# Energy Barriers in Photochemical Molecular Rearrangements. Mechanistic and Exploratory Organic Photochemistry. XL[1]

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Abstract: The photochemical rearrangement of 4,4-diphenylcyclohexenone (1) to *cis*- and *trans*-5,6-diphenyl-bicyclo[3.1.0]hexan-2-one (2) and 3,4-diphenylcyclohex-2-en-1-one (3) has been studied in further mechanistic detail. Remarkably, over a 100-nm wavelength range the quantum yield of the major reaction product was unchanged and the "excited-state fingerprint" proved insensitive to wavelength. From this it was concluded that initial excess vibrational energy of the excited state is very quickly dissipated to solvent and that intersystem crossing occurs to the same triplet excited state independent of the configuration of the singlet initially produced. In contrast to wavelength insensitivity, a dramatic dependence on reaction temperature was encountered. This was shown not to be due to viscosity effects, for the intramolecular rearrangement rate was noted to be viscosity independent. A 50° temperature increase was found to increase the quantum yield of phenyl migration approximately 6-fold. This temperature increase led to a *ca.* 16-fold rate enhancement for triplet rearrangement and only a *ca.* 2-fold increase in rate of triplet decay. It was concluded that an activation energy of about 10 kcal/mol is required for rearrangement of the excited triplet of 4,4-diphenylcyclohexenone (1). The frequency factors were 10^{13}–10^{15}. Evidence was uncovered indicating that the stereoselectivity arises only partially from a concerted pathway being energetically favored and mainly from an entropy effect favoring the concerted process. From this study it is concluded that excited-state potential energy surfaces show thermal activation barriers similar to those encountered in ground-state chemistry. Additionally, frequency factors of the same order of magnitude as in ground-state reactions, when encountered, point to excited-state transformations with molecular demands similar to those imposed in ground-state reactions. These aspects and other details of the reaction mechanism are discussed.

In our earlier research on the photochemistry of cyclohexenones we found that in contrast to 4,4-disubstituted cyclohexadienones and 4-alkylcyclohexenones,[2] 4,4-diarylcyclohexenones undergo a γ–β aryl migration with formation of a 2,4 bond.[3] The first example and one of particular interest to the present study was the photochemical rearrangement of 4,4-diphenylcyclohexenone (1) to give *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones (2a,b)[3a] and 3,4-diphenylcyclohex-2-en-1-one (3).[4]
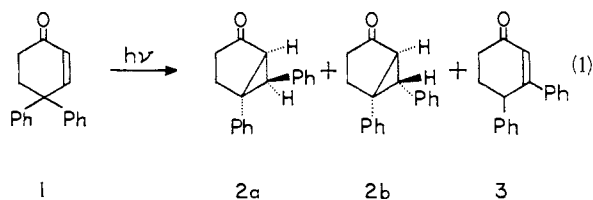
In pursuing the mechanistic aspects of this study we previously found and reported that the reaction proceeds *via* the triplet excited state of reactant 1 with a rate of 3.8×10^7 sec^{-1} for rearrangement of the triplet, and a rate of decay of reactant triplet to ground-state reactant was determined. In this previous study, a marked kinetic preference for formation of the *trans*-product stereoisomer 2a was encountered. Also, evidence was obtained that in the rearrangement electronic excitation is lost prior to the molecule reaching product geometry.[5] Thus, considerable information had been accumulated about the nature of the rearrangement, and some general features of the potential energy surface followed were uncovered.

However, it appeared that to proceed further it was necessary to inspect in greater detail this excited state to product potential energy surface. In particular we were interested in ascertaining whether there are energy barriers along the excited-state reaction coordinate in such rearrangement reactions. Whether energy barriers exist is not generally known except for a very limited number of cases such as the *cis–trans* isomerization of stilbene[6] and azobenzene,[6a,7] and the rearrangement of *o*-xylene.[8,9] Thus, the goal of the present investigation was a search for the existence of thermal barriers in the photochemical phenyl migration reaction.

Wavelength Effects. As a first step in pursuing the question of activation barriers it was necessary to de-

(1) (a) Paper XXXIX: H. E. Zimmerman and N. Lewin, *J. Am. Chem. Soc.*, 91, 879 (1969). (b) For paper XXXVIII of the series, see H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *ibid.*, 91, 434 (1969).

(2) These compounds undergo a type A rearrangement in which carbons 3 and 4 interchange places in the molecule and a 2,4 bond is formed. For a leading paper note H. E. Zimmerman and K. G. Hancock, *ibid.*, 90, 3749 (1968).

(3) (a) H. E. Zimmerman and J. W. Wilson, *ibid.*, 86, 4036 (1964); (b) H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, 89, 2033 (1967).

(4) See Zimmerman and Hancock, ref 2.

(5) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, 90, 4892 (1968).

(6) (a) D. Gegiou, K. A. Muszkat, and E. Fischer, *ibid.*, 90, 3907 (1968); (b) S. Malkin and E. Fischer, *J. Phys. Chem.*, 68, 1153 (1964).

(7) G. Zimmerman, C. Chow, and V. Paik, *J. Am. Chem. Soc.*, 80, 3528 (1958).

(8) R. B. Cundall and A. J. R. Voss, *Chem. Commun.*, 902 (1968).

(9) (a) D. Bryce-Smith and A. Gilbert, *ibid.*, 19 (1968), reported a temperature dependence of the *p*-xylene–maleic anhydride reaction but indicated this effect to derive from changes in ground-state complexation. (b) A number of investigations have been reported where quantum yields are temperature dependent. However, this does not necessarily mean that the excited rate constants for reaction have such a dependence.

Table I. Summary of Wavelength Dependence of Quantum Yields

| Run | Wavelength, nm | Quantum yields[a] | | | | Conversion, % |
		trans[b]	cis[c]	3,4-Enone[d]	Enone[e]	
1[f]	366	0.086 ±0.004	0.00053 ±0.00005	0.0056 ±0.0004	0.092 ±0.004	3.70
2[g]	366	0.083 ±0.004	0.00051 ±0.00005	0.0053 ±0.0004	0.089 ±0.004	0.88
3[f,h]	313	0.095 ±0.004	0.00062 ±0.00010	0.0068 ±0.0004	0.102 ±0.004	3.72
4[f,h]	313	0.095 ±0.004	0.00062 ±0.00010	0.0066 ±0.0004	0.103 ±0.004	2.37
5[g,h]	313	0.085 ±0.004	0.00127 ±0.00010	0.0062 ±0.0004	0.093 ±0.004	1.60
6[g,h]	254	0.095 ±0.004	0.00137 ±0.00010	0.0065 ±0.0004	0.103 ±0.004	1.54
7[g,h]	254	0.090 ±0.004	0.00123 ±0.00010	0.0058 ±0.0004	0.097 ±0.004	0.53
8[g,h]	254	0.089 ±0.004	0.00202 ±0.00010	0.0066 ±0.0004	0.097 ±0.004	1.28

[a] Errors estimated from data. [b] Appearance of trans-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [c] Appearance of cis-5,6-diphenylbicyclo-[3.1.0]hexan-2-one. [d] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [e] Disappearance of 4,4-diphenylcyclohex-2-en-1-one determined by adding the quantum yields of the individual products. [f] 7 nm half-band width. [g] 22 nm half-band width. [h] Corrected for product absorption and trans to cis interconversion.

termine the rate of thermal equilibration of the electronically excited enone molecules with their environment. An approach which promised to answer this question was investigation of the wavelength dependence of quantum yields and product distribution. Thus, if one varies the wavelength of light employed within one electronic excitation band, one will obtain different vibrational states of the same excited singlet. A priori, two extreme possibilities exist for a triplet reaction.

At one extreme either the excited singlet or the triplet formed by intersystem crossing might rapidly dissipate excess vibrational energy to solvent to give a triplet in thermal equilibrium with its surroundings. In such a case there would be no wavelength effect on the quantum yields, product distribution, or the reaction in general.

At the other extreme excess vibrational energy could be transferred to the environment more slowly than intersystem crossing and subsequent reaction. Also, the relative rates of intersystem crossing to different triplets (i.e., of different electronic configuration) could depend on excess vibrational energy. Hence, without rapid dissipation of vibrational energy different reactivity could result because the reacting triplet has excess vibrational energy or because the ratio of two reacting triplets is wavelength dependent.

For irradiation in a totally different absorption band, a different excited singlet will result, and one might anticipate again two extremes. Very rapid internal conversion of the higher energy singlet to the lowest excited singlet state or a similar internal conversion at the triplet stage of the process will again lead to a wavelength independence as long as excess vibrational energy is also rapidly dissipated. The second extreme possibility is that the configuration of the reacting triplet might depend on which excited singlet is initially generated in photolysis.

In the present work irradiation was carried out at 254, 313, and 366 nm and quantum yields were determined. These results are summarized in Table I. Most remarkably, it is seen that the total quantum yields are independent of wavelength in the entire 254 nm (112.6

kcal/mol) to 366 nm (78.1 kcal/mol) range, a range corresponding to a difference in energy utilized of 34.5 kcal/mol. The product distribution also seems insensitive to wavelength. The one exception, the quantum yield of cis-5,6-diphenylbicyclo[3.1.0]hexan-2-one (2b) at 254 nm, seems due to the experimental inaccuracy in correcting for conversion of initially formed trans isomer 2a; very minor amounts of such secondary conversion are large relative to the small amount of cis isomer 2b formed directly.

Thus, of the a priori possibilities it is seen that both internal conversion and vibrational energy transfer to the solvent are fast enough to ensure that it is the same electronic configuration and the same distribution of vibrational states which react independent of the wavelength and any excess energy employed experimentally. It is to be noted that this energy dissipation may be at the singlet stage prior to intersystem crossing or, alternatively, at the triplet stage following intersystem crossing.

Temperature Dependence. Having determined from the wavelength studies that there was rapid thermal dissipation of vibrational energy, we were able to conclude reasonably that the excited-state species was in thermal equilibrium with its solvent environment and, thus, to proceed in a study of the reaction temperature dependence.

Indeed, it was found (note Table II) that the quantum yield at 63° in t-butyl alcohol was increased about threefold over the efficiency at 20°. However, because we wished to avoid complications due to a temperature dependence of the nature of the solvent (e.g., a change in hydrogen bonding with temperature), aliphatic hydrocarbon solvents were selected for further temperature dependence studies. Even here there was concern that temperature effects might arise from secondary factors such as a decrease in viscosity with temperature.[10] That viscosity was not a factor presently

(10) A viscosity dependence of the stilbene isomerization has been reported by D. Gegiou, J. A. Muszkat, and E. Fischer, J. Am. Chem. Soc., 90, 12 (1968).

Table II. Summary of Viscosity and Temperature Dependence of Quantum Yields

Run	Solvent	Temp, °C	Viscosity, mP	Quantum yields[a]			
				trans[b]	cis[c]	3,4-Enone[d]	Enone[e]
1	t-Butyl alcohol	28	37.4[f]	0.086 ±0.004	0.00053 ±0.00010	0.0056 ±0.0004	0.092 ±0.004
2		28	37.4[f]	0.083 ±0.004	0.00051 ±0.00010	0.0053 ±0.0004	0.089 ±0.004
9		63	9.4[f]	0.231 ±0.012	0.0019 ±0.0001	0.0111 ±0.0005	0.244 ±0.012
10		63	9.4[f]	0.238 ±0.012	0.0017 ±0.0001	0.0109 ±0.0005	0.251 ±0.012
11	n-Hexane	20	3.07[g]	0.029 ±0.001	0.0001 ±0.00005	0.00003 ±0.000003	0.029 ±0.001
12		20	3.07[g]	0.028 ±0.001	0.0001 ±0.00005	0.00002 ±0.000003	0.028 ±0.001
13	n-Dodecane	20	15.02[g]	0.028 ±0.001	0.0001 ±0.00005	0.00003 ±0.000003	0.028 ±0.001
14		20	15.02[g]	0.027 ±0.001	0.0002 ±0.00005	0.00003 ±0.000003	0.027 ±0.001
15		73	6.86[g]	0.176 ±0.009	0.0013 ±0.0001	0.00034 ±0.00003	0.178 ±0.009
16		73	6.86[g]	0.180 ±0.009	0.0013 ±0.0001	0.00036 ±0.00003	0.182 ±0.009

[a] Errors estimated from data. [b] Appearance of trans-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [c] Appearance of cis-5,6-diphenylbicyclo [3.1.0]hexan-2-one. [d] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [e] Disappearance of 4,4-diphenylcyclohex-2-en-1-one determined by adding the quantum yields of the individual products. [f] A. G. Ward, Trans. Faraday Soc., 33, 88 (1937). [g] F. D. Rossini, et al., "Selected Values of Properties of Hydrocarbons," NBS Circular C461, U. S. Government Printing Office, Washington, D. C., 1947.

was demonstrated by the finding (Table II) that the quantum yield at 20° in n-hexane (viscosity: 3.07 mP at 20°) was the same as in the fivefold more viscous n-dodecane (viscosity: 15.02 mP at 20°). Additionally, this means that there is no inherent solvent difference between hexane and dodecane. This is important since the quantum yields were found to be solvent dependent (note Table II, t-butyl alcohol vs. hexane).

Interestingly, there was a marked temperature dependence of the quantum yields in the hydrocarbon solvents (note Table II) paralleling the t-butyl alcohol effect. An approximately sixfold increase in reaction efficiency resulted from a 50° temperature increase.

Control runs (see Experimental Section) showed that in the dark no thermal degradation leading to potentially troublesome contaminating impurities occurred. Similarly, there was no thermal stereoisomerization.

Temperature Dependence of Triplet Rearrangement and Decay Rates. Determination of Activation Parameters. The marked increase in quantum yields with temperature is dramatic. Nevertheless, this effect by itself tells us little since the increased temperature could be speeding up the rate of rearrangement or decreasing the competitive decay processes. Intersystem crossing already was known[4] to be of unit efficiency and thus could not be further increased. The dilemma could be resolved by a study of the temperature dependence of the rates.

Additionally, the main goal of the study was to search for activation energies and thermal barriers. To obtain such activation parameters, the dependence of the rates of triplet rearrangement on temperature was required. In our previous study[4] we measured the rate of triplet rearrangement and decay at one temperature by use of the Stern–Volmer relationship

$$1/\phi = (k_r^{tot} + k_d)/k_r + (k_q/k_r)[Q] \qquad (2)$$

Here a plot of the reciprocal of the quantum yield of a given reaction vs. quencher concentration is linear with

a slope equal to k_q/k_r. Since the rates of quenching are very close to diffusion controlled,[4] one may utilize the measured slope together with the rates of diffusion calculated from the modified Debye equation[11]

$$k_{diff} = (8RT/3000\eta) \qquad (3)$$

This allows one to solve for k_r, the rate of triplet excited-state rearrangement. Using the intercept ($k_r^{tot} + k_d)/k_r$ and the sum of the measured rate constants, k_r^{tot}, one can obtain a rate of decay (i.e., k_d) for each of the triplet reactions.

Following this approach, 2,5-dimethyl-2,4-hexadiene was used as a quencher since this had been found in earlier work[4] to give triplet destruction at close to diffusion-controlled rates. The rates of rearrangement and decay were determined by Stern–Volmer plots at different temperatures (Figures 1 and 2, Table III). In obtaining the rate constants from these Stern–Volmer plots it was necessary to take into account the dependence of k_q on temperature; the k_q's varied with temperature both due to a direct dependence on temperature and also as a result of the change in viscosity with temperature (note eq 3). Literature viscosities at the different temperatures were used (see Table II). The activation parameters were obtained from the Arrhenius and Eyring equations, using rate constants at two temperatures. Because each set of rate constants requires an entire Stern–Volmer plot and because of experimental limitations, further temperatures were not utilized.

For activation parameters to be meaningful, the nature of the potential energy surface needs to be assumed. Two possibilities seem reasonable and are presented in Figures 3 and 4. These are suggested by the rate and migratory aptitude results in our 4-p-cyanophenyl-4-phenylcyclohexenone study.[1a,3b]

If a single maximum surface is involved (i.e., Figure 4), then the activation parameters determined (note

(11) Note F. Wilkinson, Advan. Photochem., 3, 248 (1964).

Table III. Quantum Yields in Quenched Irradiations[a]

Run	Temp, °C	Enone concn × 10² M	Quencher[c] concn, M	Quantum yields[b]			
				trans[d]	cis[e]	3,4-Enone[f]	Enone[g]
17	20	1.14	0.470	0.00325 ±0.00016	0.000022 ±0.000004	0.000006	0.00327 ±0.00016
18	20	1.14	0.798	0.0020 ±0.0001	0.000012 ±0.000003	h	0.0020 ±0.0001
19	73	1.14	0.484	0.0195 ±0.0009	0.00014 ±0.00001	0.000038 ±0.000004	0.0196 ±0.0009
20	73	1.14	0.821	0.0123 ±0.0006	0.00009 ±0.00001	0.000024 ±0.000003	0.0124 ±0.0006

[a] 2,5-Dimethyl-2,4-hexadiene as quencher. [b] Errors estimated from data. [c] Correction applied for direct absorption by quencher of up to 5% of incident light. [d] Appearance 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] Disappearance of 4,4-diphenylcyclohex-2-en-1-one determined by adding the quantum yields of the individual products. [h] Below the limits of detection.

Table IV. Rates of Triplet Reaction and Decay, Slope, Intercept, k_r and k_d at 20 and 73°

Compd	Temp, °C	Slope,[a] einsteins × cm³/mol²	Intercept,[b] einsteins/ mol	Rate of reaction, sec⁻¹	Rate of decay, sec⁻¹
Enone[c]	20	569.6	36.5	7.6×10^6	2.7×10^8
	73	92.0	5.67	1.22×10^8	5.7×10^8
trans[d]	20	572.4	37.0	7.6×10^6	2.7×10^8
	73	92.8	5.75	1.21×10^8	5.7×10^8
cis[e]	20	93,410	5,915	4.6×10^4	2.7×10^8
	73	12,580	800	8.9×10^5	7.1×10^8
3,4-Enone[f]	73	47,540	2,985	2.4×10^5	7.0×10^8

[a] Least-square slopes. [b] Least-square intercepts. [c] Disappearance of 4,4-diphenylcyclohex-2-en-1-one. [d] Appearance 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-diphenyl-cyclohex-2-en-1-one.

Table V. Activation Energies, Enthalpies, Entropies, and Frequency Factors

Compd	Arrhenius activation energy, kcal/mol	Arrhenius frequency factors, sec⁻¹	Activation enthalpy, kcal/mol	Activation entropy, eu
Enone[a]	10.53	$10^{14.7}$	9.86	6.95
trans[b]	10.53	$10^{11.7}$	9.86	6.95
cis[c]	11.27	$10^{13.1}$	10.7	−0.65

[a] Disappearance of 4,4-diphenylcyclohex-2-en-1-one. [b] Appearance of trans-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [c] Appearance of cis-5,6-diphenylbicyclo[3.1.0]hexan-2-one.

Tables IV and V) have their classical significance. The calculated activation parameters are the energy and entropy change required to reach the transition state, except that here one is dealing with an electronically excited species. Ground-state product is known[4] to arise directly without intermediate formation of the product excited state: hence in Figures 3 and 4, loss of electronic excitation occurs along the latter part of the surface although it is not pictured explicitly. Whether this is a discontinous process, as a radiationless transition, or merely part of the curve is uncertain.

On the other hand, if the double maximum curve of Figure 3 is correct, the Stern–Volmer treatment for each product leads to an experimental rate constant which is the product of the rate constant for the formation of the (e.g., bridged) intermediate multiplied by the probability of this proceeding onward to the product

under consideration.[12] That is

$$k_{rA}^{exp} = k_{TI}P_{IA} \qquad (4)$$

where k_{rA}^{exp} is the experimentally determined rate constant for formation of product A, k_{TI} is the rate of formation of intermediate I from triplet, and P_{IA} is the probability of intermediate I going onward to give product A.

It is clear that the usual Arrhenius or Eyring treatments cannot be directly applied, since this involves plotting the log of a rate constant vs. $1/T$ to get an activation energy from the slope. In the present case the log of the experimental rate constant includes a probability term (i.e., P_{IA}) which is not a simple rate constant and which is known to be temperature dependent from the varying product composition with temperature. However, the ratio of experimental rate constants involves only the ratio of probabilities of intermediate going onward to products, e.g., A and B, and this ratio is a simple ratio of the rate constants. Hence the difference in activation energies obtained will be exact as will the ratio of frequency factors (or difference in activation entropies).

All of this means that if a relatively long-lived bridged species does exist, the activation parameters and frequency factors will be in error. But, if there is no return from this intermediate to ground-state reactant, then in eq 4, P_{IA} remains close to unity where A refers to trans product, since this product predominates heavily. In this event the error will be very small. To the extent that there is decay from a bridged intermediate, P_{IA} will be less than unity and perhaps temperature dependent. However, the very similar experimental rates of decay determined in the present case compared with those in the rearrangement of the p-cyanophenyl-substituted analog studied earlier[1b] suggests that decay is from the initially formed triplet where substitution by a cyano group remote from the site of excitation, the enone moiety, would have little effect on decay. In contrast, in the bridged species, one would anticipate a large effect on back migration depending on the presence or absence of a p-cyano substituent in the migrating aryl group, an effect not observed. In

(12) The mathematics involved is omitted for brevity. The kinetic conclusions are relatively straightforward in any case.
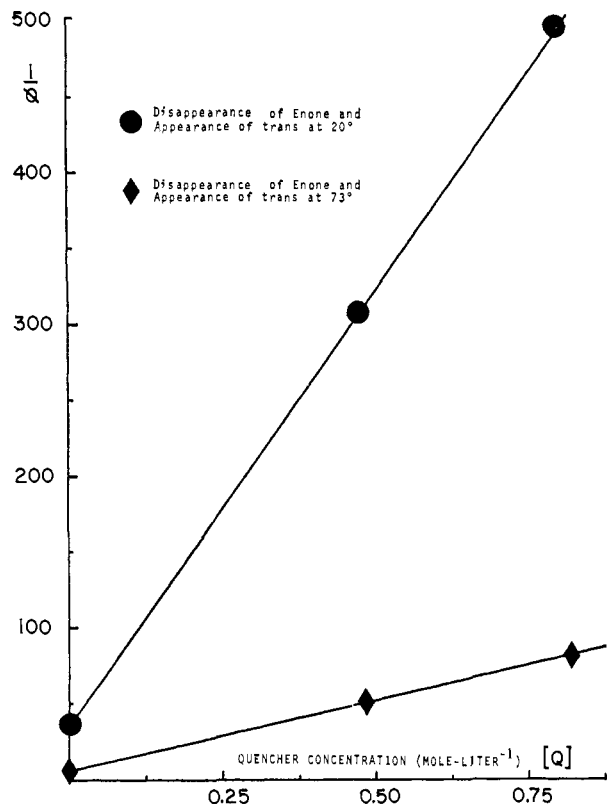
Figure 1.

Figure 2.

summary, it appears that the activation parameters are of the correct order of magnitude in addition to being exact relative to one another.

A final possibility[13a] needs to be considered. This is that the reaction proceeds by way of a ground-state intermediate such as the *trans* stereoisomer **1t** of reactant or another isomer such as the oxabicyclo-butane[13b] **6**. The kinetics of such a process would follow expression 5

$$1/\phi = K\left(\frac{k_r + k_d}{k_r} + \frac{k_q}{k_r}[Q]\right) \tag{5}$$

1t   **6**
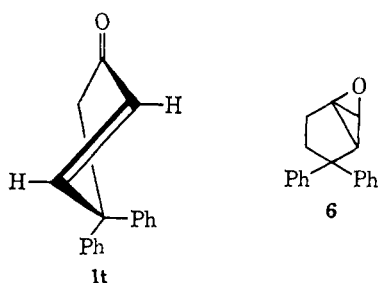
where K is the probability of the intermediate giving product rather than decaying back to reactant. This

Figure 3. Double maximum potential energy surface for the excited state: ——, excited-state surface; – – –, ground-state surface.

Figure 4. Single maximum for the excited-state surface: ——, excited-state surface; – – –, ground-state surface.

(13) (a) Such a possibility was suggested by a referee who considered **1t** and **6** as potential candidates. (b) Such oxabicyclobutanes as **6** were discussed by us earlier (H. E. Zimmerman, R. G. Lewis, J. J. Mc-Cullough, A. Padwa, S. W. Staley, and M. Semmelhack, *J. Am. Chem. Soc.*, **88**, 1065 (1966), footnote 37) as a possible route for decay and energy dissipation.
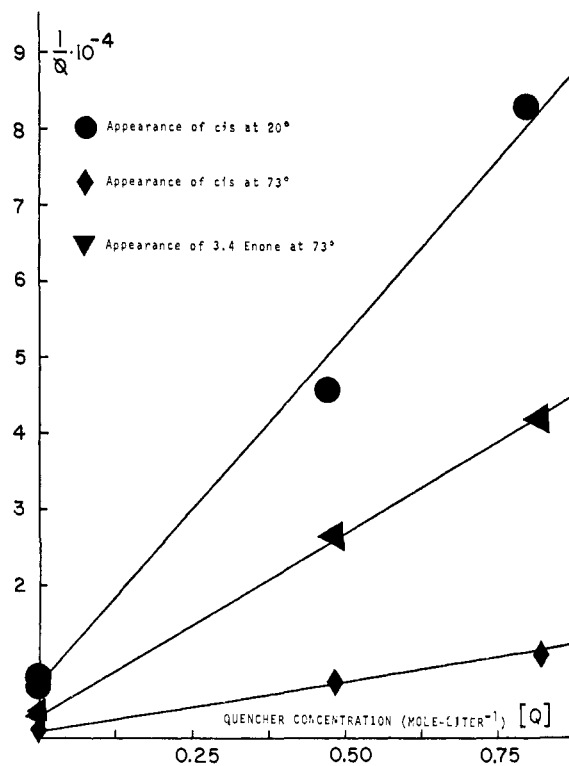
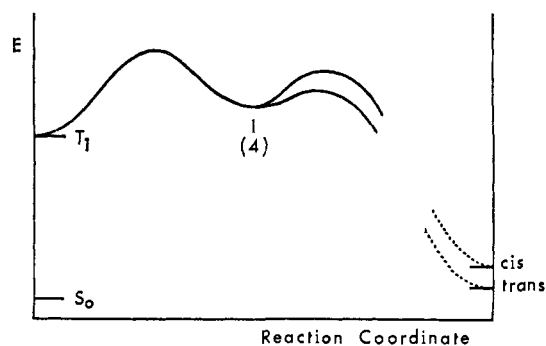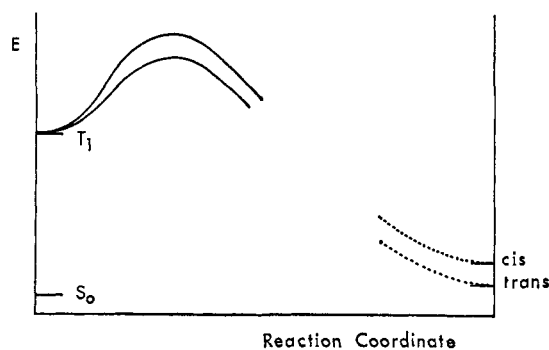situation is very similar to that considered for a double maximum excited-state surface. With such a ground-state intermediate the temperature dependence might derive from a barrier to the intermediate proceeding to product. In this extreme, K but not k_r and k_d would vary with temperature.

There are some good reasons for excluding this possibility. (1) If the *trans*-enone **1t** were the intermediate in these rearrangement reactions, then in the cases where there are both phenyl and cyanophenyl groups at carbon-4, phenyl should migrate in preference, since here migration is to the electron-deficient state β-carbon of a ground-state enone moiety. The electron deficiency should hold even for a twisted *trans*-enone. (2) In this type rearrangement[3,4] the *trans* stereoisomer of the 5,6-disubstituted bicyclo-[3.1.0]hexan-2-one invariably is kinetically preferred. Yet, models as well as reference to structure **1t** as shown reveal that one aryl group is nearly coplanar with the β C–H bond of the *trans* double bond and the other phenyl would be left to migrate. This migration leads to *cis* stereochemistry. Additionally, the –CH₂CH₂– chain of the *trans*-enone blocks one side of the *trans* double bond, and migration to the accessible side leads to the *cis*-diphenyl configuration. This stereochemistry is not observed. (3) The same aryl migration rearrangement is found in 4,4-disubstituted naphthalenones where in place of the CH₂CH₂ moiety there is a fused benzo ring. Here a *trans*-enone intermediate seems hopelessly inaccessible due to strain. (4) In the case of the oxabicyclobutane intermediate,[13b] there are two ways in which this might decay back to an unsaturated carbonyl compound. One of these decay routes leads to 3,3-diphenyl-1-cyclopentenecarboxaldehyde which is not a product of the reaction. More relevantly, the oxabicyclobutane species does not seem to be a probable intermediate in leading to a bicyclo[3.1.0]hexan-2-one. (5) Finally, if we use the rate law of eq 5, we find that a variation of K with temperature is insufficient to fit our data. An increase in the term $(k_r + k_d)$ with temperature is required. This is in accord with our interpretation above which seems simplest.

Interpretative Discussion of Results. Excited-State Energy Barriers in Photochemistry. As noted above, the wavelength independence of the quantum yields established rapid excess energy dissipation to solvent. That excess vibrational energy is rapidly distributed to solvent relative to the rate of reaction is of fundamental interest. This result is not totally unexpected for a reaction involving a reasonable activation energy (*vide infra*) as has been pointed out previously.[3] More striking is the very rapid internal conversion occurring when an upper excited singlet is initially engendered as in irradiation at 254 nm; here independent of whether the initial excitation was heavily localized in the benzene ring or the enone moiety, the same reaction ensued with the same efficiency.[14]

Most striking and perhaps the most important aspect of the present study is the observation of appreciable

(*i.e.*, *ca.* 10 kcal/mol) thermal barriers in the phenyl rearrangement reaction. The number of examples where thermal barriers have been encountered is small.[15]

Perhaps the barrier in the present study is intuitively reasonable, since the reaction does involve disruption of the electronics of the phenyl ring. Thus, it appears that despite our dealing with an electronically excited system, there is an appreciable loss in energy incurred in phenyl bridging.[16]

Although it is still too early to generalize, it seems likely that appreciable energy barriers will be encountered where extensive molecular rearrangement is involved in a photochemical reaction and that this energy derives from loss in delocalization energy and bond weakening, two factors also important in ground-state rate phenomena.

The difference between the presently studied rearrangement and the low energy barrier of *cis–trans* isomerization cases previously studied then seems reasonable, for in the stereoisomerization free rotation in the excited state should not involve very large energy demands.

The existance of barriers on the excited-state potential energy curve means that control of the course of photochemical reactions of this type can be understood by considerations not too different from ground-state reasoning except that here one has to consider the molecular structure of the electronically excited species.

Finally in this connection, an investigation of temperature dependences has practical consequences, since many reactions not observed at room temperature may become observable at elevated temperatures where thermal barriers often can be overcome. Similarly, minor photochemical products may become accessible.

Interpretative Discussion of Results. Rates of Decay. A noteworthy point is the finding (note Table IV) that there is a temperature dependence of the rate of triplet decay (*i.e.*, k_d); this corresponds to an activation energy[17] of 2.8 kcal/mol. Two aspects require comment. The first regards the fact that there actually is an activation energy and the second point concerns the small magnitude.

Concerning the first point, the existence of a barrier suggests that the lowest energy vibrational state does not decay as efficiently as a somewhat higher energy vibrational state. This might mean that there exists a point where the potential energy surfaces of triplet excited state and ground state intersect. Such a point would not be at an energy minimum but would correspond to one of the higher vibrational levels for some

(14) One may note that regardless of the site of initial excitation and independent of whether there is some coupling of the phenyl and enone chromophores, as phenyl migration begins the two moieties become strongly conjugated and two independent systems no longer remain.

(15) For the azobenzene isomerization (ref 7) a thermal barrier of 5 kcal/mol was estimated for the *trans–cis* reaction. In the stilbene *trans–cis* reaction barriers of 1.7[6b] and 3.0[6a] have been obtained. For the rearrangement of *o*-xylene a barrier of 7.7 kcal/mol was reported.[8] It should be noted that excited-state activation parameters are not correctly obtained by use of a mere plot of quantum yields against the reciprocal of temperature, since the quantum yield is given by $(k_r)/(k_r^{tot} + k_d)$. It cannot be assumed that the denominator will be constant and yet to get activation energies one needs a plot of log k_r *vs.* $1/T$.

(16) With respect to the possibility that the energy barrier is actually in the electronic ground state reached by demotion, we note the earlier work on migratory aptitudes.[1b,3b] It seems unlikely that a ground-state species formed early enough along the reaction coordinate to still leave a *ca.* 10-kcal/mol barrier would lead to *p*-cyanophenyl migration, since return to reactant should be facile in an electron-deficient ground-state migration and phenyl migration should then be strongly preferred.

(17) Alternatively, the temperature effect could derive from an increased rate of solvent collision.
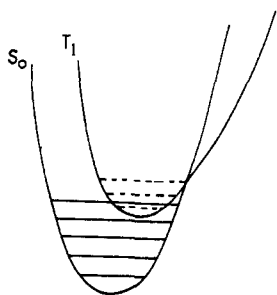
Figure 5. Possible overlap of S_0 and T_1 energy surfaces.

molecular degree of freedom as depicted in Figure 5. Thus an activation energy would be required for thermally equilibrated triplet T_1 to reach this point. Alternatively, it could be merely that an upper vibrational level of the triplet intersystem crosses to ground state more rapidly than the lower levels because of greater overlap of the vibrational wave functions.[18] Thus, it has been argued that the greater such vibrational overlap, the greater the rate of radiationless transitions.[18] One might inquire what molecular motion could be involved which would correspond to the activation energy. This might just be incipient aryl bonding with carbon 3.

However, let us turn our attention to the second point noted, namely the very small activation energy for the decay process (i.e., 2.8 kcal/mol vs. 10.53 kcal/mol) for the rearrangement of excited enone 1 to trans-5,6-diphenylbicyclo[3.1.0]hexan-2-one (2a). This means that the decay process either occurs at a point on the potential energy surface available to the excited state totally different than the rearrangement transition state or alternatively that decay occurs very much earlier but along the same general pathway. In either event, it would be difficult to say that decay and reaction have much in common.

Finally, in connection with decay, we observe from Table IV that the experimentally derived decay rates obtained from different Stern–Volmer plots are the same within experimental error for any single temperature. Since each Stern–Volmer plot derives from one compound, the identity of the k_d's provides strong circumstantial evidence that the same excited state gives rise to the several products.

Interpretative Discussion. Relative Activation Energies and Entropies. An aspect of the findings is the very similar activation energies, 11.3 kcal/mol found for formation of cis-5,6-diphenylbicyclo[3.1.0]hexan-2-one (2b) and 10.5 kcal/mol for trans-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (2a). It seems unlikely that this similarity is accidental. Rather, it is more likely that similar transition states are involved.

The frequency factors (or alternatively, entropies of activation), $10^{14.7}$ for trans-isomer formation and $10^{13.1}$ for cis stereoisomer, are of the same order of magnitude and are typical of ordinary molecular transformations.

Thus there is nothing unique about these excited-state reaction probabilities.

We do note, however, that the entropy differences at room temperature are sufficient to account for roughly three-fourths of the stereoselectivity (i.e., $T\Delta S$-$(trans)^{20°}$ = 2.04 and $T\Delta S(cis)^{20°}$ = -0.19 kcal/mol). One reasonable explanation of the less positive activation entropy for the formation of cis stereoisomer derives from the suggestion[4] that formation of the trans isomer (2a) is concerted with inversion of configuration at carbon 4 while formation of the cis isomer (2b) is nonconcerted and proceeds via the open biradical 5 (note Chart I). To the extent that an odd electron at carbon 4 needs to be stabilized, the C-4 phenyl group will have a conformational restriction and the more negative entropy of activation would result.

Chart I. Pathways Leading from 4,4-Diphenylcyclohexenone to the Bicyclic Ketone Products; Inhibition of Free Rotation as a Function of Reaction Stereochemistry
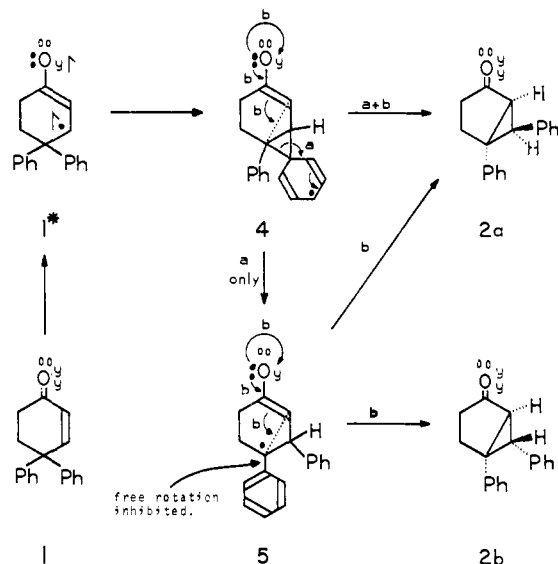
Experimental Section[19]

4,4-Diphenylcyclohex-2-en-1-one was prepared according to the method described by Zimmerman, et al.,[20] in 64.5% yield, mp 94–95°, after recrystallization from ethanol.

4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C was prepared by the synthesis described earlier.[4] From 12.076 g (13.05 mCi, 61.2 mmol) of barium radiocarbonate, the synthesis yielded 7.85 g (51.7% based on Ba[14]CO$_3$) of slightly yellow 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C, mp 92–94°. Recrystallization from 95% ethanol gave 6.46 g of pure material, mp 94–95°, specific activity 226.67 μCi/mmol.

cis and trans-5,6-diphenylbicyclo[3.1.0]hexan-2-ones were prepared by preparative photolysis following the method of Zimmerman and Hancock.[4] The cis isomer used melted at 113–114° and the trans isomer at 76–77°.

3,4-Diphenylcyclohex-2-en-1-one was prepared according to Zimmerman and Hancock.[4] Final purification was by chromatography on a 4.3 × 38 cm slurry packed column, using 5% ether–hexane, half silica gel (Davison, Grade 950, 60–200 mesh) and half silica gel containing 10% of Norit. This yielded white crystalline material, mp 100–101°.

Quantum Yield Irradiations. In all runs the microscale determination, using isotope dilution, described in detail by Zimmer-

(18) Note D. Phillips, J. Lemaire, C. S. Burton, and W. A. Noyes, Jr., Advan. Photochem., 5, 329 (1968), for a general discussion; (b) R. B. Frosch and G. W. Robinson, J. Chem. Phys., 37, 1962 (1962); 38, 1187 (1963).

(19) Melting points were observed on a hot-stage apparatus and are corrected.

(20) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, J. Am. Chem. Soc., 88, 4895 (1966).

man and Hancock[4] was employed. The specific activity was determined with a Nuclear Chicago Mark I scintillation counter.

Solvents and Quenchers. Crude *n*-dodecane (Eastman) was stirred three times with fuming sulfuric acid, water, aqueous sodium bicarbonate, and water and dried over sodium sulfate. Distillation over sodium gave a solvent which showed no absorption above 230 nm, bp 96–97° (0.13 mm). From photolysis mixtures the solvent was removed *in vacuo* (0.01 mm) at 40–50°.

2,5-Dimethyl-2,4-hexadiene was vacuum distilled (0.3 mm) under nitrogen through a 50-cm column packed with steel helices, bp 29–30°. The purity was checked by nmr. It was removed from the photolysis mixtures *in vacuo* along with the solvent.

Quantum Yields. The specific activity of the ^{14}C-labeled reactant was 226.67 μCi/mmol in all runs. The isotope dilution was performed volumetrically. From the photolysis mixture the solvent was removed *in vacuo* and the residue dissolved in 50.0 ml of a mixture of 20% benzene in hexane; 3.0-, 6.0-, 20.0-, and 21.0-ml aliquots for the 4,4-diphenylcyclohex-2-en-1-one, *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, and 3,4-diphenylcyclohex-2-en-1-one, respectively, were withdrawn and added to an accurately weighed amount of the corresponding ^{12}C compounds. Specific data for individual determinations are listed as follows: conditions of irradiation of the ^{14}C-labeled reactant (weight, solvent, wavelength, band width, amount of light) followed by isotope dilution data. The weight of each ^{12}C compound used to dilute an aliquot of the radioactive reaction mixture is followed by the number of the final recrystallization in parentheses (4,4-diphenylcyclohex-2-en-1-one, *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-ones from 10% benzene in hexane; 3,4-diphenylcyclohex-2-en-1-one from methanol), recovered weight, the melting point, the asymptotic specific activity (nCi/mmol) with standard error, the calculated amount of material recovered or produced, and finally the quantum yield. The quantum yield for disappearance of the reactant was taken as the sum of quantum yields for appearance of products, since the low conversions used made the absolute errors in the amounts of the reactant employed and recovered of the same order as the amount converted.

Run 1. 4,4-Diphenylcyclohex-2-en-1-one-4-[14]C (85.9 mg, 345.9 μmol) in 39 ml of *t*-butyl alcohol at 28°, irradiated at 366 nm, 7 nm half-band width, 139.2 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (502.2 mg, 2022 μmol) added to ^{14}C photolysate (10.31 mg, 41.51 μmol): (6), 72 mg, 94–95°, 4406 ± 22, 338.1 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (504.1 mg, 2030 μmol) added to ^{14}C photolysate (10.31 mg, 41.51 μmol): (6), 43 mg, 76–77°, 159.91 ± 0.83, 11.95 μmol produced, ϕ = 0.0858 ± 0.0040.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (506.6 mg, 2040 μmol) added to ^{14}C photolysate (34.36 mg, 138.4 μmol): (12), 24 mg, 113–114°, 3.290 ± 0.028, 0.074 μmol produced, ϕ = 0.00053 ± 0.00004.

3,4-Diphenylcyclohex-2-en-1-one (515.0 mg, 2074 μmol) added to ^{14}C photolysate (30.93 mg, 124.6 μmol): (6) 80 mg, 101–102°, 30.451 ± 0.160, 0.774 μmol produced, $\emptyset$ = 0.00556 ± 0.00040.

Run 2. 4,4-Diphenylcyclohex-2-en-1-one-4-[14]C (80.9 mg, 325.7 μmol) in 39 ml of *t*-butyl alcohol at 28°, irradiated at 366 nm, 22 nm half-band width, 32.1 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (501.6 mg, 2020 μmol) added to ^{14}C photolysate (4.85 mg, 19.53 μmol): (4), 58 mg, 94–95°, 2174 ± 11, 326.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (510.9 mg, 2057 μmol) added to ^{14}C photolysate (9.71 mg, 39.10 μmol): (6), 43 mg, 76–77°, 35.427 ± 0.180, 2.68 μmol produced, ϕ = 0.0835 ± 0.0040.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (492.7 mg, 1984 μmol) added to ^{14}C photolysate (33.98 mg, 136.8 μmol): (10), 73 mg, 113–114°, 0.789 ± 0.011, 0.0164 μmol produced, ϕ = 0.00051 ± 0.00004.

3,4-Diphenylcyclohex-2-en-1-one (493.7 mg, 1988 μmol) added to ^{14}C photolysate (32.36 mg, 130.3 μmol): (6), 103 mg, 101–102°, 7.797 ± 0.046, 0.171 μmol produced, ϕ = 0.00533 ± 0.00040.

Run 3. 4,4-Diphenylcyclohex-2-en-1-one-4-[14]C (81.2 mg, 326.9 μmol) in 39 ml of *t*-butyl alcohol, at 28°, irradiated at 313 nm, 7 nm half-band width, 119.0 μEinsteins; 80.4% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (509.8 mg, 2053 μmol) added to ^{14}C photolysate (9.74 mg, 39.22 μmol): (4), 248 mg, 94–95°, 407 ± 21, 313.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (512.1 mg, 2062 μmol) added to ^{14}C photolysate (9.74 mg, 39.22 μmol): (7) 47 mg, 76–77°, 147.22 ± 0.96, 11.11 μmol produced (corrected for inter-

conversion 11.27 μmol), ϕ = 0.0934 ± 0.0040 (corrected for interconversion 0.0947 ± 0.0040, 11.9% of light absorbed by *trans*).

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (505.3 mg, 2035 μmol) added to ^{14}C photolysate (32.48 mg, 130.8 μmol): (12), 78 mg, 113–114°; 10.657 ± 0.065, 0.239 μmol produced (corrected for interconversion 0.074 μmol), ϕ = 0.0020 ± 0.001 (corrected for interconversion ϕ = 0.00062 ± 0.00010).

3,4-Diphenylcyclohex-2-en-1-one (512.8 mg, 2065 μmol) added to ^{14}C photolysate (29.23 mg, 117.7 μmol): (7), 98 mg, 101–102°, 31.844 ± 0.170, 0.806 μmol produced, ϕ = 0.0068 ± 0.0004.

Run 4. 4,4-Diphenylcyclohex-2-en-1-one-4-[14]C (81.0 mg, 326.1 μmol) in 39 ml of *t*-butyl alcohol, at 29°, irradiated at 313 nm, 7 nm half-band width, 75.5 μEinsteins; 86.6% of light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (509.6 mg, 2052 μmol) added to ^{14}C photolysate (9.72 mg, 39.14 μmol): (4), 138 mg, 94–95°, 4129 ± 21, 316.5 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (515.5 mg, 2076 μmol) added to ^{14}C photolysate (9.72 mg, 39.14 μmol): (4), 110 mg, 76–77°, 93.295 ± 0.480, 7.12 μmol produced, (corrected for interconversion 7.19 μmol) ϕ = 0.0943 ± 0.0040 (corrected for interconversion 0.0952 ± 0.0040).

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (509.4 mg, 2051 μmol) added to ^{14}C photolysate (32.40 mg, 130.5 μmol): (12), 127 mg, 113–114°, 5.057 ± 0.031, 0.114 μmol produced (corrected for interconversion 0.0047 μmol), ϕ = 0.00151 ± 0.00010 (corrected for interconversion 0.00062 ± 0.00010).

3,4-Diphenylcyclohex-2-en-1-one (510.7 mg, 2056 μmol) added to ^{14}C photolysate (29.16 mg, 117.4 μmol): (6), 101 mg, 101–102°, 19.839 ± 0.110, 0.500 μmol produced, ϕ = 0.0066 ± 0.0004.

Run 5. 4,4-Diphenylcyclohex-2-en-1-one-4-[14]C (83.7 mg, 337.0 μmol) in 39 ml of *t*-butyl alcohol, at 28°, irradiated at 313 nm, 22 nm half-band width, 58.2 μEinsteins; 90.5% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (500.8 mg, 2016 μmol) added to ^{14}C photolysate (5.02 mg, 20.21 μmol): (5), 176 mg, 94–95°, 2210 ± 11, 330.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (506.4 mg, 2039 μmol) added to ^{14}C photolysate (10.04 mg, 40.42 μmol): (6), 67 mg, 76–77°, 65.89 ± 0.34, 4.93 μmol produced (4.96 μmol corrected for interconversion), ϕ = 0.0847 ± 0.0040 (corrected for interconversion 0.0853 ± 0.0040).

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (504.9 mg, 2033 μmol) added to ^{14}C photolysate (35.15 mg, 141.6 μmol): (12), 123 mg, 113–114°, 5.026 ± 0.031, 0.107 μmol produced (corrected for interconversion 0.074 μmol), ϕ = 0.00184 ± 0.00010 (corrected for interconversion 0.00127 ± 0.00010).

3,4-Diphenylcyclohex-2-en-1-one (498.6 mg, 2008 μmol) added to ^{14}C photolysate (33.48 mg, 134.8 μmol): (6), 86 mg, 101–102°, 16.239 ± 0.087, 0.360 μmol produced, ϕ = 0.0062 ± 0.0004.

Run 6. 4,4-Diphenylcyclohex-2-en-1-one-[14]C (86.1 mg, 346.7 μmol) in 39 ml of *t*-butyl alcohol, at 29°, irradiated at 254 nm, 22 nm half-band width, 51.7 μEinsteins; 99.76% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (506.5 mg, 2039 μmol) added to ^{14}C photolysate (5.17 mg, 20.82 μmol): (4), 201 mg, 94–95°, 2,245 ± 11, 340.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (519.7 mg, 2093 μmol) added to ^{14}C photolysate (10.33 mg, 41.64 μmol): (5), 89 mg, 76–77°, 64.011 ± 0.330, 4.93 μmol produced, ϕ = 0.0953 ± 0.004 (corrected for interconversion 0.0954 ± 0.0040).

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (487.3 mg, 1962 μmol) added to ^{14}C photolysate (36.16 mg, 145.6 μmol): (14), 91 mg, 113–114°, 3.814 ± 0.025, 0.079 μmol produced, ϕ = 0.00137 ± 0.00010.

3,4-Diphenylcyclohex-2-en-1-one (495.8 mg, 1996 μmol) added to ^{14}C photolysate (34.44 mg, 138.7 μmol): (6), 41 mg, 101–102°, 15.344 ± 0.084, 0.337 μmol produced, ϕ = 0.00652 ± 0.00040.

Run 7. 4,4-Diphenylcyclohex-2-en-1-one-4-[14]C (84.7 mg, 341.0 μmol) in 39 ml *t*-butyl alcohol, at 29°, irradiated at 254 nm, 22 nm half-band width, 18.5 μEinsteins; 99.92% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (508.3 mg, 2047 μmol) added to ^{14}C photolysate (5.08 mg, 20.45 μmol): (4) 163 mg, 94–95°, 2246 ± 11, 342.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (518.6 mg, 2088 μmol) added to ^{14}C photolysate (10.16 mg, 40.91 μmol): (5), 94 mg, 76–77°, 21.644 ± 0.16, 1.66 μmol produced, ϕ = 0.0897 ± 0.004.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (506.7 mg, 2040 μmol)

added to ^{14}C photolysate (35.57 mg, 143.2 μmol): (14), 51 mg, 113–114°, 1.102 ± 0.011, 0.0236 μmol produced, ϕ = 0.0013 ± 0.0001 (corrected for interconversion 0.0012 ± 0.0001).

3,4-Diphenylcyclohex-2-en-1-one (515.6 mg, 2076 μmol) added to ^{14}C photolysate (33.88 mg, 136.4 μmol): (6), 19 mg, 101–102°, 4.751 ± 0.030, 0.108 μmol produced, ϕ = 0.0058 ± 0.0004.

Run 8. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (83.4 mg, 335.8 μmol) in 39 ml of *t*-butyl alcohol, at 29°, irradiated at 254 nm, 22 nm half-band width, 43.9 μEinsteins; 99.84% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (532.7 mg, 2145 μmol) added to ^{14}C photolysate (5.00 mg, 20.13 μmol): (5), 138 mg, 94–95°, 2078 ± 11, 330.7 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (507.7 mg, 2044 μmol) added to ^{14}C photolysate (10.01 mg, 40.26 μmol): (6), 23 mg, 76–77°, 51.88 ± 0.27, 3.90 μmol produced, ϕ = 0.0888 ± 0.0040. (corrected for interconversion 0.0889 ± 0.0040).

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (496.5 mg, 1999 μmol) added to ^{14}C photolysate (35.03 mg, 141.1 μmol): (18), 43 mg, 113–114°, 4.380 ± 0.028, 0.092 μmol produced (0.089 corrected for interconversion), ϕ = 0.0021 ± 0.0001 (corrected for interconvesion 0.0020 ± 0.0001).

3,4-Diphenylcyclohex-2-en-1-one (496.2 mg, 1998 μmol) added to ^{14}C photolysate (33.36 mg, 134.3 μmol): (5), 95 mg, 101–102°, 13.199 ± 0.073, 0.291 μmol produced, ϕ = 0.0066 ± 0.0004.

Run 9. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (85.9 mg, 345.9 μmol) in 39 ml of *t*-butyl alcohol, at 63°, irradiated at 366 nm, 22 nm half-band width, 52.7 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (500.8 mg, 2016 μmol) added to ^{14}C photolysate (5.15 mg, 20.74 μmol): (3), 192 mg, 94–95°, 2247 ± 11, 336.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (510.2 mg, 2054 μmol) added to ^{14}C photolysate (10.31 mg, 41.51 μmol): (6), 72 mg, 76–77°, 160.986 ± 0.820, 12.17 μmol produced, ϕ = 0.231 ± 0.012.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (500.3 mg, 2014 μmol) added to the ^{14}C photolysate (36.11 mg, 145.4 μmol): (21), 26 mg, 113–114°, 4.742 ± 0.030, 0.100 μmol produced, ϕ = 0.0019 ± 0.0001.

3,4-Diphenylcyclohex-2-en-1-one (499.3 mg, 2011 μmol) added to ^{14}C photolysate (34.36 mg, 138.4 μmol): (6) 17 mg, 101–102°, 26.367 ± 0.140, 0.585 μmol produced, ϕ = 0.0111 ± 0.0005.

Run 10. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (119.7 mg, 482.0 μmol) in 39 ml of *t*-butyl alcohol, at 63°, irradiated at 366 nm, 22 nm half-band width, 53.2 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (504.4 mg, 2031 μmol) added to ^{14}C photolysate (7.18 mg, 28.91 μmol): (3), 229 mg, 94–95°, 3121 ± 16, 472.6 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (502.8 mg, 2024 μmol) added to ^{14}C photolysate (14.36 mg, 57.82 μmol): (7), 31 mg, 75–76°, 170.12 ± 0.87, 12.68 μmol produced, ϕ = 0.238 ± 0.012.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.0 mg, 2017 μmol) added to ^{14}C photolysate (50.27 mg, 202.4 μmol): (17), 12 mg, 113–114°, 4.257 ± 0.028, 0.0903 μmol produced, ϕ = 0.0017 ± 0.0001.

3,4-Diphenylcyclohex-2-en-1-one (500.4 mg, 2015 μmol) added to ^{14}C photolysate (47.88 mg, 192.8 μmol): (7), 29 mg, 101–102°, 26.047 ± 0.140, 0.579 μmol produced, ϕ = 0.0109 ± 0.0005.

Run 11. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (100.6 mg, 405.1 μmol) in 39 ml of *n*-hexane, at 20°, irradiated at 366 nm, 22 nm half-band width, 151.4 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (506.6 mg, 2040 μmol) added to ^{14}C photolysate (6.04 mg, 24.32 μmol): (5) 137 mg, 94–95°, 2683 ± 13, 407.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (499.8 mg, 2012 μmol) added to ^{14}C photolysate (12.07 mg, 48.64 μmol): (6), 111 mg, 75–76°, 59.20 ± 0.30, 4.38 μmol produced, ϕ = 0.0290 ± 0.0010.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (507.0 mg, 2041 μmol) added to ^{14}C photolysate (42.25 mg, 170.1 μmol): (14), 53 mg, 113–114°, 0.969 ± 0.010, 0.0208 μmol produced, ϕ = 0.00014 ± 0.00005.

3,4-Diphenylcyclohex-2-en-1-one (516.5 mg, 2080 μmol) added to ^{14}C photolysate (40.24 mg, 162.0 μmol): (9), 19 mg, 101–102°, 0.171 ± 0.090, 0.0039 μmol produced, ϕ = 0.000026 ± 0.000003.

Run 12. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (97.7 mg, 393.4 μmol) in 39 ml of *n*-hexane, at 20°, irradiated at 366 nm, 22 nm half-band width, 190.9 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (498.2 mg, 2006 μmol) added to ^{14}C photolysate (5.86 mg, 23.59 μmol): (5), 310 mg, 94–95°, 2626 ± 13, 391.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (500.4 mg, 2015 μmol) added to ^{14}C photolysate, (11.72 mg, 47.19 μmol): (6), 123 mg, 76–77°, 71.19 ± 0.36, 5.28 μmol produced, ϕ = 0.0276 ± 0.0010.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (505.1 mg. 2034 μmol) added to ^{14}C photolysate, (41.03 mg, 165.2 μmol): (14), 21 mg, 113–114°, 0.875 ± 0.010, 0.0187 μmol produced, ϕ = 0.00010 ± 0.00005.

3,4-Diphenylcyclohex-2-en-1-one (502.4 mg, 2023 μmol) added to ^{14}C photolysate (39.08 mg, 157.4 μmol): (7), 76 mg, 101–102°, 0.180 ± 0.010, 0.0040 μmol produced, ϕ = 0.000021 ± 0.000003.

Run 13. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (89.2 mg, 359.2 μmol) in 39 ml of *n*-dodecane, at 20°, irradiated at 366 nm, 22 nm half-band width, 165.1 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (496.7 mg, 2000 μmol) added to ^{14}C photolysate (5.35 mg, 21.54 μmol): (5), 300 mg, 94–95°, 2414 ± 12, 358.5 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (509.1 mg, 2050 μmol) added to ^{14}C photolysate (10.70 mg, 43.08 μmol): (7), 109 mg, 75–76°, 61.082 ± 0.310, 4.61 μmol produced, ϕ = 0.0279 ± 0.0010.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (504.7 mg, 2032 μmol) added to ^{14}C photolysate (37.46 mg, 150.9 μmol): (12), 49 mg, 113–114°, 1.032 ± 0.012, 0.0220 μmol produced, ϕ = 0.00013 ± 0.00005.

3,4-Diphenylcyclohex-2-en-1-one (504.1 mg, 2030 μmol) added to ^{14}C photolysate (35.68 mg, 143.7 μmol): (7), 55 mg, 101–102°, 0.207 ± 0.012, 0.0046 μmol produced, ϕ = 0.000028 ± 0.000003.

Run 14. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (90.6 mg, 364.8 μmol) in 39 ml of *n*-dodecane, at 20°, irradiated at 366 nm, 22 nm half-band width, 170.8 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (499.2 mg, 2010 μmol) added to ^{14}C photolysate (5.44 mg, 21.90 μmol): (5), 250 mg, 94–95°, 2447 ± 12, 365.6 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.5 mg, 2019 μmol) added to ^{14}C photolysate (10.87 mg, 43.77 μmol): (6), 109 mg, 75–76°, 62.330 ± 0.320, 4.63 μmol produced, ϕ = 0.0271 ± 0.0010.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (496.8 mg, 2000 μmol) added to ^{14}C photolysate (38.05 mg, 153.2 μmol): (14), 15 mg, 113–114°, 1.376 ± 0.030, 0.0290 μmol produced, ϕ = 0.00017 ± 0.00005.

3,4-Diphenylcyclohex-2-en-1-one (502.0 mg, 2021 μmol) added to ^{14}C photolysate (36.24 mg, 145.9 μmol): (7), 51 mg, 101–102°, 0.253 ± 0.013, 0.0056 μmol produced, ϕ = 0.000033 ± 0.000003.

Run 15. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (79.8 mg, 321.3 μmol) in 39 ml of *n*-dodecane, at 73°, irradiated at 366 nm, 22 nm half-band width, 125.5 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (503.2 mg, 2026 μmol) added to ^{14}C photolysate (4.79 mg, 19.29 μmol): (5), 207 mg, 94–95°, 2005 ± 10, 300.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (505.6 mg, 2036 μmol) added to ^{14}C photolysate (9.58 mg, 38.57 μmol): (6), 107 mg 75–76°, 294.69 ± 1.53, 22.09 μmol produced, ϕ = 0.176 ± 0.009.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (497.2 mg, 2002 μmol)" added to ^{14}C photolysate (33.52 mg, 135.0 μmol): (17), 33 mg, 113–114°, 7.677 ± 0.046, 0.161 μmol produced, ϕ = 0.0013 ± 0.0001.

3,4-Diphenylcyclohex-2-en-1-one (505.0 mg, 2033 μmol) added to ^{14}C photolysate (31.92 mg, 128.5 μmol): (8), 21 mg, 101–102°, 1.893 ± 0.015, 0.0425 μmol produced. ϕ = 0.00034 ± 0.00003.

Run 16. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (80.8 mg, 325.3 μmol) in 39 ml of *n*-dodecane, at 73°, irradiated at 366 nm. 22 nm half-band width, 132.4 μEinsteins.

4,4-Diphenylcyclohex-2-en-1-one (504.8 mg, 2033 μmol) added to ^{14}C photolysate (4.85 mg, 19.53 μmol): (5) 173 mg, 94–95°, 2008 ± 11, 302.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (505.4 mg, 2035 μmol) added to ^{14}C photolysate (9.70 mg, 39.06 μmol): (6), 88 mg, 75–76°, 319.08 ± 1.92, 23.91 μmol produced, ϕ = 0.180 ± 0.009.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (498.2 mg, 2006 μmol) added to ^{14}C photolysate (33.94 mg, 136.7 μmol): (15), 53 mg, 113–114°, 8.35 ± 0.05, 0.176 μmol produced, ϕ = 0.0013 ± 0.0001.

3,4-Diphenylcyclohex-2-en-1-one (502.1 mg, 2022 μmol) added to ^{14}C photolysate (32.32 mg 130.1 μmol): (7), 73 mg, 101–102°, 2.056 ± 0.020, 0.0459 μmol produced, ϕ = 0.00036 ± 0.00003.

Run 17. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (109.7 mg, 441.7 μmol) and 2,5-dimethyl-2,4-hexadiene (2.0155 g, 0.0183 mol, 0.470 M) in 38.9 ml of *n*-dodecane, at 20°, irradiated at 366 nm, 22 nm half-band width, 567.2 μEinsteins; 97.0% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (504.2 mg, 2030 μmol) added to ^{14}C photolysate (6.58 mg, 26.49 μmol): (6), 67 mg, 94–95°, 2915 ± 15, 440.8 μmol recovered

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.6 mg, 2020 μmol) added to ^{14}C photolysate (13.16 mg, 52.99 μmol): (7), 166 mg, 75–76°, 24.830 ± 0.150, 1.84 μmol produced, ϕ = 0.00324 ± 0.00016.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (500.8 mg, 2016 μmol) added to ^{14}C photolysate (46.07 mg, 185.5 μmol): (16) 71 mg, 112–114°, 0.588 ± 0.028, 0.012 μmol produced, ϕ = (2.2 ± 0.4) × 10⁻⁵.

3,4-Diphenylcyclohex-2-en-1-one (507.1 mg, 2042 μmol) added to ^{14}C photolysate (43.88 mg, 176.7 μmol): (9), 103 mg, 100–102°, 0.144, 3.3 × 10⁻³ μmol produced, ϕ = 6 × 10⁻⁶.

Run 18. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (109.7 mg, 441.7 μmol) and 2,5-dimethyl-2,4-hexadiene (3.4077 g, 0.0309 mol, 0.798 M) in 38.75 ml of *n*-dodecane, at 20°, irradiated at 366 nm, 22 nm half-band width, 926.2 μEinsteins; 94.8% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (500.6 mg, 2016 μmol) added to ^{14}C photolysate (6.58 mg, 26.49 μmol): (5), 153 mg, 94–95°, 2812 ± 14, 422.1 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (508.8 mg, 2049 μmol) added to ^{14}C photolysate (43.88 mg, 176.7 μmol): (6), 131 mg, 75–76°, 83.010 ± 0.520, 1.88 μmol produced, ϕ = 0.00203 ± 0.00010.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (503.3 mg, 2026 μmol) added to ^{14}C photolysate (46.07 mg, 185.5 μmol): (16), 62 mg, 112–114°, 0.524 ± 0.025, 1.11 × 10⁻² μmol produced, ϕ = (1.2 ± 0.3) × 10⁻⁵.

Run 19. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (110.1 mg, 443.3 μmol) and 2,5-dimethyl-2,4-hexadiene (2.0630 g, 0.0187 mol, 0.484 M) in 38.70 ml of *n*-dodecane, at 73°, irradiated at 366 nm, 22 nm half-band width, 422.1 μEinsteins; 97.6% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (506.0 mg, 2037 μmol) added to ^{14}C photolysate (6.61 mg, 26.61 μmol): (4), 210 mg, 94–95°, 2894 ± 15, 439.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (497.9 mg, 2005 μmol) added to ^{14}C photolysate (13.21 mg, 53.19 μmol): (6), 134 mg, 75–76°, 111.55 ± 0.57, 8.23 μmol produced, ϕ = 0.0195 ± 0.0009.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.2 mg, 2018 μmol) added to ^{14}C photolysate (46.24 mg, 186.2 μmol): (18), 21 mg, 113–114°, 2.808 ± 0.021, 0.0595 μmol produced, ϕ = (1.4 ± 0.2) × 10⁻⁴.

3,4-Diphenylcyclohex-2-en-1-one (501.9 mg, 2021 μmol) added to ^{14}C photolysate (44.00 mg, 177.2 μmol): (10), 19 mg, 101–102°, 0.714 ± 0.015, 0.0159 μmol produced, ϕ = (3.8 ± 0.4) × 10⁻⁵.

Run 20. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (109.7 mg, 441.7 μmol) and 2,5-dimethyl-2,4-hexadiene (3.5125 g, 0.0319 mol, 0.821 M) in 38.80 ml of *n*-dodecane, at 73°, irradiated at 366 nm, 22 nm half-band width, 685.8 μEinsteins; 94.7% of the light was absorbed by the reactant.

4,4-Diphenylcyclohex-2-en-1-one (504.7 mg, 2032 μmol) added to ^{14}C photolysate (6.58 mg, 26.49 μmol): (4), 153 mg, 94–95°, 2842 ± 15, 430.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (501.9 mg, 2021 μmol) added to ^{14}C photolysate (13.16 mg, 52.99 μmol): (7), 124 mg 75–76°, 113.32 ± 0.57, 8.42 μmol produced, ϕ = 0.0123 ± 0.0006.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (504.2 mg, 2030 μmol)

added to ^{14}C photolysate (46.07 mg, 185.5 μmol): (18), 41 mg, 113–114°, 2.930 ± 0.021, 0.0625 μmol produced, ϕ = (9.1 ± 2.0) × 10⁻⁵.

3,4-Diphenylcyclohex-2-en-1-one (500.0 mg, 2013 μmol) added to ^{14}C photolysate (43.88 mg, 176.7 μmol): (10), 24 mg, 100–102°, 0.741 ± 0.015, 0.0165 μmol produced, ϕ = (2.4 ± 0.3) × 10⁻⁵

Control Runs. Run C-1. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (171.0 mg, 688.5 μmol) in 40 ml *n*-dodecane at 75° for 3 hr. The reaction, work-up, and isotope dilution were performed in total darkness.

4,4-Diphenylcyclohex-2-en-1-one (505.2 mg, 2034 μmol) added to ^{14}C aliquot (10.26 mg, 41.30 μmol): (3), 193 mg, 94–95°, 4554 ± 23, 695.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (504.5 mg, 2031 μmol) added to ^{14}C photolysate (20.52 mg, 82.63 μmol): (7), 127 mg, 75–76°, no product formed.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (502.3 mg, 2022 μmol) added to ^{14}C aliquot (68.40 mg, 275.4 μmol): (12), 43 mg, 113–114°, no product formed.

3,4-Diphenylcyclohex-2-en-1-one was not analyzed for in this particular run, since other thermal runs showed no evidence that this product was formed.

Run C-2. In this run and run C-3 the minor conversions were found due to room fluorescent light.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (87.9 mg, 354.0 μmol) in 40 ml of *t*-butyl alcohol at 69° for 25 hr; activity 12.27 μCi/mmol.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (498.2 mg, 2006 μmol) added to ^{14}C aliquot (10.55 mg, 42.48 μmol): (6), 73 mg, 75–76°, 262.8 ± 1.4, 366.0 μmol recovered; 0% conversion.

4,4-Diphenylcyclohex-2-en-1-one (514.0 mg, 2070 μmol) added to ^{14}C aliquot (35.16 mg, 141.6 μmol): (7), 103 mg, 94–95°, 0.036 ± 0.016, 1.5 × 10⁻² μmol produced, 0% conversion.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (505.7 mg, 2036 μmol) added to ^{14}C aliquot (5.27 mg, 21.22 μmol): (11), 123 mg, 113–114°, 0.021 ± 0.007, 5.8 × 10⁻² product formed, 0% conversion.

3,4-Diphenylcyclohex-2-en-1-one (499.3 mg, 2011 μmol) added to ^{14}C aliquot (36.92 mg, 148.7 μmol): (7), 51 mg, 101–102°, 0.025 ± 0.003, 1 × 10⁻² μmol product formed, 0% conversion.

Run C-3. *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one-5-^{14}C (78.4 mg, 316.0 μmol) in 40 ml of *t*-butyl alcohol at 69° for 5 hr; activity 11.97 μCi/mmol.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (475.4 mg, 1914 μmol) added to ^{14}C aliquot (4.70 mg, 18.92 μmol): (6), 308 mg, 113–114°, 119.78 ± 0.65, 322.0 μmol recovered, 0% conversion.

4,4-Diphenylcyclohex-2-en-1-one (480.1 mg, 1933 μmol) added to ^{14}C aliquot (9.41 mg, 37.89 μmol): (5), 200 mg, 94–95°, no product formed.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (498.0 mg, 2005 μmol) added to ^{14}C aliquot (32.93 mg, 132.6 μmol): (6), 121 mg, 75–76°, 0.050 ± 0.020, 2 × 10⁻² μmol produced, 0% conversion.

3,4-Diphenylcyclohex-2-en-1-one (483.4 mg, 1946 μmol) added to ^{14}C aliquot (31.36 mg, 126.3 μmol): (7), 53 mg, 101–102°, 0.064 ± 0.010, 2.6 × 10⁻² μmol produced, 0% conversion.