Organic and Biological Chemistry

Relative Rates of Aryl Migrations in Excited-State Transformations. Mechanistic and Exploratory Organic Photochemistry. XXXIX[1]

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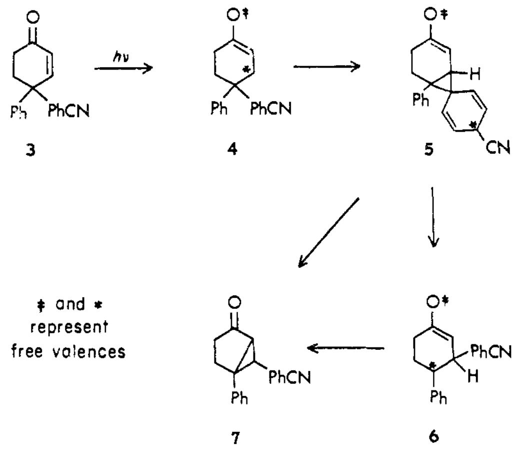
Abstract: The preferential migration of *p*-cyanophenyl relative to phenyl, previously reported in the photochemical transformation of 4-*p*-cyanophenyl-4-phenylcyclohexenone (**3**) to give isomeric 5,6-diarylbicyclo[3.1.0]hexan-2-ones, was studied in mechanistic detail. The selectivity favoring *p*-cyanophenyl over phenyl migration was shown to arise from greater ease of *p*-cyanophenyl migration rather than from reluctance of *p*-cyanophenyl to remain behind. In an intermolecular comparison, the quantum efficiency of *p*-cyanophenyl migration in 4-*p*-cyanophenyl-4-phenylcyclohexenone (**3**) was found to be 0.177 *vs.* 0.022 per phenyl group migrating in the case of 4,4-diphenylcyclohexenone (**1**). Intramolecular comparison revealed selectivity of the same order. The rates of *p*-cyanophenyl and phenyl migration in the triplet excited state of 4-*p*-cyanophenyl-4-phenylcyclohexenone (**3**) were obtained from quenching studies and were found to be 3.35×10^8 sec^{-1}, and 0.309×10^8 sec^{-1}, respectively. This showed the rate of migration of *p*-cyanophenyl in **3** to be much greater than the rate of migration of phenyl in both **1** and **3**, the rate in **1** having previously been shown to be 0.24×10^8 sec^{-1} per phenyl group. Thus a nonmigrating *p*-cyanophenyl group was slightly accelerating compared to a nonmigrating phenyl. A considerably more dramatic effect derived from substitution on the group rearranging; this is in analogy with ground-state chemistry. Strikingly, the rates of triplet decay of **1** and **3** were relatively close, implying that rearrangement and radiationless decay have little in common. It may be concluded from the present study that γ to β aryl migration of cyclohexenones does indeed involve rearrangement to a β-carbon with odd electron capabilities, and no evidence of electron deficiency is revealed. This accords with our previous assumption based on intramolecular competition between *p*-cyanophenyl and phenyl migration.

The photochemical rearrangement of 4,4-diphenylcyclohexenone (**1**) with phenyl migration to give the 5,6-diphenylbicyclo[3.1.0]hexan-2-one (**2**) stereoisomers was encountered in our exploratory studies[2] and was subsequently investigated in electronic and mechanistic detail.[3] As one approach designed to gain insight into the nature of the rearranging excited state and of the rearrangement itself, the rearrangement of 4-*p*-cyanophenyl-4-phenylcyclohexenone (**3**) was investigated[4] with the view that migratory aptitudes could be used as a probe for excited-state electronic makeup and reactivity. It was observed[4] that *p*-cyanophenyl migrated heavily in preference to phenyl. The conclusion was drawn that the rearranging excited state is not electron deficient at the β-carbon, since one would not expect a cyanophenyl group to migrate to a positive center. Rather, the β-carbon was thought to be odd electron in character. Thus in Chart I, the * seemed unlikely to represent a positive charge, since this would require an electron-deficient center on a carbon bearing a cyano group (*i.e.*, in **5**). Similar migratory aptitude studies were carried out concurrently in the case of 4-*p*-cyanophenyl-4-phenyl-1(4H)-naphthalenone[5] and 4-anisyl-4-phenylcyclohexenone.[4]

Chart I. General Mechanism Giving Rise to *p*-Cyanophenyl Migration



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[1] For paper XXXVIII see H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Am. Chem. Soc.*, **91**, 434 (1969). (b) For paper XXXVII note H. E. Zimmerman and H. Iwamura, *ibid.*, **90**, 4763 (1968).

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

[3] (a) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3794 (1968); (b) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **90**, 4892 (1968).

[4] H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, *ibid.*, **89**, 2033 (1967).

[5] H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, *ibid.*, **87**, 1138 (1965).

Table I. Quantum Yields in Direct Irradiations of 4-*p*-Cyanophenyl-4-phenylcyclohexenone

Run[a]	Enone concn, *M*	Light, μEinsteins	Quantum yields, mmol/mEinstein: Enone[b]	*trans*-**9**[c]	*cis*-**10**[c]	*trans*-**11**
1-D	0.0100	60.4	0.193 (±0.002)	0.176 (±0.002)	0.00098 (±0.00002)	0.0159 (±0.0004)
2-D	0.0132	61.7	0.197 (±0.002)	0.179 (±0.002)	0.00102 (±0.00002)	0.0167 (±0.0004)

[a] At 366 nm in benzene at 26.0°. [b] Disappearance of starting material. [c] Appearance of photoproduct.

These led to the same conclusion.

Nevertheless a serious element of uncertainty existed. As was pointed out in these papers, the conclusions rested on certain assumptions which, however reasonable, were not totally unambiguous. It was assumed that in analogy to ground-state aryl migrations, greater stabilization results from substitution of a resonance-stabilizing group on the migrating aryl group rather than on the nonmigrating aryl group remaining behind.[6] Thus if the transition-state or rate-controlling stage of the excited-state transformation were to resemble species **6** of Chart I rather than the assumed **5**, one would expect an excited state with an electron drift toward oxygen (*i.e.*, * = + and $\mp$ = −) to give the observed preferential *p*-cyanophenyl migration. This would result from the reluctance of *p*-cyanophenyl group to "remain behind" rather than from an inherent tendency of the *p*-cyanophenyl group to migrate.

Additionally, in photochemical transformations one has the competitive decay of the excited state to reactant to consider as another factor. In the cyanophenyl *vs.* phenyl comparison it was conceivable that the excited-state species in which phenyl had begun to migrate might preferentially decay back to ground-state reactant with reverse migration. If this occurred, the product distribution (phenyl *vs.* cyanophenyl migrated) would not necessarily be controlled by the ease of migration but could be dominated by relative rates of decay of two partially rearranged species (*e.g.*, **5** and its relative in which phenyl is migrating).

It was therefore necessary in the next level of subtlety to search for operational tests of these possibilities and to obtain evidence revealing the source of the intriguing migratory selectivity observed.

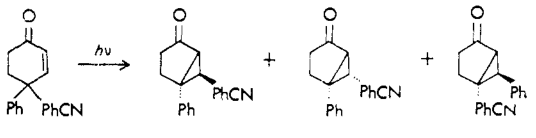
One mode of attack on the problem involved determination of efficiency of the rearrangement of 4-*p*-cyanophenyl-4-phenylcyclohexenone (**3**) relative to 4,4-diphenylcyclohexenone (**1**). If *p*-cyanophenyl migration results from a true preference over phenyl rearrangement, one might expect an enhanced quantum yield for the reaction of **3** *vs.* **1**. Conversely, if cyanophenyl migrates out of reluctance to stay behind, a diminished quantum yield should result. However, it is well recognized that relative quantum yields will give an indication of excited-state reactivities only if the competitive rates of decay are equal, and this cannot generally be taken for granted. Excited-state reaction rates provide a more meaningful guide to reactivity, and it was decided to determine the rates of triplet rearrangement.

The rates of triplet decay were also of interest because of their bearing on an important point in photochemistry, namely whether excited-state decay and reaction are related processes. If so, these should vary in parallel fashion. Specifically in the present instance, one mode of decay might involve incipient rearrangement. Then for different 4,4-diarylcyclohexenones k_r and k_d would vary similarly with structure.

Synthetic Aspects and Methods. The quantum yields were obtained by the method of isotopic dilution, following the general procedure we outlined earlier.[3] This required the synthesis of both radioactive and nonradioactive reactant and nonradioactive products. 4-*p*-Cyanophenyl-4-phenylcyclohexenone (**3**) was synthesized by the procedure described earlier by Zimmerman, Scheffer, and Rieke,[4] the last step of which involved the reaction of 4-*p*-bromophenyl-4-phenylcyclohexenone (**8**) with cuprous cyanide in N-methylpyrrolidone. This procedure allowed introduction of ^{14}C by the use of radioactive cuprous cyanide. The synthetic details are outlined in the Experimental Section.

Results

Irradiation of 4-*p*-cyano-^{14}C-phenyl-4-phenylcyclohexenone in benzene at 366 nm gave the previously reported[4] three products (eq 1), *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**9**), *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**10**), and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**11**). The quantum yields for disappearance of starting material and the appearance of photoproducts **9**, **10**, and **11** are given in Table I.



(1)

3 **9** **10** **11**

For sensitization studies propiophenone was selected, since its triplet (74 kcal/mol)[7] proved energetic enough to excite 4,4-diphenylcyclohexenone with close to unit efficiency.[3a] In these sensitized runs, enone con

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(6) In general, or at least in energetically favorable carbonium ion, free-radical, and carbanion ground-state 1,2 shifts, it is the group substituted with the delocalizing substituent which migrates with kinetic preference, although such migration leaves the free valence (*i.e.*, positive charge, odd electron density, negative charge) on a carbon bearing a phenyl group lacking the helping substituent. This effect seems to arise from the bridged transition state having the free valence heavily localized in the *para* position of the migrating group.

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

Table II. Quantum Yields in Sensitized Irradiations of 4-*p*-Cyanophenyl-4-phenylcyclohexenone

Run[a]	Enone concn, *M*	Light, μEinsteins	Sens[b] (concn, *M*)	Quantum yields, mmol/mEinstein: Enone	*trans*-**9**[c]	*cis*-**10**[c]	*trans*-**11**[c]
1-S[e,i]	0.0101	84.6	Propiophenone (0.217)	0.188 (±0.009)	0.165 (±0.008)	0.0071 (±0.0004)	0.0156 (±0.0008)
2-S[e,i]	0.0104	73.1	Propiophenone (0.219)	0.195 (±0.010)	0.172 (0.009)	0.0068 (±0.0003)	0.0159 (±0.0008)
3-S[e,f]	0.0095	137	Propiophenone (0.244)	(0.212)[d]	0.186 (±0.009)	0.0074 (±0.0004)	*g*
4-S[h–j]	0.0089	141	Benzophenone (0.146)	0.138 (±0.007)	0.125 (±0.006)	0.0010 (±0.00005)	0.0116 (±0.0006)

[a] In benzene at 26.0°. [b] Sensitizer absorbed over 98% of the light. [c] Appearance of photoproduct. [d] Calculated assuming known selectivity. [e] At 313 nm. [f] 6.4 nm half-band width. [g] Not determined. [h] At 366 nm. [i] 22 nm half-band width. [j] The error is based on the propiophenone data.

Table III. Quantum Yields in Quenched Irradiations of 4-*p*-Cyanophenyl-4-phenylcyclohexenone

Run[a]	Enone concn, *M*	Quencher[b] concn, *M*	Light, μEinsteins	Quantum yields, mmol/mEinstein[c]: Enone[d]	*trans*-**9**[e]	*cis*-**10**[e]	*trans*-**11**[e]
1-Q	0.0137	0.651[f]	62.2	0.0389 (±0.0023)	0.0351 (±0.0022)	0.00027 (±0.000017)	0.00351 (±0.00010)
2-Q	0.0170	0.289[f]	98.2	0.0887 (±0.0052)	0.0818 (±0.0052)	0.00038 (±0.000024)	0.00648 (±0.00018)
3-Q	0.0160	0.477[f]	160	0.0567 (±0.0033)	0.0519 (±0.0033)	0.00037 (±0.000023)	0.00445 (±0.00013)
4-Q	0.0195	0.935[h]	116[i]	0.0341 (±0.0020)	0.0312 (±0.0020)	*g*	0.00285 (±0.00008)

[a] In benzene at 366 nm. [b] The enone absorbed over 95% of the available light. [c] Error estimated from the scatter of the data. [d] Disappearance of starting material. [e] Appearance of photoketone. [f] 22 nm half-band width. [g] Not determined. [h] 6.4 nm half-band width. [i] Corrected for a small amount of absorbing impurity formed during the reaction. This internal filter absorbed an average of 6.7% of the light. The effect was negligible at lower quencher concentrations.

centrations of *ca.* 0.01 *M* were used to ensure that the decay rates of the sensitizer singlets[8] and triplets[9] in relation to the pseudounimolecular rate of collision[10] were in the range to allow energy transfer from triplet but not singlet sensitizer. At the same time sufficient sensitizer was used to absorb over 98% of the available light. The quantum yields in sensitized irradiations are listed in Table II.

In order to obtain the desired rate constants and further information bearing on the multiplicity, quenching studies were also carried out. The previous work on 4,4-diphenylcyclohexenone[3a] showed 2,5-dimethyl-2,4-hexadiene to be an efficient quencher. Indeed the present reaction was efficiently quenched with 2,5-dimethyl-2,4-hexadiene. The results of these quenching studies are summarized in Table III.

With the Stern–Volmer relationship (eq 2) in mind, the reciprocals of both individual quantum yields, as well as the total quantum yield, were plotted against quencher concentration [Q]. These plots are given in Figures 1, 2, 3, and 4, and are seen to be reasonably linear over the quenching range studied ($\leqslant 0.93\ M$). The slope of these plots gives k_q/k_r, the bimolecular quenching rate divided by the rate of triplet rearrangement. It is assumed that f, the efficiency of intersystem crossing, is unity (note discussion below). Thus, one can calculate k_r if k_q is known. It was assumed that the quenching process was sufficiently exothermic that quenching approached the diffusion-controlled rate.[3,11,12] The values of k_r calculated are listed in Table IV. These values were used together with the intercept, $(k_r^{\text{tot}} + k_d)/k_r$, of each Stern–Volmer plot to solve for k_d, the rate of excited-state decay to reactant ground state. In using eq 2 it should be noted that k_r^{tot} in the numerator of the intercept is the sum of all the individual reaction constants and that k_d will include

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

(Note: k_r^{tot} is the sum of all reaction rates of triplet)

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(8) F. Wilkinson and J. T. Dubois [*J. Chem. Phys.*, **39**, 3080 (1963)] found the intersystem crossing rate for acetophenone to be over 10^{10} sec^{-1}. Propiophenone has been assumed to have similar properties.

(9) S. G. Cohen, D. A. Laufer, and W. Sherman [*J. Am. Chem. Soc.*, **86**, 3060 (1964)] measured the unimolecular decay rate of triplet acetophenone as *ca.* 10^5 sec^{-1} in solution. A similar rate is taken for propiophenone.

(10) (a) F. Wilkinson, *Advan. Photochem.*, **3**, 241 (1964); (b) H. L. J. Bäckström and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955). A bimolecular diffusion rate of 10^{10} l. mol^{-1} sec^{-1} was assumed by those authors. Note ref 3, footnote 17a for discussion of this point.

(11) Since 4,4-diphenylcyclohexenone was found to be quenched by 2,5-dimethyl-2,4-hexadiene in a close to a diffusion-controlled process and since the *p*-cyanophenyl derivative should have a triplet energy equal to that of the unsubstituted enone diffusion control is presently a reasonable assumption.

(12) In the previous study this quencher was one of the most efficient,[3a] justifying the approximation. As P. J. Wagner and I. Kochevar [*J. Am. Chem. Soc.*, **90**, 2232 (1968)] have noted there are reasons for expecting concave upward Stern–Volmer plots if there is perfect diffusion control and nearest neighbor quenching becomes important at higher quencher concentrations.

Table IV. Rates of Reaction and Rates of Decay

$1/\phi$ *vs.* [Q]	Slope[a]	Intercept[b]	$k_r{}^a \times 10^{-8}$ sec^{-1}	$k_d \times 10^{-8}$ sec^{-1}
Disappearance of **3**	27.2 ± 2.2	5.13 ± 0.10	3.68 ± 0.30	15.2
Appearance of **9**	29.8 ± 2.6	5.63 ± 0.11	3.35 ± 0.29	15.2
Appearance of **10**	4166 ± 504	1000 ± 20	0.0240 ± 0.0029	20.3
Appearance of **11**	323.8 ± 11.9	61.4 ± 1.5	0.309 ± 0.0114	15.3

[a] Errors for slopes are standard deviations. [b] Errors are based on direct irradiation data.

Table V. Product Ratios[a]

	9/11	**9/10**	**11/10**
Direct runs	10.92 ± 0.18	166.5 ± 17.3	15.27 ± 1.72
Sensitized runs (propiophenone)	10.69 ± 0.18	24.48 ± 1.17	2.257 ± 0.095
Sensitized run[b] (benzophenone)	10.77 ± 0.18	125.0 ± 5.97	11.60 ± 0.49
Quenched runs	11.13 ± 1.04	169.4 ± 40.3	15.14 ± 3.02

[a] Mean values and standard deviations, based on listings in Tables I, II, III and additional data listed in the Experimental Section (runs without actinometry). [b] Error was estimated assuming the same scatter as in the propiophenone series.

all modes of decay whether radiative, nonradiative, or involving incipient reaction.

Interpretative Discussion

Reaction Multiplicity. The first matter requiring discussion is the reaction multiplicity. The conclusions of the earlier study[4] that the triplet excited state is responsible for the aryl migration were confirmed. Thus, reference to Tables I and II shows that sensitization by propiophenone led to the same quantum yield, within experimental error, as obtained in direct irradiation runs. Additionally, the product "fingerprint,"[3,13] as determined by quantum yields of major stereoisomers of the cyanophenyl and phenyl migrated products, was the same in the direct irradiation runs as in the propiophenone-sensitized runs where the triplet excited state of the reactant was artificially generated. Similarly, the ratio of these products was insensitive to the extent of quenching in the 2,5-dimethyl-2,4-hexadiene runs (note later discussion). If more than one excited state were involved in the reactions, *e.g.*, one being the lowest energy triplet, then one would expect that the product distribution would change with increasing concentration of quencher. Even with equal (*i.e.*, diffusion controlled) quenching efficiencies, this is so, since in the two cases quenching will be competing against different rates of decay and rates of reaction. Thus it can easily be shown that eq 3 holds in such a case. Here ϕ_{AI} is the

$$\phi_{AI}/\phi_{BII} = (f_A k_{rAI}/f_B k_{rBII})(k_{rB}{}^{tot} + k_{dB} + k_{qB}[Q])/(k_{rA}{}^{tot} + k_{dA} + k_{qA}[Q]) \quad (3)$$

quantum yield of product I derived from excited state A and ϕ_{BII} is the quantum yield of product II derived from excited state B; the k_r's, k_d's, k_q's, and Q have their usual meaning except that the $k_r{}^{tot}$'s represent the sum of all reaction rates deriving from the given excited excited state, A or B. In the numerator and denominator, as the quencher concentration [Q] is increased, the unequal terms $(k_{rB}{}^{tot} + k_{dB})$ and $(k_{rA}{}^{tot} + k_{dA})$ begin less and less to dominate ratio of quantum yields and thus the product distribution. Hence ϕ_{AI}/ϕ_{BII} is a function of [Q].[14]

A further diagnostic test as to whether one or more excited states give rise to the observed products derives from eq 4 which predicts that products which originate from the same excited state will give the same value for the expression $S_i\Phi_{0i}$, where S_i is the slope of the plot of $1/\Phi_i$ *vs.* [Q] for a given product, and Φ_{0i} is the quantum yield of product i in absence of quencher. This is due to the fact the right side of the equation remains constant as long as one excited state is involved. We note that eq 4 also equals $k_q\tau$ which is the slope of

$$S_i\Phi_{0i} = k_q/(k_r{}^{tot} + k_d) \quad (4)$$

the more commonly used plot of Φ_0/Φ *vs.* [Q]. However, the common plot is incapable of giving k_r and k_d and was not used in the present work.

Thus both sensitization and quenching tests confirm the involvement of a single triplet excited state in the formation of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**9**) and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**11**). Table V lists the product distribution in direct, sensitized, and quenched runs. Table VI gives the $S_i\Phi_{0i}$ values.

Table VI. $S_i\Phi_i$ Values[a]

Product	$S_i\Phi_i$
trans-5-Phenyl-6-*p*-cyanophenylbicyclo-[3.1.0]hexan-2-one (**9**)	5.28
trans-5-*p*-Cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (**11**)	5.28
cis-5-Phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**10**)	4.12

[a] The data were obtained from Tables I and IV.

One further point requires comment. We note in Table II that in propiophenone- (E_T = 74 kcal/mol)

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

(14) Interestingly, this prediction of a dependence of product distribution on quencher concentration does not depend on different efficiencies of quenching. For cases where the excited states do not differ in ease of quenching, the two k_q's (numerator and denominator) will have equal values, yet again a product dependence will result. However, the prediction does depend on the excited states (*e.g.*, A and B) not being rapidly equilibrated.

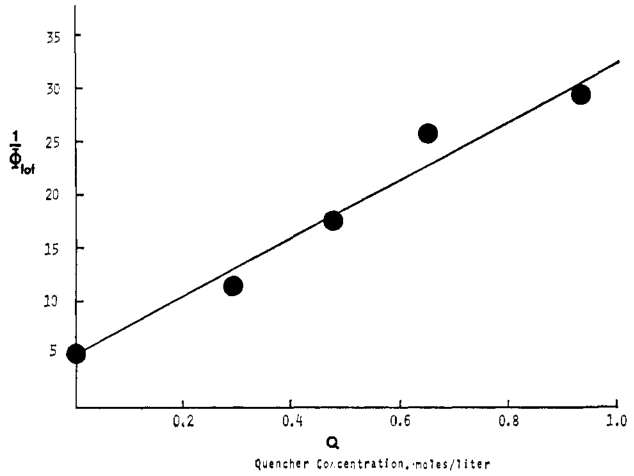

Figure 1. Stern–Volmer plot of total quantum yield.

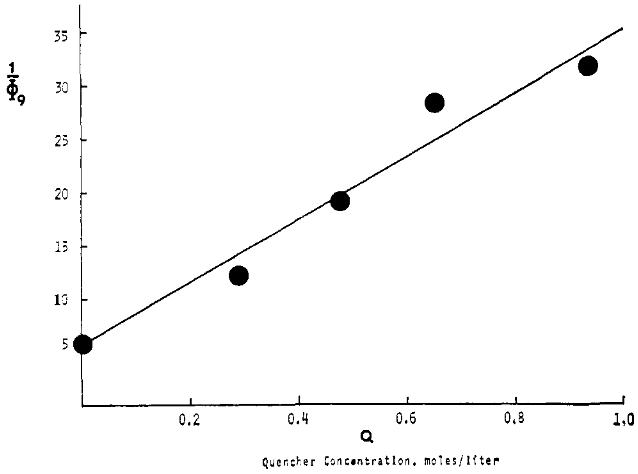

Figure 2. Stern–Volmer plot of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one.

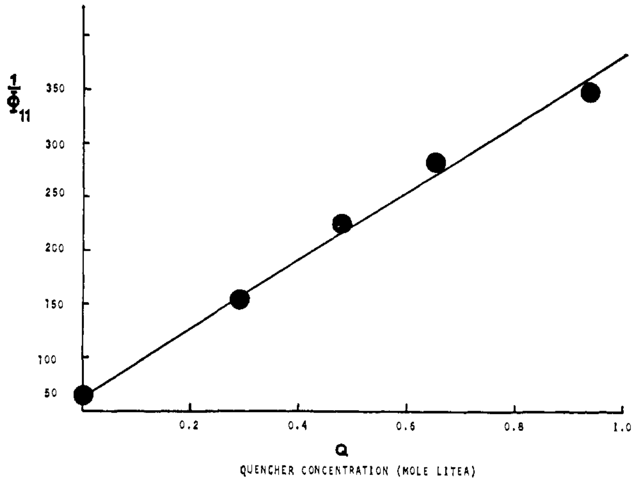

Figure 3. Stern–Volmer plot of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one.

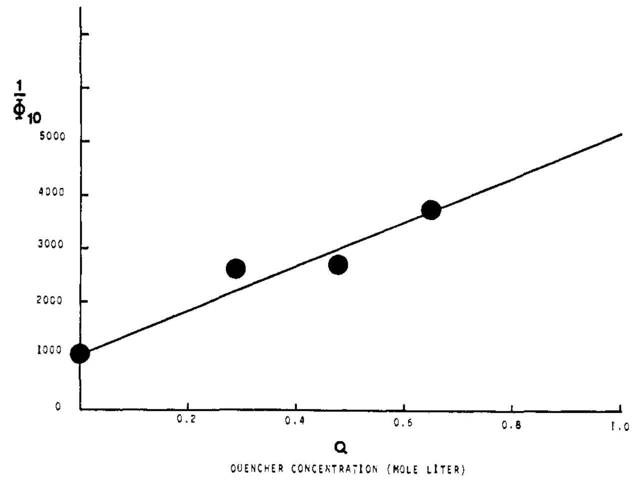

Figure 4. Stern–Volmer plot of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexane-2-one.

sensitized runs the quantum yield of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**10**) is strikingly enhanced. A trivial explanation is secondary conversion of a small amount of the major stereoisomer, *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**9**). However, it can be seen from Table II that the quantum yield for this product is independent of light absorbed and band width. Thus this does not appear to be an experimental artifact. Adding to this conclusion is the observation that the lower energy sensitizer benzophenone (E_T = 68.5 kcal/mol) afforded product ratios approaching that of the direct and quenched runs (note Table V). The observation seems to suggest that with the higher energy sensitizer a higher energy triplet[15] is being formed to varying extents with different stereoselectivity characteristic of this triplet. However, the invariance of migratory aptitudes to sensitizer energy would have to mean that such a higher energy triplet has the same odd electron character in the same degree as the lower triplet. This effect is unusual and is the subject of further study. The effect is absent in direct and quenched runs as seen from the fingerprint invariance.

Discussion of Reaction Efficiency and Source of Migratory Selectivity. As has been noted in the introductory section (*vide supra*), it was an *a priori* possibility that the preferential *p*-cyanophenyl migration resulted from reluctance of this group to remain behind on carbon-4. However, the quantum efficiency of formation of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (**9**) in the present work was found to be 0.177 (Table I). In contrast, the efficiency for a single phenyl group migration[16] in 4,4-diphenylcyclohexenone (**1**) to give *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**12**) was only 0.022[3a] (note Chart II). Thus, the rearrangement involving a migrating *p*-cyanophenyl group is indeed more efficient than one involving a migrating phenyl group and this then cannot be a

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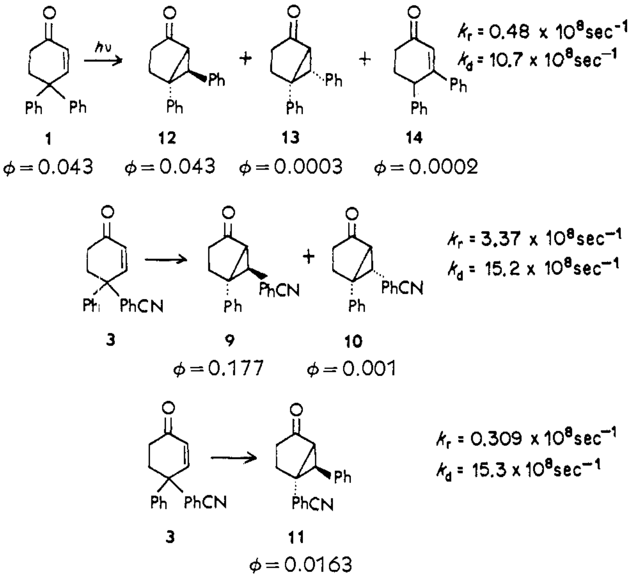
(15) Recent reports of involvement of second triplets in photochemical reactions have been by: (a) R. S. H. Liu and D. M. Gale, *J. Am. Chem. Soc.*, **90**, 1897 (1968); (b) R. S. H. Liu and J. R. Edman, *ibid.*, **90**, 213 (1968); (c) P. de Mayo, J.-P. Pete, and M. Tchir, *ibid.*, **89**, 5712 (1967); (d) N. C. Yang and Robert L. Loeschen, *Tetrahedron Letters*, 2571 (1968).

(16) Since we were interested in the efficiency of migration of a single aryl group, for statistical reasons the quantum yield of 0.043 for diphenylcyclohexenone is halved. Similarly the rate is corrected statistically.

result of reluctance of the *p*-cyanophenyl group to migrate.

Discussion of the Triplet Rearrangement. The importance of knowing the source of enhanced quantum efficiency of the *p*-cyanophenyl migration has been stressed. As noted in Table IV and outlined in Chart II the rate of *p*-cyanophenyl migration with phenyl nonmigrating was found to be 3.35×10^8 sec^{-1} from the quenching studies. This contrasts with the previously determined[3a] rate of 0.24×10^8 sec^{-1} for migration of a single phenyl[16] with phenyl nonmigrating. Thus, cyanophenyl has an advantage of over tenfold. Additionally, it is of interest to inspect the effect of a nonmigrating *p*-cyanophenyl group. It was found (Table IV) that the rate of phenyl migration with *p*-cyanophenyl nonmigrating was 0.309×10^8 sec^{-1}. Consequently, a nonmigrating *p*-cyanophenyl group is slightly accelerating.

Chart II. Quantum Yields, Rates of Rearrangement, and Rates of Decay



These results tell us that in the excited-state rearrangement, at the rate-controlling stage of the process, the free valence is much more heavily localized at the *para* position of the migrating aryl group than in the nonmigrating aryl substituent. This parallels the ground-state situation described above.[6] Additionally, the stabilization by the cyano group both in the migrating and nonmigrating aryl group rules out an electron deficiency in the aryl groups as a result of any electron drift toward oxygen in the excited state. Instead the results accord nicely with the picture in which the β-carbon of the excited state has odd electron character.[4] Finally, loss of electronic excitation, either by an electronic transition or by intersection of the excited- and ground-state potential energy curves, cannot precede the rate-limiting and irreversible stage of the reaction; otherwise, an electron-rich oxygen and electron-deficient aryl group would lead to reversal of selectivity.

The Question of Relationship of Decay and Reaction of Excited States. Another aspect of interest which resulted from the quenching experiments is the rate of decay of 4-*p*-cyanophenyl-4-phenylcyclohexenone triplet, k_d, which was found to be 15.2×10^8 sec^{-1} (note Table IV and Chart II). This is remarkably close to the decay rate for the triplet of 4,4-diphenylcyclohexenone (Chart II) which was reported[3a,17] as $k_d = 10.7 \times 10^8$ sec^{-1}. Thus, despite rates of rearrangement which differ by an order of magnitude, the decay rates are relatively invariant. This is both striking and important since one might have conceived of incipient but unsuccessful migration as constituting one mode of decay. In fact it has been considered that photochemical transformations are closely related to radiationless decay processes leading back to ground state.[18] Of course most photochemical reactions could be stated to constitute radiationless decay processes giving rise to compounds other than the initial reactant, but this is a truism, since in relatively few photochemical reactions does the excited state of the product seem to be formed.[19] Rather, the excited state of reactant more commonly seems to go directly to ground state of the product.[3] However, in the photochemistry under investigation, the decay to product seems to have little in common with the decay back to reactant. In general in our studies, where rearrangement rates and decay rates have been measured,[20] the rates of decay (*i.e.*, the k_d's) have varied less than two powers of ten in cases where rates of unimolecular triplet rearrangement have varied over five powers of ten. It presently seems likely that the correlation between decay to reactant and product will best fit processes not involving major molecular change, perhaps processes such as the stilbene *cis–trans* isomerization.

Experimental Section[21]

4-*p*-Cyanophenyl-4-phenylcyclohexenone. This material was prepared according to the procedure of Zimmerman, Rieke, and Scheffer.[4]

The following is a large-scale adaptation of previously described procedures.[4]

Preparative Photolysis of 4-*p*-Cyanophenyl-4-phenylcyclohexenone. The photolysis was carried out by dissolving 11.4 g of the enone in 1 l. of freshly purified benzene. The irradiation was carried out in an immersion well under nitrogen, with a 450-W Hanovia medium-pressure lamp with a Pyrex filter. The reaction was monitored by removing aliquots and checking their infrared spectra. At the completion of the reaction the 5.95-μ carbonyl band characteristic of the starting material was replaced by a new band at 5.80 μ. The reaction was complete after 4 hr and gave rise to 11.5 g of crude oil.

Separation of Isomeric 5,6-Diarylbicyclo[3.1.0]hexan-2-ones. The crude oil (9.12 g) was chromatographed on a 3.5×90 cm silica gel column (Davison, Grade 950, 60–200 mesh), slurry packed in 20% ether in hexane. Elution in 1-l. fractions gave: 1–6, 25% ether in hexane, nil; 7–12, 30% ether in hexane, 4.94 g of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one, mp 139–

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(17) Calculated from the data in ref 3a, for the quencher used in our experiments (2,5-dimethyl-2,4-hexadiene).

(18) Such a possibility has received comment by G. S. Hammond, 12th Reaction Mechanisms Conference, Brandeis University, Waltham, Mass., June 1968.

(19) One example where product excited state results is the deprotonation of the singlet excited state of phenols and protonation of heterocyclic bases. Here the excited state is detected by its characteristic fluorescence. For a discussion, references, and examples note A. Weller, *Progr. Reaction Kinetics*, 1, 187 (1961).

(20) Note ref 3a for a summary of some of these k_r's and k_d's.

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

140°, which on recrystallization from 1:1 benzene-ether melted at 140–141°. Fractions 13–20, 30% ether in hexane, weighed 1.79 g and consisted of a mixture of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Fractions 21–27, 45% ether in hexane, afforded 1.81 g of *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one, identified by ir. This on recrystallization from 1:1 ether–benzene melted at 158–160°.

A mixture of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one from several photolysis runs (7.1 g) was chromatographed on a 4 × 100 cm silica gel column, slurry packed in 25% ether in hexane. Elution in 1-l. fractions gave: 1–9, nil; 10–16, 3.24 g of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one, mp 139–140°. Fraction 17, 0.31 g, was a mixture of the photoketones. Fractions 18–27, 2.05 g, gave *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]-hexan-2-one, mp 159–160°.

The following was an alternative procedure of preparing 5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. 4-*p*-Bromophenyl-4-phenylcyclohexenone (10.0 g, 30.6 mmol) was photolyzed under nitrogen in 1 l. of benzene for 12 hr using a 450-W Hanovia medium-pressure mercury immersion lamp with Pyrex filter. After concentration under reduced pressure the residue was added to 7.00 g (78.2 mmol) of cuprous cyanide and 35 ml of N-methylpyrrolidone. The mixture was refluxed under nitrogen for 2 hr and then poured into 150 ml of water which contained 6.1 g of sodium cyanide. Benzene extraction and concentration *in vacuo* afforded an oil which was chromatographed on a 4.5 × 60 cm silica gel column, slurry packed in 25% ether in hexane. Elution in 1 l. fractions gave: fractions 1–4, 25% ether in hexane, 0.224 g of uncharacterized gum; 5–7, 0.67 g of a mixture of *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one and *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one. Fractions 8–12 gave 1.77 g of *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one, which after three recrystallizations from 1:1 ether–benzene gave 1.41 g of material, mp 159–160°.

Cuprous Cyanide-^{14}C. A modification of the procedure of Reid and Weaver was used.[22] A solution of potassium cyanide-^{14}C (*ca.* 0.5 mCi, 0.0207 mmol), 0.6105 g (9.375 mmol) of nonradioactive potassium cyanide, and 1.2757 g (10.121 mmol) of sodium sulfite in 50 ml of water was added under a stream of nitrogen and with stirring to 2.5084 g of cupric sulfate (15.72 mmol) in 50 ml of water and 0.05 ml of 12 *N* sulfuric acid. The reaction mixture was stirred for 30 min while the effluent gases were slowly swept into a trap which contained alkaline potassium permanganate. The supernatant liquid and subsequent washings of the solid residue with water, ethanol, and finally ether were removed by suction through a filter stick. The cuprous cyanide, thus obtained as a white solid, was used in the same flask in the next step.

4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone. Dry cuprous cyanide-^{14}C (*ca.* 9.3 mmol) prepared as above and 3.00 g (9.175 mmol) of 4-*p*-bromophenyl-4-phenylcyclohexenone in 7.0 ml of freshly distilled N-methylpyrrolidone were heated for 2 hr at a bath temperature of 165°. The following procedure was adopted to prevent emulsion formation. After cooling, the partially solid reaction mixture was treated alternately with benzene and 20% aqueous potassium cyanide to give a total volume of 500 ml of benzene and 100 ml of aqueous potassium cyanide. The benzene layer was washed with 50 ml of aqueous potassium cyanide and five 100-ml portions of water and concentrated *in vacuo*. The residue was chromatographed on a 3.5-cm diameter column of Woelm alumina (activity 2, 250 g), packed with 15% ether in hexane. Elution with 15% ether in hexane in 1-l. fractions gave: fractions 1–2, 0.0164 g of impure starting material; 6–15, 2.30 g of 4-*p*-cyano-^{14}C-phenyl-4-phenylcyclohexenone, mp 79–80°. Three crystallizations from ether afforded 1.5 g of material, mp 81–82°; $\lambda_{\max}$ (benzene) 337 nm (ϵ 29), specific activity 75.90 μCi/mmol. The mother liquors from the above crystallizations contained less pure radioenone.

Quantum Yields. All determinations were carried out in benzene at 26.0°. Specific data for individual determinations are listed as follows: conditions of irradiation of the ^{14}C reactant (weight, activity, solvent, wavelength, band width, amount of light), followed by isotope dilution data. The amount of each ^{12}C compound used to dilute an aliquot of radioactive reaction mixture is followed by the number of the final recrystallization (in parentheses) from ether or 1:1 ether–benzene, the melting point, asymptotic specific activity (nCi/mmol) with standard error, calculated amount of material recovered or produced, and finally the quantum yield.

The quantum yield for the disappearance of starting material was obtained as the sum of quantum yields for the appearance of the products, since the low conversions used made the errors in the amounts of the reactant employed and recovered of the same order as the amount converted.

Run 1-D. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1039 g, 380.1 μmol), activity 75.90 μCi/mmol, in 38.0 ml of benzene, irradiated at 366 nm, 22 nm half-band width, 60.4 μEinsteins. The photolysate was made up to 100.0 ml with benzene.

The photolysate (5.0 ml, 19.00 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.5624 g, 2058 μmol): (5), 81–82°, 671.5 ± 3.5; 367.4 μmol recovered.

The photolysate (10.0 ml, 38.01 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.5238 g, 1916 μmol): (7), 140–141°, 42.14 ± 0.22; 10.65 μmol produced, $\phi = 0.176$.

The photolysate (25.0 ml, 95.0 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.1995 g, 729.9 μmol): (7), 159–160°, 25.07 ± 0.13; 0.965 μmol produced, $\phi = 0.0159$.

The photolysate (60.0 ml, 228.1 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.4844 g, 1722 μmol): (8), 158–160°, 1.517 ± 0.011; 0.05903 μmol produced, $\phi = 0.00098$.

Run 2-D. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1370 g, 501.2 μmol), activity 75.90 μCi/mmol, in 38.0 ml of benzene, irradiated at 366 nm, half-band width 22 nm, 61.7 μEinsteins. The photolysate was made up to 100 ml with benzene.

The photolysate (5.0 ml, 25.1 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.5813 g, 2127 μmol): (6), 81–82°, 859.80 ± 4.38; 487.4 μmol recovered.

The photolysate (10.0 ml, 50.12 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.5350 g, 1957 μmol): (7), 140–141°, 42.89 ± 0.25; 11.07 μmol produced, $\phi = 0.179$.

The photolysate (20.0 ml, 100.2 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2586 g, 946.1 μmol): (7), 159–160°, 16.53 ± 0.09; 1.031 μmol produced, $\phi = 0.0167$.

The photolysate (65.0 ml, 325.8 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.4950 g, 1811 μmol): (8), 158–160°, 1.718 ± 0.009; 0.06307 μmol produced, $\phi = 0.00102$.

Run 1-S. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1045 g, 382.3 μmol), activity 75.90 μCi/mmol, and propiophenone (1.1081 g, 8259 μmol), in 38.0 ml of benzene, irradiated at 313 nm, 22 nm half-band width, 84.6 μEinsteins; 98.3% of the available light was absorbed by the sensitizer.

The photolysate (5.0 ml, 19.11 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.8854 g, 3239 μmol): (5), 81–82°, 426.07 ± 2.13; 365.9 μmol recovered.

The photolysate (10.0 ml, 38.23 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.9946 g, 3639 μmol); (7), 140–141°, 29.14 ± 0.15; 13.96 μmol produced, $\phi = 0.165$.

The photolysate (20.0 ml, 76.46 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2359 g, 863.1 μmol): (7), 159–160°, 23.28 ± 0.15; 1.322 μmol produced, $\phi = 0.0156$.

The photolysate (65.0 ml, 248.5 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.6036 g, 2208 μmol): (8), 158–160°, 20.73 ± 0.11; 0.6035 μmol produced, $\phi = 0.0071$.

Run 2-S. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1081 g, 395.5 μmol), activity 75.90 μCi/mmol, and propiophenone (1.1164 g, 8321 μmol), in 38.0 ml, irradiated at 313 nm, 22 nm half-band width, 73.1 μEinsteins; 98.2% of the available light was absorbed by the sensitizer. The photolysate (5.0 ml, 19.77 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (1.0526 g, 3851 μmol): (5), 81–82°, 373.7 ± 1.9; 381.2 μmol recovered.

The photolysate (10.0 ml, 39.55 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.9788 g, 3581 μmol): (5), 140–141°, 26.68 ± 0.14; 12.59 μmol produced, $\phi = 0.172$.

The photolysate (20.0 ml, 79.1 μmol) plus *trans*-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.1955 g, 7153 μmol): (6), 159–160°, 24.69 ± 0.13; 1.164 μmol produced, $\phi = 0.0159$.

The photolysate (65.0 ml, 257.1 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.8140 g, 2978 μmol): (8), 158–160°, 8.280 ± 0.042; 0.5008 μmol produced, $\phi = 0.0068$.

Run 3-S. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1000 g, 365.9 μmol), activity 36.77 μCi/mmol, and propiophenone (1.2582 g, 9378 μmol), in 38.0 ml, irradiated at 313 nm, 6.4 nm half-band width, 137 μEinsteins; 98.5% of the light was absorbed by the sensitizer. The reaction mixture was made up to 87.501 g with benzene.

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[22] A. Murray and D. L. Williams, "Organic Syntheses with Isotopes," Interscience Publishers, New York, N. Y., 1958, p 164.

The photolysate (2.6336 g, 11.01 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (1.2290 g, 4497 μmol): (5), 140–141°, 6.268 ± 0.035; 25.47 μmol produced, $\phi = 0.186$.

The photolysate (84.868 g, 354.9 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.5217 g, 1909 μmol): (9), 158–160°, 18.90 ± 0.099; 1.012 μmol produced, $\phi = 0.0074$.

Run 4-S. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.0949 g, 347.2 μmol), activity 75.90 μCi/mmol, and benzophenone (1.0361 g, 5685 μmol), in 39.0 ml of benzene, irradiated at 366 nm, 22 nm band width, 141 μEinsteins; 98.6% of the available light was absorbed by the sensitizer. The reaction mixture was made up to 100.0 ml (87.542 g) with benzene.

The photolysate (4.4413 g, 17.62 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.4977 g, 1821 μmol): (5), 81–82°, 688.0 ± 3.8; 328.3 μmol recovered.

The photolysate (4.4191 g, 17.53 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (1.2073 g, 4417 μmol): (7), 140–141°, 15.27 ± 0.085; 17.59 μmol produced, $\phi = 0.125$.

The photolysate (4.4343 g, 17.59 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2875 g, 1052 μmol): (8), 159–160°, 5.987 ± 0.033; 1.638 μmol produced, $\phi = 0.0116$.

The photolysate (74.248 g, 294.5 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (1.8059 g, 6607 μmol): (9), 158–160°, 0.1374 ± 0.0009; 0.1410 μmol produced, $\phi = 0.0010$.

Run 1-Q. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1423 g, 5206 μmol), activity 75.90 μCi/mmol, and 2,5-dimethyl-2,4-hexadiene (2.7556 g, 25008 μmol), were irradiated in 38.0 ml of benzene at 366 nm, half-band width 22 nm, 62.2 μEinsteins; 95.4% of the light was absorbed by the reactant.

The photolysate (5.0 ml, 26.03 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (1.0152 g, 3714 μmol): (4), 81–82°, 526.4 ± 2.7; 518.8 μmol recovered.

The photolysate (10.0 ml, 52.06 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.8418 g, 3080 μmol): (6), 140–141°, 5.384 ± 0.031; 2.185 μmol produced, $\phi = 0.0351$.

The photolysate (20.0 ml, 104.0 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2038 g, 745.6 μmol): (7), 159–160°, 4.440 ± 0.027; 0.2187 μmol produced, $\phi = 0.00351$.

The photolysate (65.0 ml, 338.4 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.6140 g, 2246 μmol): (9), 158–160°, 0.3656 ± 0.0055; 0.01664 μmol produced, $\phi = 0.00027$.

Run 2-Q. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1771 g, 648.0 μmol), activity 36.77 μCi/mmol, and 2,5-dimethyl-2,5-hexadiene (1.2096 g, 10980 μmol), in 30.0 ml of benzene, were irradiated at 366 nm, half-band width 22 nm, 98.2 μEinsteins; 98.3% of the light was absorbed by the reactant.

The photolysate (5.0 ml, 32.40 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.5840 g, 2137 μmol): (4), 81–82°, 535.3 ± 2.7; 632.7 μmol recovered.

The photolysate (10.0 ml, 64.80 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.9942 g, 3637 μmol): (7), 140–141°, 8.100 ± 0.045; 8.034 μmol produced, $\phi = 0.0818$.

The photolysate (20.0 ml, 129.6 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2397 g, 877.0 μmol): (7), 159–160°, 5.327 ± 0.031; 0.6337 μmol produced, $\phi = 0.00648$.

The photolysate (65.0 ml, 4212 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.5217 g, 1909 μmol): (7), 158–160°, 0.04641 ± 0.00054; 0.03715 μmol produced, $\varphi = 0.00038$.

Run 3-Q. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1659 g, 607.0 μmol), activity 36.77 μCi/mmol, and 2,5-dimethyl-2,4-hexadiene (2.0004 g, 18154 μmol), in 38.8 ml of benzene, were irradiated at 366 nm, half-band width 22 nm, 160 μEinsteins; 97.1% of the available light was absorbed by the reactant.

The photolysate (5.0 ml, 30.35 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.4293 g, 1571 μmol): (3), 81–82°, 663.7 ± 3.4; 577.4 μmol recovered.

The photolysate (25.0 ml, 151.7 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.8682 g, 3176 μmol): (5), 140–141°, 24.053 ± 0.125; 8.317 μmol produced, $\phi = 0.0519$.

The photolysate (25.0 ml, 151.7 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2531 g, 926.0 μmol): (6), 159–160°, 7.077 ± 0.039; 0.7130 μmol produced, $\phi = 0.00445$.

The photolysate (45.0 ml, 273.1 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.2879 g, 1053 μmol): (9), 158–160°, 0.9298 ± 0.0119; 0.0592 μmol produced, $\phi = 0.00037$.

Run 4-Q. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.2072 g, 758.1 μmol), activity 36.77 μCi/mmol, and 2,5-dimethyl-2,4-hexadiene (4.0017 g, 36316 μmol), in 38.85 ml of benzene, were irradiated at 366 nm, half-band width 6.4 nm, 116 μEinsteins (corrected for 6.7% average absorption by an internal filter formed in the course of the reaction), where 95.4% of the light was absorbed by the reactant at the beginning of the reaction. The reaction mixture was made up to 100.0 ml (86.595 g) with benzene.

The photolysate (4.3519 g, 38.16 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (1.0143 g, 3711 μmol): (4), 81–82°, 366.94 ± 1.87; 743.0 μmol recovered.

The photolysate (21.7049 g, 190.0 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (1.1186 g, 4093 μmol): (6), 140–141°, 7.677 ± 0.042; 3.615 μmol produced, $\phi = 0.0312$.

The photolysate (21.6916 g, 189.9 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2611 g, 955.3 μmol): (7), 159–160°, 3.184 ± 0.018; 0.3302 μmol produced, $\phi = 0.00285$.

Runs without Actinometry. **Run 1-O.** 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1030 g, 376.8 μmol), activity 75.90 μCi/mmol, in 38.0 ml of benzene, irradiated at 366 nm, 22 nm half-band width. The photolysate was made up to 100.0 ml with benzene.

The photolysate (10.0 ml, 37.68 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.5222 g, 1911 μmol): (5), 81–82°, 1304 ± 6.9; 333.9 μmol recovered.

The photolysate (10.0 ml, 37.68 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.4992, 1826 μmol): (7), 140–141°, 155.5 ± 0.81; 37.50 μmol produced.

The photolysate (40.0 ml, 150.7 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.4429 g, 1620 μmol): (7), 159–160°, 65.14 ± 0.34; 3.475 μmol produced.

The photolysate (40.0 ml, 150.7 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.4786 g, 1751 μmol): (8), 158–160°, 3.855 ± 0.03; 0.2229 μmol produced.

Run 2-O. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1130 g, 413.4 μmol), activity 75.90 μCi/mmol, in 38.0 ml of benzene, irradiated at 366 nm, 22 nm half-band width. The photolysate was made up to 100.0 ml with benzene.

The photolysate (5.0 ml, 20.67 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.4714 g, 1.725 μmol): (4), 81–82°, 866.9 ± 4.5; 398.5 μmol recovered.

The photolysate (5.0 ml, 20.67 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.5088 g, 1862 μmol): (6), 140–141°, 28.95 ± 0.15; 14.21 μmol produced.

The photolysate (35.0 ml, 144.7 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2472 g, 904.4 μmol): (9), 159–160°, 37.50 ± 0.20; 1.277 μmol produced.

The photolysate (55.0 ml, 227.4 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.4114 g, 1505 μmol): (9), 158–160°, 2.780 ± 0.018; 0.1003 μmol produced.

Run 3-O. 4-*p*-Cyano-^{14}C-phenyl-4-phenylcyclohexenone (0.1980 g, 724.4 μmol), activity 36.77 μCi/mmol, and 2,5-dimethyl-2,4-hexadiene (2.0828 g, 18,900 μmol), in 39.05 ml of benzene, were irradiated at 366 nm, 22 nm half-band width. The reaction mixture was made up to 83.307 g (100.0 ml) with benzene.

The photolysate (4.4054 g, 36.55 μmol) plus 4-*p*-cyanophenyl-4-phenylcyclohexenone (0.9214 g, 337.1 μmol): (4), 81–82°, 375.6 ± 1.92; 689.5 μmol recovered.

The photolysate (8.7918 g, 72.95 μmol) plus *trans*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (1.2732 g, 4658 μmol): (6), 140–141°, 12.73 ± 0.067; 16.02 μmol produced.

The photolysate (21.8978 g, 181.7 μmol) plus *trans*-5-*p*-cyanophenyl-6-phenylbicyclo[3.1.0]hexan-2-one (0.2849 g, 1042 μmol): (6), 159–160° 13.63 ± 0.07; 1.541 μmol produced.

The photolysate (52.211 g, 433.2 μmol) plus *cis*-5-phenyl-6-*p*-cyanophenylbicyclo[3.1.0]hexan-2-one (0.4841 g, 1771 μmol): (9), 158–160°, 1.049 ± 0.008; 0.08447 μmol produced.

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