg, 134.0 μmol): 5, 104 mg, 99.0–100.0°, 1.964 $\pm$ 0.010; 0.966 μmol produced; $\phi = 2.9\,(\pm 0.3) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (467.8 mg, 1884 μmol) plus ^{14}C mixture (45.8 mg, 184.3 μmol): 6, 100 mg, 94.0–95.0°, 0.059 $\pm$ 0.005; 0.020 μmol produced; $\phi = 0.61\,(\pm 1.0) \times 10^{-4}$.

Run V-6. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (103.7 mg, 417.6 μmol) and 4.917 g of 1,3-cyclohexadiene (0.0614 mol, 1.614 *M*), 259 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (422.6 mg, 1702 μmol) plus ^{14}C mixture (16.6 mg, 66.8 μmol): 4, 38 mg, 76.0–77.0°, 444.8 $\pm$ 1.4; 400.1 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (343.9 mg, 1385 μmol) plus ^{14}C mixture (29.0 mg, 117.0 μmol): 5, 96 mg 116.0–118.0°, 12.24 $\pm$ 0.04; 4.94 μmol produced; $\phi = 0.0191 \pm 0.0019$.

3,4-Diphenylcyclohex-2-en-1-one (316.4 mg, 1274 μmol) plus ^{14}C mixture (29.0 mg, 117.0 μmol): 5, 16 mg 99.0–100.0°, 1.561 $\pm$ 0.017; 0.579 μmol produced; $\phi = 2.2\,(\pm 0.3) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (367.7 mg, 1481 μmol) plus ^{14}C mixture (29.0 mg, 117.0 μmol): 5, 100 mg, 94.0–95.0°, 0.176 $\pm$ 0.004; 0.076 μmol produced; $\phi = 2.9\,(\pm 1.5) \times 10^{-4}$.

Run V-7. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (149.4 mg, 601.7 μmol) and 9.217 g of 2,5-dimethyl-2,4-hexadiene (0.0836 mol, 2.20 *M*), 762 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (520.9 mg, 2098 μmol) plus ^{14}C mixture (17.9 mg, 72.2 μmol): 5, 33 mg, 76.0–77.0°, 404.5 $\pm$ 1.3; 595.8 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (425.3 mg, 1713 μmol) plus ^{14}C mixture (17.9 mg, 72.2 μmol): 6, 58 mg, 116.0–118.0°, 11.23 $\pm$ 0.03; 13.07 μmol produced; $\phi = 0.0172 \pm 0.0017$.

3,4-Diphenylcyclohex-2-en-1-one (535.6 mg, 2157 μmol) plus ^{14}C mixture (47.8 mg, 192.5 μmol): 5, 29 mg, 99.0–100.0°, 2.430 $\pm$ 0.011; 1.33 μmol produced; $\phi = 1.8\,(\pm 0.2) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (626.6 mg, 2524 μmol) plus ^{14}C mixture (65.7 mg, 264.8 μmol): 5, 125 mg, 94.0–95.0°, 0.040 $\pm$ 0.005; 0.019 μmol produced; $\phi = 0.24\,(\pm 1.0) \times 10^{-4}$.

Run V-8. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (97.4 mg, 392.3 μmol) and 7.952 g of 1,3-cyclohexadiene (0.0993 mol, 2.62 *M*) irradiated at 313 mμ (1.5-mμ band width), 29.8 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (540.7 mg, 2178 μmol) plus ^{14}C mixture (11.7 mg, 47.1 μmol): 4, 101 mg, 76.0–77.0°, 264.2 $\pm$ 0.8; 399.8 μmol recovered.

cis,-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (485.4 mg, 1955 μmol) plus ^{14}C mixture (85.7 mg, 345.2 μmol): 6, 56 mg, 116.0–118.0°, 2.163 $\pm$ 0.010; 0.392 μmol produced; $\phi = 0.0132 \pm 0.0013$.

Run V-9. *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (105.2 mg, 423.7 μmol) and 8.462 g of 1,3-cyclohexadiene (0.1056 mol, 2.78 *M*), 251 μE.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (431.1 mg, 1736 μmol) plus ^{14}C mixture (12.6 mg, 50.8 μmol): 4, 71 mg, 76.0–77.0°, 336.9 $\pm$ 1.1; 408.2 μmol recovered.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (400.5 mg, 1613 μmol) plus ^{14}C mixture (12.6 mg, 50.8 μmol): 5, 75 mg, 116.0–118.0°, 3.058 $\pm$ 0.018; 3.35 μmol produced; $\phi = 0.0134 \pm 0.0013$.

3,4-Diphenylcyclohex-2-en-1-one (419.7 mg, 1690 μmol) plus ^{14}C mixture (33.7 mg, 135.6 μmol): 5, 95 mg, 99.0–100.0°, 0.847, $\pm$ 0.008; 0.364 μmol produced; $\phi = 1.5\,(\pm 0.2) \times 10^{-3}$.

4,4-Diphenylcyclohex-2-en-1-one (424.1 mg, 1708 μmol) plus ^{14}C mixture (46.3 mg, 186.4 μmol): 5, 35 mg, 94.0–95.0°, 0.556 $\pm$0.007; 0.17 μmol produced; $\phi = 7.0\,(\pm 5.0) \times 10^{-4}$.

Run VI-1. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (94.6 mg, 381.0 μmol) and 0.366 g of 1,3-cyclohexadiene (0.0046 mol, 0.120 *M*), 192 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (374.8 mg, 1509 μmol) plus ^{14}C mixture (18.9 mg, 76.2 μmol): 4, 143 mg, 116.0–118.0°, 555.9 $\pm$ 1.8; 367.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (481.3 mg, 1938 μmol) plus ^{14}C mixture (18.9 mg, 76.2 μmol): 4, 47 mg, 76.0–77.0°, 19.64 $\pm$ 0.08; 15.91 μmol produced; $\phi = 0.0828 \pm 0.0083$.

3,4-Diphenylcyclohex-2-en-1-one (476.0 mg, 1917 μmol) plus ^{14}C mixture (56.8 mg, 228.6 μmol): 6, 59 mg, 99.0–100.0°, 1.198 $\pm$ 0.008; 0.320 μmol produced; $\phi = 1.7\,(\pm 0.4) \times 10^{-3}$.

Run VI-2. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (92.5 mg, 372.5 μmol) and 1.100 g of 2,5-dimethyl-2,4-hexadiene (0.0100 mol, 0.263 *M*), 163 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (435.5 mg, 1754 μmol) plus ^{14}C mixture (18.5 mg, 74.5 μmol): 4, 175 mg, 116.0–118.0°, 465.3 $\pm$ 1.6; 354.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (495.6 mg, 1996 μmol) plus ^{14}C mixture (18.5 mg, 74.5 μmol): 5, 51 mg, 76.0–77.0°, 16.87 $\pm$ 0.04; 14.09 μmol produced; $\phi = 0.0864 \pm 0.0087$.

3,4-Diphenylcyclohex-2-en-1-one (457.4 mg, 1842 μmol) plus ^{14}C mixture (55.5 mg, 223.5 μmol): 5, 94 mg, 99.0–100.0°, 1.276 $\pm$ 0.008; 0.327 μmol produced; $\phi = 2.0\,(\pm 0.5) \times 10^{-3}$. .

Run VI-3. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (96.1 mg, 387.0 μmol) and 2.102 g of 2,5-dimethyl-2,4-hexadiene (0.0191 mol, 0.502 *M*), 122 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (460.6 mg, 1855 μmol) plus ^{14}C mixture (19.2 mg, 77.4 μmol): 4, 106 mg, 116.0–118.0° 460.1 $\pm$ 1.5; 370.7 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (459.6 mg, 1851 μmol) plus ^{14}C mixture (19.2 mg, 77.4 μmol): 5, 34 mg, 76.0–77.0°, 12.68 $\pm$ 0.03; 9.80 μmol produced; $\phi = 0.0803 \pm 0.0081$.

3,4-Diphenylcyclohex-2-en-1-one (537.2 mg, 2164 μmol) plus ^{14}C mixture (57.7 mg, 232.2 μmol): 5, 67 mg, 99.0 –100.0°, 1.056 $\pm$ 0.008; 0.318 μmol produced; $\phi = 2.6\,(\pm 0.6) \times 10^{-3}$.

Run VI-4. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (106.3 mg, 428.1 μmol) and 4.156 g of 2,5-dimethyl-2,4-hexadiene (0.0377 mol, 0.992 *M*), 163 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (384.7 mg, 1549 μmol) plus ^{14}C mixture (21.3 mg, 85.6 μmol): 4, 144 mg, 116.0–118.0°, 600.0 $\pm$ 1.9; 408.5 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (512.9 mg, 2066 μmol) plus ^{14}C mixture (21.3 mg, 85.6 μmol): 4, 95 mg, 76.0–77.0°, 19.92 $\pm$ 0.06; 17.21 μmol produced; $\phi = 0.105 \pm 0.011$.

3,4-Diphenylcyclohex-2-en-1-one (723.4 mg, 2913 μmol) plus ^{14}C mixture (63.8 mg, 256.9 μmol): 5, 121 mg, 99.0–100.0°, 0.914 $\pm$ 0.008; 0.371 μmol produced; $\phi = 2.3\,(\pm 0.6) \times 10^{-3}$.

Run VI-5. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (99.8 mg, 401.9 μmol) and 4.192 g of 2,5-dimethyl-2,4-hexadiene (0.0380 mol, 1.001 *M*), 114 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (402.5 mg, 1621 μmol) plus ^{14}C mixture (20.0 mg, 80.4 μmol): 5, 130 mg, 116.0–118.0°, 550.5 $\pm$ 1.8; 390.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (481.0 mg, 1937 μmol) plus ^{14}C mixture (20.0 mg, 80.4 μmol): 5, 36 mg, 76.0–77.0°, 9.560 $\pm$ 0.024; 7.74 μmol produced; $\phi = 0.068 \pm 0.017$.

3,4-Diphenylcyclohex-2-en-1-one (508.3 mg, 2047 μmol) plus ^{14}C mixture (59.9 mg, 241.2 μmol): 5, 175 mg, 99.0–100.0°, 0.520 $\pm$ 0.007; 0.148 μmol produced; $\phi = 1.3\,(\pm 1.0) \times 10^{-3}$.

Run VI-6. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (101.5 mg, 408.8 μmol) and 4.197 g of 2,5-dimethyl-2,4-hexadiene (0.0381 mol, 1.003 *M*) irradiated at 313 mμ (1.5-mμ band width), 3.91 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (412.8 mg, 1663 μmol) plus ^{14}C mixture (12.2 mg, 49.1 μmol): 4, 106 mg, 116.0–118.0°, 345.9 ± 1.1; 412.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.8 mg, 2021 μmol) plus ^{14}C mixture (89.3 mg, 359.7 μmol): 5, 56 mg, 76.0–77.0°, 1.882 ± 0.007; 0.362 μmole produced; $\phi = 0.086 \pm 0.009$.

Run VI-7. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (156.7 mg, 631.1 μmol) and 4.166 g of 2,5-dimethyl-2,4-hexadiene (0.0378 mol, 1.399 *M*) in 27.0 ml of benzene, 194 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (432.6 mg, 1742 μmol) plus ^{14}C mixture (31.3 mg, 126.2 μmol): 4, 74 mg, 116.0–118.0°, 787.4 ± 2.5; 613.4 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (559.7 mg, 2254 μmol) plus ^{14}C mixture (31.3 mg, 126.2 μmol): 4, 52 mg, 76.0–77.0°, 19.86 ± 0.07; 18.72 μmol produced; $\phi = 0.0966 \pm 0.0097$.

3,4-Diphenylcyclohex-2-en-1-one (622.6 mg, 2507 μmol) plus ^{14}C mixture (94.0 mg, 378.7 μmol): 6, 78 mg, 99.0–100.0°, 1.161 ± 0.008; 0.430 μmol produced; $\phi = 2.2\,(\pm 0.5) \times 10^{-3}$.

Run VI-8. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (107.7 mg, 433.8 μmol) and 5.531 g of 1,3-cyclohexadiene (0.0691 mol, 1.816 *M*), 75.4 μE.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (373.5 mg, 1504 μmol) plus ^{14}C mixture (21.5 mg, 86.8 μmol): 4, 100 mg, 116.0–118.0°, 642.8 ± 2.1; 426.6 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (469.0 mg, 1889 μmol) plus ^{14}C mixture (21.5 mg, 86.8 μmol): 5, 26 mg, 76.0–77.0°, 8.998 ± 0.039; 7.10 μmol produced; $\phi = 0.0942 \pm 0.0095$.

3,4-Diphenylcyclohex-2-en-1-one (451.4 mg, 1818 μmol) plus ^{14}C mixture (64.6 mg, 260.3 μmol): 5, 42 mg, 99.0–100.0°, 1.028 ± 0.008; 0.260 μmol produced; $\phi = 3.5\,(\pm 0.9) \times 10^{-3}$.

Acknowledgment. Support of this research by National Institutes of Health Grant GM 07487, the National Science Foundation, and ARO(D) is gratefully acknowledged. K. G. H. expresses appreciation for a National Institutes of Health Predoctoral Fellowship.

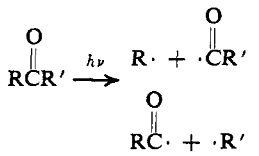
The Photochemistry of the β,γ-Cyclopropyl Ketones (−)-*cis*- and -*trans*-4-Caranone

David C. Heckert and Paul J. Kropp

Contribution from the Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239. *Received January 22, 1968*

Abstract: On irradiation under a variety of conditions the β,γ-cyclopropyl ketone (−)-*cis*-4-caranone (**9**) was found to undergo facile rearrangement, affording principally an approximately 3:1 mixture of cyclopentanone (**10**) and cyclobutanone (**11**) photoproducts. The cyclopentanone appeared to be a single epimer and was assigned the *trans* structure **10b**, whereas two epimeric cyclobutanones were obtained, which were assigned the *cis* and *trans* structures **11a** and **11b**, respectively. Analogous behavior was exhibited by (−)-*trans*-4-caranone (**22**). In neither case was there any detectable interconversion of the *cis* and *trans* epimers **9** and **22** during irradiation, in contrast to the previously observed photochemical epimerization of 2-methylcyclohexanones. In the presence of *t*-butylamine, an amide, assumed to be **24**, was also obtained, but in less than 1% yield. Hence the presence of the cyclopropane ring at the β,γ position facilitates type-I cleavage of the 4,5 bond to afford a cyclopropylcarbinyl radical (*cf.* **12**) at the expense of cleavage toward the more highly alkyl-substituted C-3 position (*cf.* **20**). Further mechanistic implications are discussed.

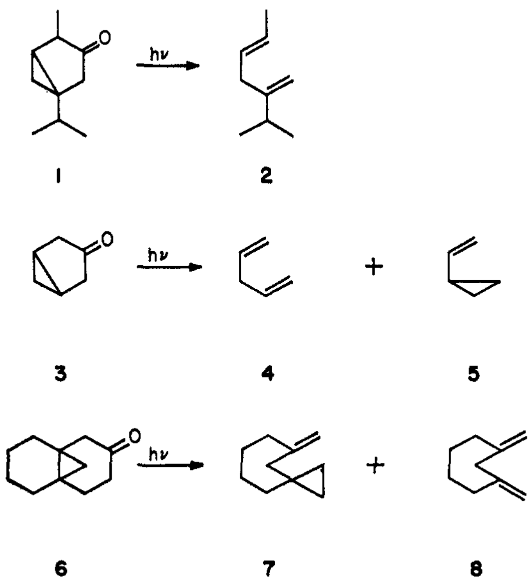
One of the principal consequences of photoexcitation of aliphatic ketones is the familiar Norrish type-I homolytic cleavage of the bonds joining the carbonyl group and the α-carbon atoms.[1]



$$\mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}' \xrightarrow{h\nu} \begin{array}{l} \mathrm{R}\cdot + \cdot\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{R}' \\ \mathrm{R}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\cdot + \cdot\mathrm{R}' \end{array}$$

Studies on both the gas and liquid phase photochemistry of bicyclic β,γ-cyclopropyl ketones, though limited in number, have indicated that in each case the major mode of decomposition is a double α cleavage leading to decarbonylation.[2-4] This is illustrated in Chart I with the bicyclo[3.1.0]hexan-3-ones

Chart I



---

(1) See, for example, J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 379–381.

(2) R. H. Eastman, J. E. Starr, R. St. Martin, and M. K. Sakata, *J. Org. Chem.*, **28**, 2162 (1963).

(3) L. D. Hess, Ph.D. Dissertation, University of California, Riverside, Calif., 1966 [*Dissertation Abstr.*, **B27**, 433 (1966)]; L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967); see also ref 1, p 412.

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