Electronic Details of the Photochemical Phenyl Migration in 4,4-Diphenylcyclohexenone.[1] Mechanistic Organic Photochemistry. XXXI

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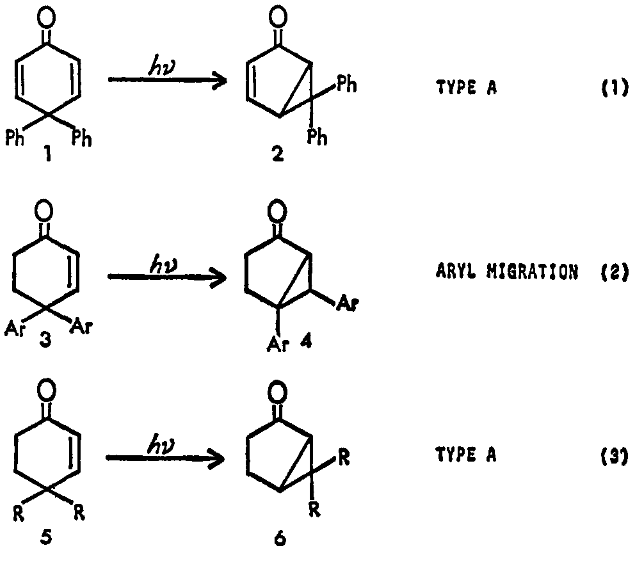
Abstract: The photochemical reaction of 4,4-diphenylcyclohex-2-en-1-one (**7**) to give *trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (**8**), *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**9**), and 3,4-diphenylcyclohex-2-en-1-one (**10**) was examined in mechanistic detail. Inverse isotope dilution determination of quantum yields was employed and found to be a powerful and generally useful method. A "fingerprint" identification technique demonstrated that the reactive excited state was a triplet. An unusually large energy gap between efficient sensitization and quenching was noted and is discussed. The phenyl migration was found to be 20 times less efficient and at least 500-fold slower than the type A rearrangement of 4,4-diphenylcyclohexadienone (**1**) studied earlier. These facts confirmed the postulated role of the second double bond in the type A rearrangement and provided further evidence that the facility of an excited-state reaction is a function of the energy demands of the reaction route. A striking kinetic stereoselectivity of 140:1 favoring formation of the *trans* isomer **8** was encountered. This apparently general stereochemical course is considered. A modest solvent effect on the quantum yield for formation of the bicyclic ketones **8**, **9** was observed, with no corresponding change in the stereoselectivity. A large solvent effect on the efficiency of 3,4-diphenylcyclohex-2-en-1-one (**10**) formation was noted. The phenyl migration reaction was concluded to be more efficient than the type A process of aliphatic enones.

The photochemistry of cyclohexenones and dienones has been the object of intensive study. This is not surprising in view of the dramatic and varied photochemical rearrangements known to occur.

Three rearrangements in the series have been of particular interest (eq 1–3). The general transformation of 4-substituted cyclohexadienones to 6-substituted bicyclo[3.1.0]hex-3-en-2-ones (eq 1), in which the β and γ carbons exchange places, has been termed a type A rearrangement.[2] The example of 4,4-diphenylcyclohexadienone (**1**) has been studied in detail.[3,4] In the second case of interest, 4,4-diarylcyclohexenones (*e.g.*, **3**, eq 2), $\gamma \rightarrow \beta$ aryl migration was found predominant instead.[5-7] Aliphatic cyclohexenones (*e.g.*, **5**, eq 3) also rearrange photochemically to type A products[2,8] reminiscent of the dienone transformation, but a different mechanism must be involved.[2]

The finding that in the case of 4,4-diphenylcyclohex-2-en-1-one (**7**) phenyl migration occurred in preference to a type A rearrangement suggested the tenuous argument that the processes in Chart I become progressively less efficient[5] (*i.e.*, eq 1 > eq 2 > eq 3). Thus, since phenyl migration had been an *a priori* possibility in the dienone **1**, but an experimentally unobserved result, C-3 to C-5 bonding in the excited state and subsequent rearrangement to give a type A product must have been a more efficient process. Aryl migration occurred in cyclohexenones lacking the second double bond, but when no aryl substituent was present as a potential migrating group, then an inefficient mechanism leading to a type A product was enforced. This logic, although reasonable, was imperfect because it utilized intramolecular competition between two processes to predict the relative efficiencies of these pathways in different molecules. Therefore, it was of interest to place comparison of the three rearrangements on a firm quantitative basis by examining the 4,4-diphenylcyclohexenone rearrangement in mechanistic detail.

Chart I. Cyclohexenone and Dienone Rearrangements



A Precise Method of Quantum Yield Determination. When this study was initiated it was clear that for compounds of higher molecular weights, a precise method of analysis was needed. In the case of volatile materials mass spectrometry and vpc allow low-conversion de-

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[1] For paper XXX, note H. E. Zimmerman and R. L. Morse, *J. Am. Chem. Soc.*, **90**, 954 (1968).

[2] (a) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *ibid.*, **88**, 159 (1966); (b) *ibid.*, **88**, 1965 (1966).

[3] H. E. Zimmerman and D. I. Schuster, *ibid.*, **84**, 4527 (1962).

[4] H. E. Zimmerman and J. S. Swenton, *ibid.*, **89**, 906 (1967).

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

[6] H. E. Zimmerman and K. G. Hancock, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, O-130.

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

[8] (a) W. W. Kwie, B. A. Shoulders, and P. D. Gardner, *ibid.*, **84**, 2268 (1962); (b) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963); (c) B. Nann, D. Gravel, G. Schorta, H. Wehrli, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **46**, 2473 (1963).

Table I. Quantum Yields in Direct Irradiations of 4,4-Diphenylcyclohex-2-en-1-one

Run[a]	Enone concn, M	Light, mEinsteins	Quantum yields, mmol/mEinsteins[b]			
			Enone[c]	*trans*[d]	*cis*[e]	3,4-Enone[f]
1[g,j]	0.0054	3.45	0.042 (±0.002)	0.042 (±0.002)	0.0001 (±0.0002)	*l*
2[g,j]	0.0062	6.16	0.047 (±0.002)	0.047 (±0.002)	0.0002 (±0.0002)	0.0002 (±0.0001)
3[h,j]	0.012	0.177	0.043 (±0.002)	0.042 (±0.002)	0.0006 (±0.0002)	0.0002 (±0.0001)
4[h,j]	0.013	0.217	0.044 (±0.002)	0.043 (±0.002)	0.0004 (±0.0002)	*l*
5[i–k]	0.010	1.06	0.042 (±0.002)	0.042 (±0.002)	0.0003 (±0.0002)	0.0001 (±0.0001)
6[i,k,m]	0.011	0.297	0.042 (±0.002)	0.042 (±0.002)	*l*	*l*
7[i,k,n]	0.011	0.318	0.078 (±0.003)	0.073 (±0.003)	0.0003_4 (±0.0001)	0.0048 (±0.0005)
8[i,k,n]	0.011	0.244	0.084 (±0.003)	0.078 (±0.003)	0.0004_1 (±0.0001)	0.0052 (±0.0005)

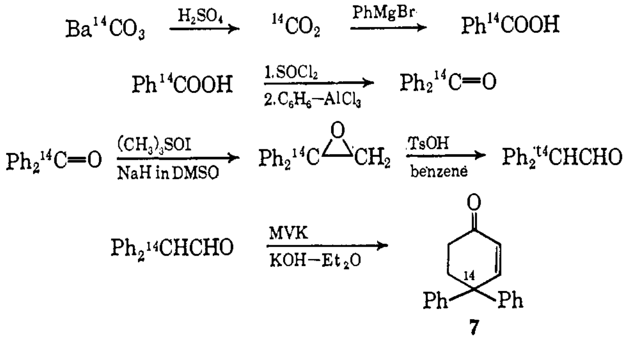
[a] At 366 mμ in benzene at 24.0°. [b] Error estimated from scatter of experimental data. [c] Disappearance of 4,4-diphenylcyclohex-2-en-1-one. [d] Appearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [e] Appearance of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [f] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [g] Macrophotolysis apparatus. [h] Microapparatus and monochromator A. [i] Microapparatus, monochromator B. [j] Van Slyke analysis. [k] Liquid scintillation analysis. [l] Not determined. [m] Using tritiated material. [n] In *t*-butyl alcohol at 27.0°.

terminations with accuracy. A similarly powerful method for nonvolatile organic compounds was required so that even minor products could be studied at low conversion. Isotope dilution was selected.[9]

Labeling of organic molecules was accomplished both by specific synthesis with carbon-14 and by catalytic tritiation of the reactant. A simple method for tritium labeling merely involved exchange between tritium oxide and organic substrate in dioxane solution in the presence of typical hydrogenation catalysts.

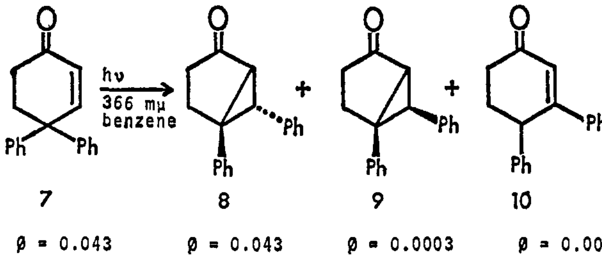
The bulk of this work, however, employed 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C as the labeled material. Preparation (note Chart II) was begun by carbonating phenylmagnesium bromide with radiocarbon dioxide,[10] conversion of the product benzoic acid to benzoyl chloride and thence *via* Friedel–Crafts acylation of benzene to benzophenone-carbonyl-^{14}C. Dimethyloxosulfonium methylide[11] was used to convert the radioactive benzophenone into 1,1-diphenylethylene oxide-1-^{14}C, which was then rearranged to diphenylacetaldehyde with *p*-toluenesulfonic acid. Condensation of 2,2-diphenylacetaldehyde-2-^{14}C with methyl vinyl ketone[12,13] gave 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C in 27% over-all yield based on barium carbonate-^{14}C (Chart II).

Chart II. Synthesis of 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C



The general procedure for microdetermination of quantum yields involved irradiation through a Bausch and Lomb monochromator of *ca.* 100-mg quantities of radioactive reactant. This method allowed conversions below 1% and assay of even minor products with low (*e.g.*, 10^{-4}) quantum yields.

Quantum Yields, Product Distribution, and Stereochemistry. The dual problems of reaction efficiency and mechanism were attacked simultaneously with quantum yield studies. Irradiation of 4,4-diphenylcyclohexenone (**7**) in benzene at 366 mμ gave three ketonic photoproducts, two of which had been identified[5] as *trans*- and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**8** and **9**). The third ketone has now been identified as 3,4-diphenylcyclohex-2-en-1-one (**10**) by isolation and comparison with an authentic sample. The quantum yields for disappearance of starting material and appearance of the three photoproducts, **8**, **9**, and **10**, determined by inverted isotope dilution, are given in eq 4 and Table I. Comparison of runs using ^{3}H-



(4)

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(9) Since completion of these studies, E. F. Ullman and W. A. Henderson, Jr. [*J. Am. Chem. Soc.*, 88, 4942 (1966)], have reported an example of isotope dilution used for quantum yields. In the present work it has proven a general and accurate method. (b) Except where rigorously shown to be accurate, assay by relatively nonspecific methods as uv absorption change can lead to erroneous results due to occurrence of minor but strongly absorbing by-products. Even in the case of vpc, impurities with identical retention times may cause inaccuracy.

(10) W. G. Dauben, J. C. Reid, and P. E. Yankwich, *Anal. Chem.*, 19, 828 (1947).

(11) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 87, 1353 (1965). We thank Professor Corey for prepublication communication of experimental details.

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

(13) N. C. Ross and R. Levine, *J. Org. Chem.*, 29, 2341, 2346 (1964)

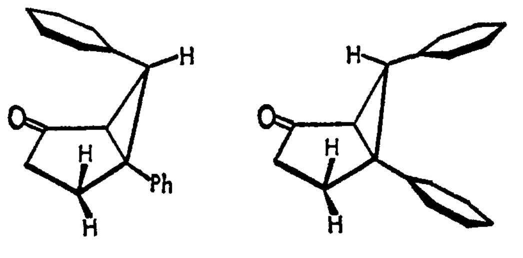


Figure 1. Conformations minimizing repulsions in final products: *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (left) and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (right).

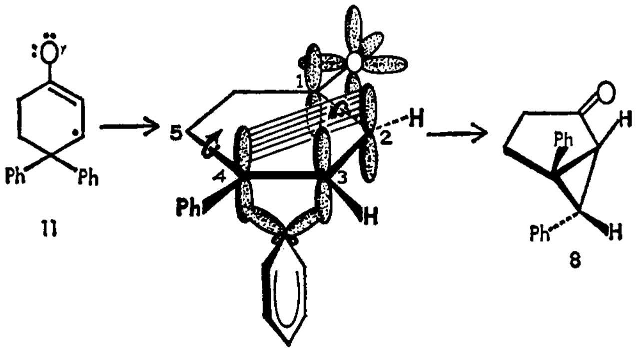
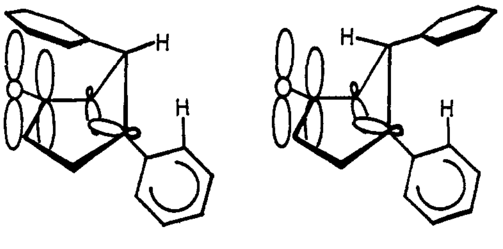


Figure 2. The stereochemical course of aryl migration with inversion of configuration at C-4.



14 or 15-TRANS 14 or 15-CIS

Figure 3. van der Waals repulsions as *trans*-5,6-diphenylbicyclo-[3.1.0]hexan-2-one (left) and *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (right) are being formed; note overlap control of the conformation of the C-4 phenyl group (cyclohexane numbering).

and ^{14}C-enones (runs 1–5 *vs.* 6) indicated no noticeable isotope effect.[14]

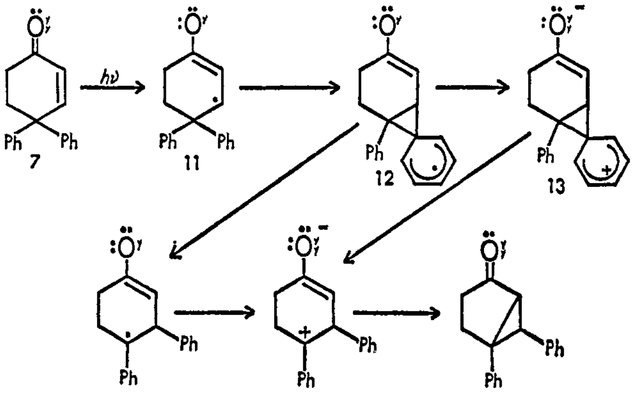
The formation of bicyclic ketone products **8** and **9** from the enone excited state was remarkably stereoselective. Thus, *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one was favored over the *cis* isomer by about 140:1. The ratio was independent of the extent of conversion, ruling out either the formation or destruction of either the *cis* or *trans* isomer in a secondary reaction. This is not surprising since the bicyclic ketone products were transparent at the 366-mμ wavelength used for irradiation.

The observed stereochemistry corresponds to inversion of configuration at C-4 (*vide infra*). This stereochemical course was not the obvious case of mutual avoidance of the two phenyl groups in the product due to van der Waals forces, since the *trans* isomer **8** has the phenyl group at C-5 *endo* to the five-membered ring, and models suggested little difference between the phenyl–phenyl interaction in the *cis*-ketone **9** and the *endo*-phenyl–C-4-methylene interaction in the *trans* compound **8** (Figure 1).

One of two reasonable explanations for the stereoselectivity is a concerted reaction pathway. In the excited state produced by n–π* excitation (**11**), migration of phenyl from C-4 to C-3 generates an incipient p orbital at C-4 (Figure 2). The back lobe of this orbital is situated favorably for overlap with the top lobe of the p orbital at C-2. Thus, rotation about the 1–2 and 4–5 bonds in a disrotatory fashion allows formation of a σ bond between C-2 and C-4 concertedly with phenyl migration from C-4 to C-3. Such a synchronous geometric change leads exclusively to the *trans*-bicyclic ketone **8**.

A second way to rationalize the preferred formation of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**8**), alternative to the concerted mechanism, is stereoelectronic control (Chart III). As noted above, the difference in van der Waals repulsions for the *trans* and *cis* isomers **8** and **9**, once formed, does not appear appreciable (Figure 1). This is because the phenyl groups in the products are free to assume the lowest energy conformations. The same is not true of the transient species in which bond 2–4 (cyclohexane numbering) is being formed. Specifically, the open species **14** or **15** in the nonconcerted pathway suggested originally by Wilson and Zimmerman[5] (Chart III) has a conformational requirement imposed on the phenyl group stabilizing the free valence at C-4. This restriction on free rotation of the C-4 phenyl group remains until 2,4-bonding has been completed. Thus, as illustrated in Figure 3, the phenyl group at C-4 is conformationally fixed; the increased phenyl–phenyl interaction in the pre-*cis* species **14** or **15** could account for preferential formation of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**8**). In any case, an open species such as **14** or **15** seems likely to intervene at least in the formation of the minor stereoisomer.

Chart III. Nonconcerted Mechanism of Wilson and Zimmerman



Similar kinetic preferences for *trans* isomer formation have been noted earlier.[1,7] The inversion of configuration at C-4 thus appears general for photochemical aryl migrations in 4,4-diarylcyclohex-2-en-1-ones (**3**).

Finally, it seems reasonable that 3,4-diphenylcyclohexenone (**10**) arises by hydride migration from C-3 to C-4 in species **15**.

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(14) In the use of tritium, in particular, it is important to ascertain that secondary isotope effects are absent.

Table II. Quantum Yields in Sensitized Irradiations of 4,4-Diphenylcyclohex-2-en-1-one

Run[a]	Enone concn, M	Light, mEinsteins	Sensitizer (concn, M[b])	Quantum yields, mmol/mEinsteins[c]			
				Enone[d]	*trans*[e]	*cis*[f]	3,4-Enone[g]
1[h,k]	0.0098	0.316	Benzophenone[n] (0.13)	0.014 (±0.001)	0.014 (±0.001)	[o]	[o]
2[i,k]	0.0020	8.15	Acetophenone[m] (0.31)	0.015 (±0.003)	0.015 (±0.003)	0.0001 (±0.0002)	0.0001 (±0.0001)
3[i,k]	0.0060	8.02	Acetophenone[m] (0.43)	0.038 (±0.003)	0.038 (±0.003)	0.0002 (±0.0002)	0.0001 (±0.0001)
4[j,k]	0.012	0.170	Acetophenone[m] (0.59)	0.032 (±0.003)	0.031 (±0.003)	0.0005 (±0.0002)	[o]
5[j,k]	0.011	0.196	Acetophenone[m] (0.29)	0.030 (±0.003)	0.030 (±0.003)	0.0004 (±0.0002)	[o]
6[h,k]	0.011	0.218	Propiophenone[m] (0.21)	0.036 (±0.003)	0.036 (±0.003)	[o]	[o]
7[h,l]	0.011	0.286	Propiophenone[m] (0.21)	0.040 (±0.003)	0.039 (±0.003)	0.0003 (±0.0002)	0.0002 (±0.0001)
8[h,l,p]	0.011	0.243	Propiophenone[m] (0.27)	0.088 (±0.003)	0.077 (±0.003)	0.0035 (±0.0005)	0.0066 (±0.0005)

[a] In benzene at 24.0°. [b] Sensitizer absorbing ≥97% of incident light. [c] Error estimated from data. [d] Disappearance of 4,4-diphenylcyclohex-2-en-1-one. [e] Appearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [f] Appearance of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one. [g] Appearance of 3,4-diphenylcyclohex-2-en-1-one. [h] Microapparatus, monochromator B. [i] Macroapparatus. [j] Microapparatus, monochromator A. [k] Van Slyke analysis. [l] Liquid scintillation analysis. [m] 313 mμ. [n] 366 mμ. [o] Not determined. [p] In *t*-butyl alcohol at 27.0°.

Multiplicity and Reaction Rate. The 4,4-diphenylcyclohexadienone (eq 1) and 4,4-dialkyl- (and 4-alkyl-4-aryl-) cyclohexenone (eq 3) rearrangements were known to proceed *via* triplet excited states.[2,4] For a meaningful comparison of the reactivities of **1** and **5** with that of 4,4-diphenylcyclohexenone (**7**) it was necessary to categorize the multiplicity of the latter reaction. The excited species responsible for the striking stereoselectivity was determined by photosensitization (Table II). Under conditions in which over 97% of incident light at 313 mμ was absorbed by propiophenone, the same distribution of products was found as in the direct irradiations. The quantum yield for disappearance of 4,4-diphenylcyclohexenone averaged 0.038, corresponding to *ca.* 90% efficiency in sensitization. Acetophenone likewise gave the same product distribution, but benzophenone was less efficient in sensitization.

Enone concentrations of *ca.* 10^{-2} M were used to ensure that the decay rates of propiophenone singlets[15] and triplets[16] were large and small, respectively, relative to the pseudo-unimolecular rate of collision[17] of enone ground states with sensitizer excited states.

The distribution of products with propiophenone photosensitization constitutes a "fingerprint" characteristic of the triplet state. Obtaining the same product distribution and similar quantum efficiencies (*i.e.*, the same "fingerprint") identifies the reactive state in the direct irradiation as a triplet.[1,7]

Naphthalene was an effective quencher. Up to 80% of the reaction could be quenched with 2.0 M naphthalene (Table III). Additionally, the reciprocal of the quantum yield was found to vary linearly with quencher concentration [Q] (Figure 4) in accordance with the Stern–Volmer expression (eq 5). In order to estimate

$$\frac{1}{\phi} = \frac{k_r + k_d}{k_r} + \frac{k_q}{k_r}[Q] \tag{5}$$

the rate of rearrangement, k_r, from the slope of the plot (k_q/k_r), it was necessary to assign a value for the bimolecular quenching rate constant k_q. Since quenching of 4,4-diphenylcyclohexenone (E_T = 69 kcal/mol)[18] by naphthalene (E_T = 61 kcal/mol)[19] was expected to be exothermic by almost 8 kcal/mol, it had been anticipated that energy transfer would be diffusion controlled.[20] Experimental verification of this expectation was sought by examination of quenching by piperylene, 1,3-cyclohexadiene, and 2,5-dimethyl-2,4-hexadiene.

Table III. Quantum Yields in Quenched Irradiations of 4,4-Diphenylcyclohex-2-en-1-one

Run[a]	Enone concn, M	Naphthalene concn, M[b]	Light, mEinsteins	Quantum yields, mmol/mEinstein[c] enone and *trans*[d]
1[e]	0.006	0.213	5.51	0.030 ± 0.0015
2[f,h]	0.011	0.500	0.138	0.023 ± 0.0011
3[f]	0.020	0.798	0.090	0.018 ± 0.0009
4[f]	0.022	1.02	0.174	0.016 ± 0.0008
5[g]	0.022	1.34	0.495	0.011 ± 0.0005
6[g]	0.022	1.68	0.527	0.010 ± 0.0005
7[g,h]	0.021	2.01	0.621	0.0083 ± 0.0004[i]

[a] At 366 mμ in benzene at 24.0°, Van Slyke analysis. [b] Correction applied for direct absorption by quencher of up to 8% of incident light. [c] Error estimated from data. [d] Disappearance of 4,4-diphenylcyclohex-2-en-1-one and appearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one equal within experimental error. [e] Macrophotolysis apparatus. [f] Microapparatus, monochromator B. [g] *cis*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one and 3,4-diphenylcyclohex-2-en-1-one were below the limits of detection as indicated in run 2. [h] Corrected for spillage before isotopic dilution.

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(15) 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 a similar lifetime.

(16) 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.

(17) (a) F. Wilkinson [*Advan. Photochem.*, **3**, 241 (1964)] gives 10^{10} l. mol^{-1} sec^{-1} for the bimolecular rate of diffusion in benzene. Using this figure, pseudo-unimolecular rates of collision of excited propiophenone singlets and triplets with enone substrate will be 10^8 sec^{-1} at the 0.01 M concentration used. This is too slow for singlet transfer (note ref 15) to compete but fast enough for triplet transfer to take place (ref 16). (b) Note the same value suggested by H. L. J. Bäckström and K. Sandros, *J. Chem. Phys.*, **23**, 2197 (1955).

(18) G. A. Zimmerman, Ph.D. Thesis, University of Wisconsin, 1965, reported the 0–0 band of a weak phosphorescence spectrum of 4,4-diphenylcyclohexenone at 416 mμ.

(19) G. N. Lewis and M. Kasha, *J. Am. Chem. Soc.*, **66**, 2100 (1944).

(20) G. Porter and F. Wilkinson [*Proc. Roy. Soc.* (London), **A264**, 1 (1961)] have suggested that bimolecular triplet energy transfer exothermic by more than 3 kcal/mol is diffusion controlled.

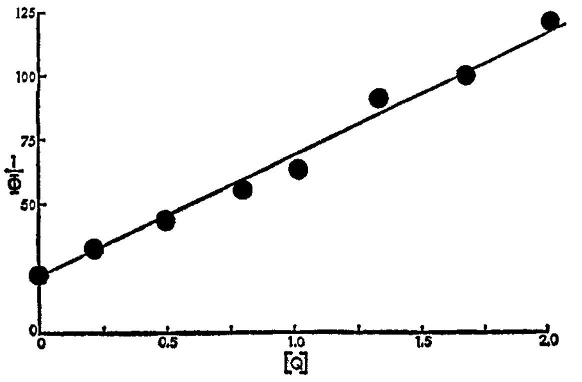

Figure 4. Stern–Volmer plot of quenching of 4,4-diphenylcyclohexenone with naphthalene.

Contrary to expectation, it was found that the three dienes quenched the enone rearrangement at three different rates, all different from the bimolecular rate of quenching observed with naphthalene (Table IV, Figure 5). The trend in these experiments seems to be an increase of quenching rate (or efficiency) with decrease of the triplet energy of the acceptor (Table V).

Table IV. Quantum Yields in Quenched Irradiations of 4,4-Diphenylcyclohex-2-en-1-one

Run[a]	Enone concn, *M*	Quencher[b] (concn, *M*)	Light, mEinsteins	Quantum yields, mmol/mEinstein[c] enone and *trans*[d]
1[e]	0.011	1,3-Pentadiene (0.392)	0.192	0.0221 ± 0.0011
2[e]	0.010	1,3-Pentadiene (1.34)	0.276	0.0096 ± 0.0005
3[f]	0.011	2,5-Dimethyl-2,4-hexadiene (0.392)	0.636	0.0084 ± 0.0004
4[f]	0.013	2,5-Dimethyl-2,4-hexadiene (0.698)	0.393	0.0063 ± 0.0003
5[f]	0.010	2,5-Dimethyl-2,4-hexadiene (1.20)	0.624	0.0037 ± 0.0002
6[f]	0.011	1,3-Cyclohexadiene (0.394)	0.482	0.0077 ± 0.0004
7[f]	0.010	1,3-Cyclohexadiene (0.639)	0.639	0.0034 ± 0.0002

[a] At 366 mμ in benzene at 24.0°, microapparatus with monochromator B. [b] Correction applied for direct absorption by quencher of up to 8% of incident light. [c] Error estimated from data. [d] Disappearance of 4,4-diphenylcyclohex-2-en-1-one and appearance of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one equal within experimental error. [e] Van Slyke analysis. [f] Liquid scintillation analysis.

Table V. Variation of Quenching Rate with the Triplet Energy of the Quencher

Quencher[a]	Triplet energy	k_q/k_r,[b] M^{-1}	"k_r",[c] sec^{-1}
Naphthalene	61[d]	46.6	2.15 × 10^8
1,3-Pentadiene	59[e]	61.7	1.62 × 10^8
2,5-Dimethyl-2,4-hexadiene	58[e]	209.4	0.48 × 10^8
1,3-Cyclohexadiene	53[f]	262.1	0.38 × 10^8

[a] In benzene at 24.0°, 366 mμ. [b] Least-squares slopes from Table IV and Figure 5. [c] Assuming k_q is 1.0 × 10^{10} l. mol^{-1} sec^{-1}. [d] Ref 19. [e] R. E. Kellogg and W. T. Simpson, *J. Am. Chem. Soc.*, **87**, 4230 (1965). [f] A. J. Fry, R. S. H. Liu, and G. S. Hammond, *ibid.*, **88**, 4781 (1966).

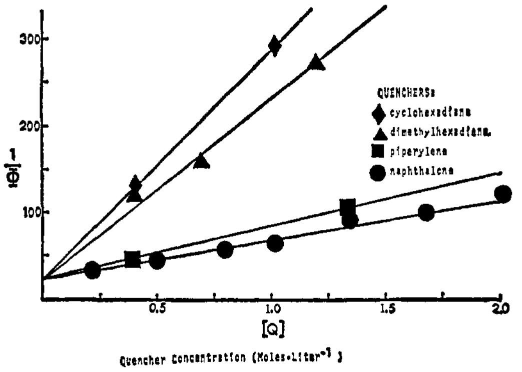

Figure 5. Stern–Volmer plots of variation of quenching rate with triplet energy of quencher for 4,4-diphenylcyclohexenone.

An alternate possibility was variation of the quenching rate with viscosity of the medium. The rate of quenching the valerophenone triplet has been reported by Wagner[21] to vary over a fivefold range during a 15-fold change in solvent viscosity. In the present work, however, the modest differences in viscosity of benzene solutions caused by changing quenchers were found inadequate to produce the fivefold change in k_q/k_r that was observed.[22] Additionally, had viscosity been important, piperylene should have been a very effective quencher; this was not the case.

In view of the large drop in triplet energy between 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene, and the rather small change in quenching rate, it seemed reasonable to suppose a limiting value of 1.0 × 10^{10} l. mol^{-1} sec^{-1} (*i.e.*, the rate of diffusion in benzene) had finally been attained. Thus, the rate of the rearrangement of the 4,4-diphenylcyclohexenone triplet was estimated as 3.8 × 10^7 sec^{-1}.

There is one point of concern, however. In an intriguing study dealing with the quenching of γ-methylvalerophenone with 2,4-hexadien-1-ol, Wagner suggested that there are reasons for expecting concave upward Stern–Volmer plots at higher quencher concentrations in diffusion-controlled reactions.[23] Furthermore, Wagner suggested that linearity at high (*e.g.*, above 0.1 *M*) quencher concentrations should signify less than a diffusion-controlled quenching rate. Neither the present work nor the high quencher concentration Stern–Volmer studies of other workers[24–26] provide evidence for nonlinear plots, and the experimental curve of Wagner was close to linear.

It is possible that solvent and quencher distribution around any molecule (*e.g.*, enone **7**) may not be statistical, with a solvent cage tending to exclude quencher from the cage. Thus there might be fewer quenchers as nearest neighbors than calculated on a macroscopic concentration basis. The rate of diffusion then corresponds to a process of penetrating the solvent cage, the immediate destruction of triplets by nearest neighbors at high quencher concentrations would not result,

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[21] P. J. Wagner, Abstracts, 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967, R-118.

[22] Oswald viscometry for benzene itself and for 1.0 *M* solutions of piperylene, 2,5-dimethyl-2,4-hexadiene, and naphthalene in benzene afforded 5.99, 5.30, 5.71, and 6.97 mP, respectively.

[23] P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 5715 (1967).

[24] E. Y. Y. Lam, D. Valentine, and G. S. Hammond, *ibid.*, **89**, 3482 (1967).

[25] D. J. Patel and D. I. Schuster, *ibid.*, **89**, 184 (1967).

[26] P. E. Eaton and W. S. Hurt, *ibid.*, **88**, 5038 (1966).

and linear Stern–Volmer behavior would be maintained. Alternatively, at modest concentrations the fraction of nearest neighbors might be low enough to afford approximate linearity.

It has been common practice in the literature to accept quenching of a photochemical reaction by high concentrations of dienes as *prima facie* evidence for involvement of a triplet excited state. However, several groups of workers have now accumulated examples of diene quenching of singlet excited states of aromatic hydrocarbons,[27] azo compounds,[28] and fluorenone,[29] despite the diene singlet being of higher energy than the molecule being quenched. The omnipresent possibility that quenching by dienes involves singlets rather than triplets and the complications attending interpretation of Stern–Volmer plots[21,23] reinforce the earlier suggestion[1b,5] that sensitization is really the *sine qua non* evidence for triplet excited states.[30] Identical product distributions under both triplet photosensitization and direct irradiation conditions and similar quantum efficiencies under the two different conditions—the "fingerprint" technique—provide very strong evidence for reactive triplets. Forearmed with fingerprint identification of the triplet, it is then possible to interpret carefully quenching phenomena.

Still, quenching where several products are formed can be used to provide some information on multiplicity. This involves an extension of the fingerprint method described above. Failure of the product distribution to change with extent of quenching can be taken to mean that only one multiplicity species is responsible for the reactions observed and quenched. It would be fortuitous for two species of different configuration to give the same product distribution, and with different extents of quenching the two multiplicity species would be participating in the over-all reaction to differing extents.

Mechanistic Conclusions. Taken together, the sensitization and quenching experiments indicated that a minimum of 90% of the reaction of 4,4-diphenylcyclohexenone (7), and probably all of it, involved the intermediacy of a triplet state. The 0–0 band at 416 mμ (69 kcal/mol) and vibrational spacing (1590 cm^{-1}) in the phosphorescence spectrum[18] were reasonable for an n–π* ketone triplet, produced by intersystem crossing from the initially generated n–π* singlet.

It may be noted that while sensitization became efficient only in the 74-kcal/mol range (*i.e.*, propiophenone), nevertheless quenching was efficient only when 1,3-cyclohexadiene (53 kcal/mol)[31] and 2,5-dimethyl-2,4-hexadiene (58 kcal/mol)[32] were used. This was paradoxical since it is commonly assumed[20] that a 3-kcal/mol energy difference between donor and acceptor is sufficient to allow diffusion-controlled energy transfer. Yet the spread between efficient sensitizers (*e.g.*, 74 kcal/mol) and quenchers (58 kcal/mol) of the 4,4-diphenylcyclohexenone system is about 16 kcal/mol—too large a gap for simple reliance on the 3-kcal figure.

The literature holds observations which may be relevant. One deals with the cycloaddition of cyclopentenone to cyclohexene studied by de Mayo.[33] Successful, but incomplete, sensitization with acetophenone (74 kcal/mol), unsuccessful sensitization with benzophenone (68.5 kcal/mol), and emission at 61 kcal/mol prompted the suggestion of an unreactive low-lying triplet (T_1) state at 61 kcal/mol with the conclusion that the reaction occurred from the higher energy T_2 state. Relatedly, Hammond[24] found a triplet state for cyclohex-2-en-1-one at 61 kcal/mol based on Saltiel plots,[34] and he concluded that the configuration was probably π–π*. The search for a higher energy n–π* triplet in this molecule was unsuccessful.

It is possible that the inefficient sensitization and quenching of 4,4-diphenylcyclohexenone is a result of a gradual approach to diffusion-controlled energy transfer. Alternatively, the apparent discrepancy between triplet energies of efficient sensitizers and quenchers might be indicative of involvement of two cyclohexenone triplet states. The higher triplet, lying at *ca.* 70 kcal/mol and accessible by photosensitization with energetic triplets such as propiophenone (74 kcal/mol),[35] would be the one responsible for the weak emission observed from 4,4-diphenylcyclohexenone.[36] The lower triplet, perhaps lying in the 61-kcal/mol range noted by Hammond,[24] would be quenched only by dienes with relatively low triplet energies (*e.g.*, 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene). The difference between the two triplets might be geometric[37]—the higher triplet T_2 having a relatively planar π system and occurring more often in somewhat constrained cyclohexenones, the lower triplet (T_1) being twisted at the β-carbon[38] and occurring as the emitting state only in simple, flexible cyclohexenones. The large energy gap observed between efficient sensitizers and quenchers would then be the result of rapid internal conversion from T_2 to T_1 at room temperature and subsequent reaction from or quenching of the lower triplet. Being of different geometry than T_2 (*i.e.*, non-Franck–Condon) this species would not be as efficiently formed by sensitization.

Solvent Dependence. Irradiation of 4,4-diphenylcyclohexenone in *t*-butyl alcohol was found to affect both quantum efficiency and product distribution. The change from benzene to *t*-butyl alcohol solvent caused an 85% increase in the quantum yield for disappearance of enone (Table I). The stereoselectivity favoring *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one (**8**)

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[27] L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, 88, 3665 (1966).

[28] S. D. Andrews and A. C. Day, *Chem. Commun.*, 477 (1967).

[29] L. A. Singer and G. A. Davis, *J. Am. Chem. Soc.*, **89**, 158 (1967).

[30] However, for an alternative viewpoint, see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 164; also J. Saltiel in "Survey of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press Inc., New York, N. Y., 1964, p 299.

[31] See Table V, footnote *f*.

[32] See Table V, footnote *e*.

[33] P. de Mayo, J. P. Pete, and M. Tchir, *J. Am. Chem. Soc.*, **89**, 5712 (1967).

[34] (a) G. S. Hammond, *et al.*, *ibid.*, **86**, 3197 (1964); (b) W. G. Herkstroeter and G. S. Hammond, *ibid.*, **88**, 4769 (1966).

[35] W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *ibid.*, **86**, 4537 (1964).

[36] A number of cyclohexenones examined by Zimmerman and McCullough (ref 2, footnote 28) consistently had triplet energies in the 68–71-kcal/mol range.

[37] This discussion places no electronic specifications on the two triplets; both may be n–π* or π–π*, or there may be one of each.

[38] This matter has been discussed by R. Hoffmann (discussions at the International Symposium on Organic Photochemistry, Strasbourg, France, July 20–24, 1964), who reported that twisting of the β-carbon in cyclohexenones is predicted by extended Hückel calculations for the n–π* excited state.

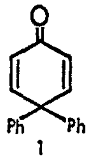
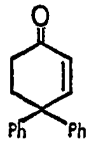
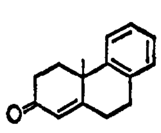
over the *cis* isomer **9** was essentially unchanged, but the proportion of 3,4-diphenylcyclohex-2-en-1-one (**10**) in the product mixture increased 16-fold. Photosensitization with propiophenone (100% efficiency) indicated a triplet state was still involved (Table II).

One possible explanation for the general increase in quantum efficiency observed is a reduced rate of decay, since any factor affecting the electronic environment of the carbonyl oxygen, such as hydrogen bonding, should markedly affect spin–orbit coupling and thus intersystem crossing decay to the ground state. Second, hydrogen bonding at oxygen in the excited state or a subsequent species (such as zwitterion **15**, Chart III) would make hydride migration from C-3 to C-4 more efficient relative to cyclopropane ring formation.[39] In the nonhydroxylic solvent, collapse of the enolate moiety of **15** and the cationic center at C-4 must be especially favorable, whereas the hydrogen-bonded enolate–cationic -C-4 collapse will be less favorable. Such hydrogen bonding or hydrogen transfer at the oxygen should not, however, alter the stereoselectivity.

Another possibility is that change of solvent brings about an inversion of two close-lying triplets. In a polar solvent, a π–π^* state might become lower in energy and take part. Such a triplet could at least be responsible for the greatly enhanced formation of 3,4-diphenylcyclohexenone (**10**).[40]

Conclusion on Reaction Efficiency. The values found for the quantum yield and triplet rearrangement rate of 4,4-diphenylcyclohexenone strongly support the qualitative order of reaction efficiencies suggested by Wilson and Zimmerman[5] (Chart I). The quantum yield, 0.043, is indeed intermediate in magnitude between 4,4-diphenylcyclohexadienone (**1**) (0.85)[4] and alkylated enones such as the tetrahydrophenanthrone **16** (0.0084)[2] (Chart IV). The rate of rearrangement found for **7** is also intermediate. The now inescapable conclusion is that the phenyl migration rearrangement (eq 2, Chart I) is one of intermediate efficiency, interposed between more efficient and less efficient type A processes, and occurs only when the second double bond, prerequisite to C-3 to C-5 bonding in the excited state, is not present (*cf.* Chart IV). One final point is worth noting: it is apparent from Chart IV that the decay rate is relatively insensitive to molecular change in this series of ketones, varying less than 100-fold while the rearrangement rate changes by a factor of 10^5. For this reason, the quantum yield appears to be a very good qualitative guide to the rate of rearrangement.

Chart IV. Quantum Yields and Rearrangement Rates of Cyclohexenones and Dienones

	Ref	ϕ	k_r, sec^{-1}	k_d, sec^{-1}
 **1**	4	0.85	$\geq 2.0 \times 10^{10}$	$\geq 3.5 \times 10^9$
 **7**	Present work	0.043	3.8×10^7	8.4×10^8
 **16**	**2**	0.0084	2.9×10^5	3.9×10^7

Experimental Section[41]

4,4-Diphenylcyclohex-2-en-1-one. Slight modification of the method of Zimmerman, Keese, Nasielski, and Swenton[12] gave a 77% yield of 4,4-diphenylcyclohex-2-en-1-one, mp 94–95° after recrystallization from ethanol.

Benzoic Acid-carboxyl-^{14}C. An adaptation of the procedure of Dauben[10] was used. Barium radiocarbonate (1.5 mCi in 5.89 g, 29.8 mmol), excess sulfuric acid, and 27.3 ml of a 1.13 *M* solution of phenylmagnesium bromide in ether gave 3.1 g (85% based on barium carbonate) of benzoic acid-carboxyl-^{14}C, mp 120–121°.

Benzophenone-carbonyl-^{14}C. Acylation of benzene with benzoyl-carbonyl-^{14}C chloride was done according to Vogel.[42] Radioactive benzoic acid was diluted to 20 g (0.16 mol) with inactive acid (Eastman). Standard treatment with thionyl chloride gave the acid chloride which was treated with excess benzene and aluminum chloride (24 g, 0.18 mol) to give after distillation and crystallization from ethanol 27.4 g (92%) benzophenone-carbonyl-^{14}C, mp 45–48° (γ form), specific activity 17.1 μCi/mol.

1,1-Diphenylethylene-1-^{14}C Oxide. A modification of Corey's procedure[11] was employed. Trimethyloxosulfonium iodide prepared according to Kuhn and Trischmann[43] (34.2 g, 0.155 mol) in 250 ml of DMSO, benzophenone-carbonyl-^{14}C (25.0 g, 0.137 mol) in 50 ml of DMSO, and sodium hydride (7.1 g of a 54% mineral oil suspension, 0.16 mol) gave 25.8 g (96% crude) of 1,1-diphenylethylene-1-^{14}C oxide, mp 49–53° (lit.[44] mp 56°), used without further purification: ir (CCl$_4$), 3.25, 3.29, 3.33, 6.70, 6.92, 7.44, 7.70, 9.86, 10.72, and 11.06 μ; nmr (CCl$_4$), τ 2.75 singlet (10 H, aromatic) and 6.89 singlet (2 H, CH$_2$).

2,2-Diphenylacetaldehyde-2-^{14}C. 1,1-Diphenylethylene-1-^{14}C oxide (25.8 g, 0.13 mol) dissolved in 50 ml of dry benzene was added dropwise to 1.6 g of *p*-toluenesulfonic acid in 300 ml of benzene, dried previously by azeotropic removal of water with a Dean–Stark trap. After 3-hr reflux under nitrogen, the mixture was cooled, extracted with saturated aqueous bicarbonate and with water, dried, filtered, and concentrated *in vacuo*. The residue was distilled at reduced pressure, giving 17.3 g of 2,2-diphenylacetaldehyde-2-^{14}C, bp 111–114° (0.5 mm) (64% from benzophenone), which was used immediately.

4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C. The synthesis of Zimmerman, *et al.*,[12] for inactive material was used with slight modification. 2,2-Diphenylacetaldehyde-2-^{14}C (17.3 g, 88.2 mmol), 7.6 ml of freshly distilled methyl vinyl ketone (90.4 mmol), and 110 ml of ether were mixed and cooled to 0°. A solution of 1.48 g of potassium hydroxide (26.7 mmol) in 8.9 ml of 95% ethanol was added slowly, and the mixture stirred 2 hr at 0°, 2 hr at 25°. Precipitated solid was redissolved by addition of 15 ml of benzene, and the organic phase was extracted with water, acid, and water, dried, and concentrated *in vacuo*, then chromatographed on a 5.5 × 150 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry-packed in 2% ether in hexane. Elution in 500-ml fractions gave the following: fractions 1–8, 2% ether in hexane, nil; 9–18, 5%, nil; 19–28, 10%, 63 mg of radiobenzophenone; 29–38, 15%, nil; 39–53, 25%, 14.3 g of 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C (27% basedon Ba^{14}CO$_3$), mp 92–95°; 54–57, 30%, nil. Recrystallization from ethanol twice gave 13.3 g of 4,4-diphenylcyclohex-2-en-1-one-4-^{14}C, mp 94–95° (lit.[12] 91–94°), specific activity 17.0

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[39] An alternative mechanism for formation of 3,4-diphenylcyclohex-2-en-1-one is β elimination of a proton from C-3 of **15** with tautomerism to the conjugated isomer **10** in work-up. The mild work-up in the isotope dilution runs argues against this.

[40] Such a phenomenon has been reported by G. Porter and P. Suppan, *Proc. Chem. Soc.*, 191 (1964).

[41] Melting points were observed on a hot-stage apparatus and are corrected.

[42] A. I. Vogel, "Practical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1962, p 734.

[43] R. Kuhn and H. Trischmann, *Ann.*, **611**, 117 (1958).

[44] A. Klages and J. Kessler, *Chem. Ber.*, **39**, 1753 (1906).

μCi/mmol. This material was isotopically diluted before use in quantum yield determinations.

***cis-* and *trans*-5,6-Diphenylbicyclo[3.1.0]hexan-2-one.** In a typical preparatory photolysis, 11.5 g (0.0463 mol) of 4,4-diphenylcyclohex-2-en-1-one in 750 ml of dry benzene was irradiated 40 hr under deoxygenated nitrogen[45] through a Pyrex filter with a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well. After removal of solvent, the residue was chromatographed on a 3.4 × 100 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry-packed in 5% ether in hexane. Elution in 250-ml fractions gave the following: fractions 1–3, 5% ether in hexane, nil; 4–9, 10%, nil; 10–22, 15%, 8.00 g of *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one; 23, 16%, 0.08 g of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one; 24–30, 16%, 2.13 g of the *cis*-photoketone, contaminated with photoketone C (*vide infra*); 31–37, 17%, 0.94 g of the *cis*-photoketone, containing *ca.* 15% photoketone C. Three crystallizations of material from fractions 13–22 from ethanol gave 6.1 g of pure *trans*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 76–77° (lit.[5] mp 73–74°). Four crystallizations of material from fractions 23–37 from ethanol gave 2.4 g of pure *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 116–118° (lit.[5] mp 116.5–117.5°). The mother liquors from fractions 23–37 were subjected to liquid-liquid partition chromatography[3] on a 1.5 m × 42 mm column whose stationary phase was a 60% by weight suspension on Celite (Eagle-Picher, Celatom FW 80) of the lower phase of the two-phase mixture of cyclohexane--dimethylformamide–ethyl acetate–water (100:40:25:3, v/v). Elution with the upper phase in 20-ml fractions gave 270 mg of photoketone C, mp 97–99°, in fractions 119–217, and 450 mg of *cis*-5,6-diphenylbicyclo[3.1.0]hexan-2-one, mp 114–117°, in fractions 128–138.

Characterization of Photoketone C. Two crystallizations of photoketone C (*vide supra*) from ethanol and 10% benzene in hexane gave 190 mg of white crystals, mp 99–100°, shown to be 3,4-diphenylcyclohex-2-en-1-one by comparison of ir and nmr spectra and mixture melting point, 99–100°.[46]

3,4-Diphenylcyclohex-2-en-1-one. Methyl vinyl ketone (8.15 ml, 0.10 mol) was added to a stirred solution of 19.6 g (0.10 mol) of desoxybenzoin in 300 ml of diethyl ether at 0° under nitrogen. Potassium hydroxide (1.69 g, 0.030 mol) in 15 ml of 95% ethanol was added over 30 min and the mixture was stirred 1 hr at 0°. The slurry was poured onto 200 g of ice and 35 ml of 1 *N* hydrochloric acid, and the solid aldol adduct was separated by filtration. The filtrate was extracted with water, dried, and concentrated *in vacuo*. The solid adduct and filtrate residue were dissolved in 300 ml of 95% ethanol and 20 ml of concentrated hydrochloric acid and refluxed 2 hr. The cooled mixture was taken up into ether, extracted with water, dried, and concentrated. Crystallization from 90% methanol gave 11.0 g (45%) of slightly yellow 3,4-diphenylcyclohex-2-en-1-one, mp 97–99°. Recrystallization from methanol gave 8.90 g of white crystals, mp 99–100° (lit.[46] mp 99–99.5°). Spectral properties were as follows: ir (CCl$_4$), 3.25, 3.29, 3.39, 3.41, 6.01, 6.24, 6.70, 6.91, 7.50, 7.99, 8.56, 11.31, 14.30, and 14.46 μ; nmr (CCl$_4$), τ 2.80 (singlet over multiplet, 10 H, aromatic), 3.47 (singlet, 1 H, vinyl), 5.78 (triplet, 1 H, allylic methine, J = 3.0 cps), 7.38–8.07 (multiplet, 4 H, two CH$_2$).

Catalytic Tritiation with Rhodium on Alumina. Tritium oxide (46.0 μl, 100 mCi/g, Volk Radiochemicals) was injected into a mixture of 118 mg (0.475 mmol) of 4,4-diphenylcyclohex-2-en-1-one and 49.6 mg of 5% rhodium on alumina[47] in 9.0 ml of dioxane (spectroquality) under nitrogen. After stirring 60 hr at 90°, the solution was taken up in 100 ml of benzene, filtered through sodium sulfate, extracted 20 times with water, dried, and concentrated *in vacuo*. One impurity (not the ring-hydrogenation product) was revealed by tlc (silica gel G, 20% ethyl acetate in hexane).

The concentrate was diluted with 113 mg of untritiated enone and the whole chromatographed on a 1.6 × 60 cm column of silica gel (Davison 950, 60–200 mesh) slurry-packed in 5% ether in hexane. Elution in 125-ml fractions gave the following: fractions 1–4, 5% ether in hexane, 23.3 mg; 5–15, 15%, 227 mg; 16, 15%, 1.5 mg. Recrystallization from benzene of the material in fractions 5–15 gave 180 mg (78%) of 4,4-diphenylcyclohex-2-en-1-one, mp 93–94°, 135 μCi/mmol.

This recrystallized tritiated enone (175 mg, 0.705 mmol) dissolved in 8.0 ml of dioxane and 4.0 ml of 20% aqueous sodium hydroxide was refluxed 12 hr under nitrogen. Work-up involved ten extractions with water, drying, and concentration *in vacuo*. Crystallization from 10% benzene in hexane gave 157 mg (63% over-all) of 4,4-diphenylcyclohex-2-en-1-one, mp 93–94°, activity 0.53 μCi/mmol. Repetition of the base treatment and work-up followed by crystallization from 10% benzene in hexane gave 146 mg (59% over-all) of 4,4-diphenylcyclohex-2-en-1-one, mp 94–95°, activity 0.079 μCi/mmol.

Catalytic Tritiation with Palladium on Charcoal. Tritium oxide (50.0 μl, 100 mCi/g) was injected into a mixture of 253 mg (1.02 mmol) of 4,4-diphenylcyclohex-2-en-1-one and 50.0 mg of 30% palladium on charcoal in 9.0 ml of dioxane under nitrogen. Stirring at reflux 240 hr, followed by filtration, 12 aqueous extractions, drying, and concentration gave material homogeneous to tlc (silica gel G, 20% ethyl acetate or 20% chloroform in hexane). Chromatography in 125-ml fractions on a 1.6 × 60 cm column of silica gel (Davison 950, 60–200 mesh) slurry-packed in 5% ether in hexane gave the following: fractions 1–2, 5% ether in hexane, 16.4 mg; 3–4, 10%, 12.4 mg; 5–6, 10%, nil; 7–11, 15%, 241 mg; 12, 15%, nil. Crystallization from 10% benzene in hexane of material in fractions 7–11 gave 236 mg (93%) of 4,4-diphenylcyclohex-2-en-1-one, mp 93–94°, activity 19.0 μCi/mmol.

Tritiated enone (230 mg, 0.926 mmol) was stirred with 4.0 ml of 20% aqueous sodium hydroxide in 9.0 ml of dioxane 12 hr at 90° under nitrogen. The mixture was taken up in 50 ml of ether, extracted seven times with water, dried, and concentrated *in vacuo*. Crystallization from 10% benzene in hexane gave 220 mg (87% over-all) of 4,4-diphenylcyclohex-2-en-1-one, mp 93.5–95.0°, activity 1.25 μCi/mmol. Repetition of the basic exchange procedure and work-up returned 218 mg (99%) of 4,4-diphenylcyclohex-2-en-1-one, mp 93.5–94.5°, activity 1.27 μCi/mmol. Chromatography in 125-ml fractions on a 1.6 × 60-cm column of alumina (Fisher, 80–200 mesh) dust-packed in 5% ether in hexane gave the following: fractions 1–2, 5% ether in hexane, 5.3 mg; 3–4, 10%, 1.3 mg; 5–10, 20%, nil; 11–12, 40%, 3.3 mg; 13–14, 60%, nil; 15–18, 80%, 218 mg; 19–20, 80%, nil. Crystallization from 10% benzene in hexane of the material in fractions 15–18 gave 206 mg (82% over-all) of 4,4-diphenylcyclohex-2-en-1-one, mp 94–95°, activity 0.90 μCi/mmol.

Catalytic Tritiation with Platinum Black.[48] Platinum oxide trihydrate (68.6 mg, 0.244 mmol) was reduced at atmospheric pressure in 8.0 ml of dioxane, then flushed with nitrogen. 4,4-Diphenylcyclohex-2-en-1-one (251 mg, 1.01 mmol) was introduced in 2.0 ml of dioxane, followed by 50.0 μl of tritium oxide, activity 100 mCi/g. After stirring 120 hr at 90° under nitrogen the organic solution was taken into hexane, filtered, extracted 12 times with water, dried, and concentrated *in vacuo*. Chromatography in 125-ml fractions on a 1.6 × 60 cm column of silica gel (Davison 950, 60–200 mesh) slurry-packed in 5% ether in hexane gave the following: fractions 1–4, 5% ether in hexane, 3.3 mg; 5–8, 10%, 0.5 mg; 9–12, 15%, 243 mg of 4,4-diphenylcyclohex-2-en-1-one, mp 92.5–94.0°, activity 8.40 μCi/mmol.

Treatment of the 243 mg of tritiated enone from chromatography with 4.0 ml of 20% aqueous sodium hydroxide in 8.0 ml of dioxane 12 hr at 90° under nitrogen was followed by dilution with 50 ml of ether, extraction with water, drying, and concentration *in vacuo* to give 238 mg (95% over-all) of 4,4-diphenylcyclohex-2-en-1-one, mp 93–94°, activity 0.94 μCi/mmol. Repetition of the base treatment and work-up was followed by chromatography on a 1.6 × 60 cm column of silica gel (Davison 950, 60–200 mesh) slurry-packed in 5% ether hexane. Elution in 125-ml fractions gave the following: fractions 1–2, 5% ether in hexane, 3.5 mg; 3–4, 10%, 0.4 mg; 5–6, 15%, nil; 7–10, 20%, 230 mg of 4,4-diphenylcyclohex-2-en-1-one, mp 94–95°, activity 0.91 μCi/mmol. Material from fractions 7–10 was rechromatographed on a 1.6 × 60 cm column of alumina (Fisher, 80–200 mesh) dust-packed in 5% ether in hexane. Elution in 125-ml fractions gave the following: fractions 1–2, 5% ether in hexane, 3.4 mg; 3–4, 10%, 1.2 mg; 5–6, 20%, nil; 7–8, 40%, nil; 9–12, 70%, 215 mg (86% over-all) of 4,4-diphenylcyclohex-2-en-1-one, mp 93.5–94.5°, activity 0.89 μCi/mmol.

Quantum Yield Equipment. Quantum yield photolyses were performed on both macro- and microscales. The irradiation vessel for macroruns consisted of two identical consecutive compartments 12.5 cm in diameter with 5-cm optical paths, quartz-faced, and

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[46] E. C. Dodds, R. L. Huang, W. Lawson, and R. Robinson, *Proc. Roy. Soc.* (London), **140B**, 470 (1953).

[47] (a) W. K. Hall and F. E. Lutinski, *J. Catalysis*, **2**, 518 (1963); (b) G. C. Bond and J. M. Winterbottom, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1967, U-1.

[48] (a) L. C. Leitch, *Can. J. Chem.*, **32**, 813 (1954); (b) J. L. Garnett, L. J. Henderson, W. A. Sollich, and G. V. D. Tiers, *Tetrahedron Letters*, **15**, 516 (1961).

fitted for thermostating, stirring, and nitrogen purging. The light source for macroruns was a General Electric AH6 high-pressure mercury arc centered at the focus of a parabolic aluminum reflector 13.7 cm long and 14.0 cm in diameter. Light was filtered through a 2.0-mm Corex D plate (Corning 9700) and through three 2.4-cm water-cooled compartments separated by 12.5-cm diameter quartz disks. The filtered light intensity was monitored with an RCA 935 phototube mounted between filter and reaction vessels.

Microphotolyses were carried out on an L-shaped optical bench in quartz-faced[49] thermostated cells 26 mm i.d., with a 10-cm optical path, under deoxygenated nitrogen[45] and with stirring. A 2 × 2 × $^1/_{16}$ in. quartz plate mounted at 45° proved a convenient beam splitter. One actinometer cell was situated perpendicularly to the main optical path and level with the beam splitter. Two light sources were used: A, a General Electric 1000-W AH6 lamp focused on a Bausch and Lomb 500-mm grating monochromator with a water-cooled collecting lens; and B, an Osram HBO 200-W super-pressure mercury lamp in series with a Bausch and Lomb high-intensity monochromator.

Filter Combinations. Four sets of three-component filters were designed for use in the macrophotolysis apparatus. Transmission spectra of the filters were recorded immediately before and following photolyses in a cell containing three 2.4-cm compartments, using a 7.2-cm water cell as reference. Variation in filter transmission over the course of a photolysis was always less than 1% at the transmission maximum. Cobalt sulfate heptahydrate, nickel sulfate hexahydrate, and stannous chloride dihydrate salts were employed.

Filter A was made up of the following: cell 1, 1.0 *M* cobalt salt (281.1 g/l.) in 5% sulfuric acid; cell 2, 0.1 *M* nickel salt (26.3 g/l.) in 5% sulfuric acid; cell 3, 0.2 *M* tin salt (45.1 g/l.) in 15% hydrochloric acid; transmission, 0% below 325 mμ, 50% at 350 mμ, 1% at 395–425 mμ, 0% above 425 mμ.

Filter B was made up of the following: cell 1, 1.0 *M* cobalt salt (281.1 g/l.) in 5% sulfuric acid; cell 2, 0.3 *M* nickel salt (78.8 g/l.) in 5% sulfuric acid; cell 3, 0.11 *M* tin salt (24.8 g/l.) in 11% hydrochloric acid; transmission, 0% below 320 mμ, 33% at 340 mμ, 0% above 370 mμ.

Filter C was made up of the following: cell 1, 1.0 *M* cobalt salt (281.1 g/l.) in 5% sulfuric acid; cell 2, 0.4 *M* nickel salt (105.1 g/l.) in 5% sulfuric acid; cell 3, 0.09 *M* tin salt (20.3 g/l.) in 11% hydrochloric acid; transmission, 0% below 315 mμ, 39% at 338 mμ, 0% above 370 mμ.

Filter D was made up of the following: cell 1, 1.0 *M* cobalt salt (281.1 g/l.) in 5% sulfuric acid; cell 2, 0.1 *M* nickel salt (26.3 g/l.) in 5% sulfuric acid; cell 3, 0.7 *M* tin salt (157.8 g/l.) in 15% hydrochloric acid; transmission, 0% below 335 mμ, 31% at 357 mμ, 1% at 390–425 mμ, 0% above 425 mμ.

Quantum Yield Irradiations. The same basic procedure was employed in both macro- and microscale determinations. Each determination involved run 1 with actinometer solution in two consecutive, identical cells, run 2 with the organic reactants in the first cell and actinometer in the second, and run 3, identical with run 1. In practice, less than 5% of incident light was transmitted by the first cell. In runs done on the optical bench, the transmission to reflection ratio of the quartz-beam splitter (*ca.* 10:1) was calculated during runs 1 and 3. Available light was indicated by runs 1 and 3, and by collection of light deflected by the beam splitter into a ferrioxalate cell during run 2. Available light in quenched runs was corrected, when necessary, for direct absorption of part of the incident light by quencher.

Potassium ferrioxalate actinometry[50] was employed. After irradiation of 0.006 *M* ferrioxalate in 0.1 *N* sulfuric acid, 2.00-ml aliquots were withdrawn, treated with 3.0 ml of 0.1% 1,10-phenanthroline monohydrochloride in water and 2.0 ml of buffer (49.3 g of sodium acetate and 10.0 ml of concentrated sulfuric acid diluted to 1 l. with water), and diluted to 25.0 ml with water. Absorbance of the ferrous phenanthroline complex was measured at 510 mμ on a Beckman Model DU spectrometer and ferrous ion production read from a calibration graph after subtraction of the optical density of a blank. Quantum efficiencies for ferrioxalate were taken as 1.21, 1.24, and 1.25 at 366, 313, and 256 mμ.[50] The apparatus was checked at 366 mμ with uranyl oxalate[51] actinometry.

Ca. 0.01 *M* solutions of radioactive substrates in benzene were irradiated at 24.0 ± 0.1°, except where otherwise indicated. Ultraviolet spectra recorded immediately before and after photolysis were within 0–5% of calculated spectra assuming Beer's law. After removal of solvent *in vacuo* (and quencher or sensitizer, when present), the ^{14}C organic residue was diluted volumetrically. Aliquots were withdrawn volumetrically for isotopic dilution with accurately weighed excesses of pure ^{12}C photoproducts and starting material.

Quenchers and Sensitizers. Naphthalene (Baker and Adamson resublimed grade) was recrystallized from methanol, then resublimed at 40° (0.1 mm) before use, and was removed from ^{14}C-photolysate by chromatography of the mixture on silica gel (Davison, Grade 950, 60–200 mesh). Naphthalene was eluted with 5% ether in hexane; photoproducts were then eluted with 25% ether in hexane. Naphthalene removed showed no contamination with radioactive material.

Piperylene (Aldrich) was distilled under nitrogen before use and was removed after photolysis along with solvent under reduced pressure. 2,5-Dimethyl-2,4-hexadiene (Aldrich) was distilled, bp 134°, before use through an H. S. Martin spinning-band column. Only fractions showing correct nmr integration were retained. When used as quencher, 2,5-dimethyl-2,4-hexadiene was removed by chromatography on a 1-m silica gel column with 5% ether in hexane eluent or by short-path distillation at 35° (0.1 mm). 1,3-Cyclohexadiene (Aldrich) was distilled from hydroquinone at room temperature under nitrogen immediately before use and was removed following photolysis *in vacuo* along with solvent.

Acetophenone (Matheson Coleman and Bell) was distilled, bp 91° (36 mm), before use and was removed by short-path distillation at 35° (0.1 mm). Propiophenone (Pennsylvania Coal Products) was distilled twice, bp 41° (0.15 mm), before use and was removed by short-path distillation at 40° (0.01 mm). Benzophenone (Eastman) was distilled, bp 112 (0.3 mm), recrystallized from 95% ethanol, and vacuum-dried before use. Removal was accomplished by chromatography on silica gel with 10% ether in hexane eluent. Analysis showed no radioactive contamination.

Viscosity Measurements.[52] The viscosity of 1.00 *M* solutions of quenchers (*vide supra*) in benzene was measured at 25.0 ± 0.1° with an Ostwald viscometer previously calibrated with water.[52] Densities, fall times (average of four determinations), and viscosities (millipoise) were as follows: naphthalene (6.408 g in 50.0 ml, 1.00 *M*), 0.8911 g/ml, 141.6 ± 0.3 sec, 6.97; piperylene (3.407 g in 50.0 ml, 1.00 *M*), 0.8540 g/ml, 113.6 ± 0.3 sec, 5.30; 2,5-dimethyl-2,4-hexadiene (5.514 g in 50.0 ml, 1.00 *M*), 0.8553 g/ml, 121.7 ± 0.3 sec, 5.71; pure benzene, 0.8714, 125.0 ± 0.3 sec, 5.99 (lit.[53] 6.02 mP).

Specific Activity of ^{14}C Compounds. Assay was accomplished by combustion and/or liquid scintillation. In the first method, combustion with Van Slyke reagents[54] was followed by vacuum-line distillation of carbon dioxide into a Bernstein–Ballentine ionization tube, calibrated with standard radiobenzoic acid. Propane was used as the ionizing gas and the ionization rate was determined on a proportional counter and scaler (Baird–Atomic). In the second method, 1–10-mg samples in a scintillator solution of 4.0 g of PPO (2,5-diphenyloxazole, Nuclear-Chicago) and 0.05 g of POPOP (1,4-bis[2-(5-phenyloxazoyl)]benzene, Nuclear-Chicago) in 1 l. of toluene (Matheson Coleman and Bell, scintillation grade) were counted in a Nuclear-Chicago Mark I scintillation system. Quench correction was done by channels ratio on a ^{133}Ba external standard; secondary checks were provided by the net external standard count rate and by straight channels ratios on ^{14}C samples.

Quantum Yields. Specific data for individual determinations are listed as follows: first, conditions for the irradiation of ^{14}C-labeled reactant (weight, solvent, wavelength, and amount of light), followed by isotope dilution data. The weight of each ^{12}C compound used to dilute an aliquot of the labeled reaction mixture is followed by the number of the final recrystallization (from 10% benzene in hexane or 5% methanol in hexane), recovered weight, melting point, asymptotic specific activity (nCi/mmol) with standard error; calculated amount of starting material recovered or product produced; and quantum yield. The quantum yield for

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[49] An epoxy adhesive not containing aromatic or other low-energy chromophores was used to cement quartz faces to Pyrex cells.

[50] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

(51) W. G. Leighton and G. S. Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).

(52) The pycnometer and viscometer were supplied and calibrated by Professor J. C. Nichol.

(53) E. W. Washburn, Ed., "International Critical Tables," Vol. V, McGraw-Hill Book Co. Inc., New York, N. Y., 1929, p 12.

(54) (a) D. D. Van Slyke and J. Folch, *J. Biol. Chem.*, **136**, 509 (1940); (b) D. D. Van Slyke, J. Plarin, and T. R. Weisiger, *ibid.*, **191**, 299 (1951).

disappearance of reactant has been obtained only as the sum of quantum yields for appearance of products, since the low conversions made the absolute errors in amounts of reactant used and recovered comparable in magnitude to their difference.

Run I-01. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (1.004 g, 4044 μmol), specific activity 8.64 μCi/mmol, in 750 ml of benzene at 25.0° irradiated in the macroapparatus (filter A) at 325–400 mμ, 3.45 mEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (901.0 mg, 3629 μmol) added to ^{14}C-photolysate (99.3 mg, 399.9 μmol): 6, 47 mg, 94.0–95.0°, 801.0 ± 6.0; 3,749 μmol recovered.

trans-5-6-Diphenylbicyclo[3.1.0]hexan-2-one (452.1 mg, 1821 μmol) added to ^{14}C-photolysate (44.0 mg, 177.2 μmol): 5, 33 mg, 76.0–77.0°, 29.8 ± 0.3; 144 μmol produced; ϕ = 0.0417 ± 0.002.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (111.3 mg, 448.2 μmol) added to ^{14}C-photolysate (11.9 mg, 48.1 μmol): 7, 14 mg, 116.0–118.0°, 0.11 ± 0.10; 0.49 μmol produced; ϕ = 1.4 (± 2.0) × 10^{-4}.

Run I-02. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (1.153 g, 4644 μmol), activity 11.76 μCi/mmol, in 750 ml of benzene at 25.0° irradiated in the macroapparatus (filter A) at 325–400 mμ, 6.16 mEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (885.0 mg, 3,564 μmol) added to ^{14}C-photolysate (93.7 mg, 377.4 μmol): 6, 207 mg, 94.0–95.0°, 1050.0 ± 4.0; 4298 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (456.9 mg, 1840 μmol) added to ^{14}C-photolysate (49.9 mg, 201.1 μmol): 7, 97 mg, 76.0–77.0°, 79.7 ± 0.3; 289 μmol produced; ϕ = 0.047 ± 0.002.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (126.7 mg, 510.3 μmol) added to ^{14}C-photolysate (14.0 mg, 56.3 μmol): 8, 19 mg, 116.0–118.0°, 0.35 ± 0.06; 1.25 μmol produced; ϕ = 2.0 (± 2.0) × 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (166.9 mg, 672.2 μmol) added to ^{14}C-photolysate (23.6 mg, 94.9 μmol): 5, 37 mg, 100.0–101.0°, 0.355 ± 0.060; 0.99 μmol produced; ϕ = 1.6(± 1.0) × 10^{-4}.

Run I-03. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (113.4 mg, 456.7 μmol), activity 11.76 μCi/mmol, in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 366 mμ, 177.4 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (594.5 mg, 2394 μmol) added to ^{14}C-photolysate (45.4 mg, 182.7 μmol): 6, 295 mg, 94.0–95.0°, 815.7 ± 2.4; 446.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (410.7 mg, 1654 μmol) added to ^{14}C-photolysate (45.4 mg, 182.7 μmol): 6, 97 mg, 76.0–77.0°, 21.35 ± 0.14; 7.52 μmol produced; ϕ = 0.0424 ± 0.002.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (304.0 mg, 1224 μmol) added to ^{14}C-photolysate (22.7 mg, 91.3 μmol): 9, 44 mg, 116.0–118.0°, 0.217 ± 0.067; 0.11 μmol produced; ϕ = 6.4 (± 2.0) × 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (307.2 mg, 1237 μmol) added to ^{14}C-photolysate (45.4 mg, 182.7 μmol): 5, 18 mg, 99.0–100.0°, 0.159 ± 0.059; 0.042 μmol produced; ϕ = 2.4(± 1.0) × 10^{-4}.

Run I-04. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (120.1 mg, 483.7 μmol), activity 11.76 μCi/mmol, in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 366 mμ, 217.0 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (573.6 mg, 2310 μmol) added to ^{14}C-photolysate (36.0 mg, 145.1 μmol): 6, 250 mg, 94.0–95.0°, 679.5 ± 2.2; 471.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (427.6 mg, 1722 μmol) added to ^{14}C-photolysate (36.0 mg, 145.1 μmol): 6, 103 mg, 76.0–77.0°, 19.30 ± 0.20; 9.42 μmol produced; ϕ = 0.0434 ± 0.002.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (448.5 mg, 1806 μmol) added to ^{14}C-photolysate (48.0 mg, 193.5 μmol): 14, 95 mg, 116.0–118.0°, 0.247 ± 0.065; 0.095 μmol produced; ϕ = 4.4 (± 2.0) × 10^{-4}.

Run I-05. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (97.9 mg, 394.3 μmol), activity 11.76 μCi/mmol, in 38.0 ml of benzene irradiated through monochromator B (band width 30 mμ) at 366 mμ 1.083 mEinsteins; analysis by Van Slyke method, checked by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (406.5 mg, 1637 μmol) added to ^{14}C-photolysate (19.6 mg, 78.9 μmol): 4, 197 mg, 94.0–95.0°, 480.7 ± 1.9; 348.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (612.7 mg, 2468 μmol) added to ^{14}C-photolysate (39.2 mg, 157.7 μmol): 4, 357 mg, 76.0–77.0°, 85.87 ± 0.44; 45.4 μmol produced; ϕ = 0.0419 ± 0.002.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (395.8 mg, 1,594 μmol) added to ^{14}C-photolysate (39.2 mg, 157.7 μmol): 10, 78 mg, 116.0–118.0°, 0.846 ± 0.076; 0.286 μmol produced; ϕ = 2.6 (± 2.0) × 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (318.6 mg, 1283 μmol) added to ^{14}C-photolysate (39.2 mg, 157.7 μmol): 5, 9 mg, 99.0–100.0°, 0.494 ± 0.010; 0.13 μmol produced; ϕ = 1.2 (± 1.0) × 10^{-4}.

Run I-06. 4,4-Diphenylcyclohex-2-en-1-one-$^{3}H_{x}$[55] (102.2 mg, 411.6 μmol), activity 10.9 μCi/mmol, in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 297.2 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (553.7 mg, 2230 μmol) added to ^{3}H-photolysate (40.9 mg, 164.6 μmol): 4, 114 mg, 94.0–95.0°, 727.3 ± 2.3; 398.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (512.1 mg, 2062 μmol) added to ^{3}H-photolysate (61.3 mg, 247.0 μmol): 4, 36 mg, 76.0–77.0°, 39.85 ± 0.19; 12.6 μmol produced; ϕ = 0.0424 ± 0.002.

Run I-07. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (102.4 mg, 412.4 μmol), activity 12.12 μCi/mmol, in 38.0 ml of *t*-butyl alcohol at 27.0° irradiated through monochromator B (band width 22 mμ) at 366 mμ, 318.1 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (478.1 mg, 1925 μmol) added to ^{14}C-photolysate (12.3 mg, 49.5 μmol): 4, 108 mg, 94.0–95.0°, 291.3 ± 0.9; 395.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (421.6 mg, 1698 μmol) added to ^{14}C-photolysate (12.3 mg, 49.5 μmol): 4, 68 mg, 76.0–77.0°, 19.89 ± 0.09; 23.3 μmol produced; ϕ = 0.0732 ± 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (408.6 mg, 1646 μmol) added to ^{14}C-photolysate (45.1 mg, 181.5 μmol): 11, 22 mg, 116.0–118.0°, 0.345 ± 0.004; 0.107 μmol produced; ϕ = 3.4 (± 1.0) × 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (360.3 mg, 1451 μmol) added to ^{14}C-photolysate (32.8 mg, 132.0 μmol): 6, 72 mg, 99.0–100.0°, 4.044 ± 0.015: 1.51 μmol produced; ϕ = 4.8(± 0.5) × 10^{-3}.

Run I-08. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (105.6 mg, 425.3 μmol), activity 12.12 μCi/mmol, in 38.0 ml of *t*-butyl alcohol at 27.0° irradiated through monochromator B (band width 22 mμ) at 366 mμ, 243.5 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (485.8 mg, 1957 μmol) added to ^{14}C-photolysate (12.7 mg, 51.0 μmol): 4, 148 mg, 94.0–95.0°, 308.1 ± 1.0; 424.9 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (462.1 mg, 1861 μmol) added to ^{14}C-photolysate (12.7 mg, 51.0 μmol): 5, 52 mg, 76.0–77.0°, 14.80 ± 0.05; 19.0 μmol produced; ϕ = 0.0779 ± 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (410.2 mg, 1652 μmol) added to ^{14}C-photolysate (46.5 mg, 187.1 μmol): 11, 84 mg, 116.0–118.0°, 0.325 ± 0.005; 0.101 μmol produced; ϕ = 4.1 (± 1.0) × 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (430.4 mg, 1733 μmol) added to ^{14}C-photolysate (33.8 mg, 136.1 μmol): 5, 119 mg, 99.0–100.0°, 2.82 ± 0.02; 1.26 μmol produced; ϕ = 5.2 (±0.5) × 10^{-3}.

Run II-01. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (92.4 mg, 372.5 μmol), activity 11.76 μCi/mmol, and 861 mg of benzophenone (4,730 μmol, 0.125 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 315.6 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (424.6 mg, 1,710 μmol) added to ^{14}C-photolysate (18.5 mg, 745.1 μmol): 4, 161 mg, 94.0–95.0°, 489.4 ± 1.9; 371.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (552.8 mg, 2226 μmol) added to ^{14}C-photolysate (37.0 mg, 149.0 μmol): 4, 168 mg, 76.0–77.0°, 9.61 ± 0.15; 4.55 μmol produced; ϕ = 0.014 ± 0.001.

Run II-02. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (375.1 mg, 1,511 μmol), activity 11.76 μCi/mmol, and 28.0 g of acetophenone (0.232 mol, 0.311 *M*) in 750 ml of benzene at 25.0° irradiated in the macroapparatus (filter B) at 320–370 mμ, 8153 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (1.022 g, 4114 μmol) added to

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(55) 4,4-Diphenylcyclohex-2-en-1-one tritiated by the platinum black method was mixed with material tritiated by rhodium on alumina catalysis which had not been purged of α-tritium by treatment with base. This mixture was recrystallized from 10% benzene in hexane to give 4,4-diphenylcyclohex-2-en-1-one, constant specific activity 10.9 μCi/mmol, for use in this study.

^{14}C-photolysate (120.0 mg, 483.4 μmole): 6, 292 mg, 94.0–95.0°, 1127.0 $\pm$ 5.0; 1,362 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (483.0 mg, 1945 μmol) added to ^{14}C-photolysate (60.0 mg, 241.7 μmol): 7, 69 mg, 76.0–77.0°, 118.0 $\pm$ 1.0; 123.3 μmol produced; ϕ = 0.015 $\pm$ 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (292.4 mg, 1178 μmol) added to ^{14}C-photolysate (30.0 mg, 120.9 μmol): 7, 99 mg, 116.0–118.0°, 0.707 $\pm$ 0.062; 0.89 μmol produced; ϕ = 1.1 ($\pm$ 2.0) $\times$ 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (285.7 mg, 1151 μmol) added to ^{14}C-photolysate (30.0 mg, 120.9 μmol): 7, 65 mg, 100.0–101.0°, 0.817 $\pm$ 0.074; 1.00 μmol produced; ϕ = 1.2 ($\pm$1.0) $\times$ 10^{-4}.

Run II-03. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (1.122 g, 4,518 μmol), activity 11.76 μCi/mmol, and 38.45 g of acetophenone (0.320 mol, 0.427 *M*) in 750 ml of benzene at 25.0° irradiated in the macroapparatus (filter C) at 315–370 mμ, 8020 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (1,000 mg, 4,028 μmol) added to ^{14}C-photolysate (112.2 mg, 451.8 μmol): 4, 686 mg, 94.0–95.0°, 1116.0 $\pm$ 3.0; 4222 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (535.3 mg, 2156 μmol) added to ^{14}C-photolysate (56.1 mg, 225.9 μmol): 5, 301 mg, 76.0–77.0°, 82.16 $\pm$ 0.41; 303.3 μmol produced; ϕ = 0.0378 $\pm$ 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (292.0 mg, 1176 μmol) added to ^{14}C-photolysate (33.7 mg, 135.5 μmol): 7, 116 mg, 117.0–118.0°, 0.502 $\pm$ 0.050; 1.67 μmol produced; ϕ = 2.1 ($\pm$ 2.0) $\times$ 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (282.8 mg, 1139 μmol) added to ^{14}C-photolysate (33.7 mg, 135.5 μmol): 7, 100 mg, 100.0–101.0°, 0.350 $\pm$ 0.062; 1.13 μmol produced; ϕ = 1.4 ($\pm$ 1.0) $\times$ 10^{-4}.

Run II-04. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (109.1 mg, 439.4 μmol), activity 11.76 μCi/mmol, and 2.673 g of acetophenone (0.0223 mol, 0.586 *M*) in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 313 mμ, 169.6 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (597.9 mg, 2408 μmol) added to ^{14}C-photolysate (34.9 mg, 140.6 μmol): 4, 288 mg, 94.0–95.0°, 662.1 $\pm$ 2.6; 448.7 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (465.5 mg, 1875 μmol) added to ^{14}C-photolysate (34.9 mg, 140.6 μmol): 5, 79 mg, 76.0–77.0°, 10.65 $\pm$ 0.13; 5.31 μmol produced; ϕ = 0.0313 $\pm$ 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (342.4 mg, 1379 μmol) added to ^{14}C-photolysate (39.3 mg, 158.2 μmol): 13, 56 mg, 116.0–118.0°, 0.243 $\pm$ 0.061; 0.079 μmol produced; ϕ = 4.7 ($\pm$ 2.0) $\times$ 10^{-4}.

Run II-05. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (103.8 mg, 418.0 μmol), activity 11.76 μCi/mmol, and 1.309 g of acetophenone (0.0109 mol, 0.287 *M*) in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 313 mμ, 196.4 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (619.2 mg, 2494 μmol) added to ^{14}C-photolysate (37.4 mg, 150.5 μmol): 5, 332 mg, 94.0–95.0°, 662.7 $\pm$ 2.2; 413.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (582.7 mg, 2347 μmol) added to ^{14}C-photolysate (37.4 mg, 150.5 μmol): 5, 231 mg, 76.0–77.0°, 10.50 $\pm$ 0.15; 5.82 μmol produced; ϕ = 0.0297 $\pm$ 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (426.0 mg, 1716 μmol) added to ^{14}C-photolysate (29.1 mg, 117.0 μmol): 13, 78 mg, 116.0–118.0°, 0.149 $\pm$ 0.063; 0.078 μmol produced; ϕ = 4.0 ($\pm$ 2.0) $\times$ 10^{-4}

Run II-06. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (105.1 mg, 423.3 μmol), activity 11.76 μCi/mmol, and 1.046 g of propiophenone (0.0078 mol, 0.205 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 313 mμ, 218.2 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (842.7 mg, 3394 μmol) added to ^{14}C-photolysate (42.0 mg, 169.3 μmol): 4, 467 mg, 94.0–95.0°, 551.5 $\pm$ 2.1; 417.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (489.2 mg, 1970 μmol) added to ^{14}C-photolysate (63.1 mg, 254.0 μmol): 5, 123 mg, 76.0–77.0°, 27.78 $\pm$ 0.31; 7.77 μmol produced; ϕ = 0.0356 $\pm$ 0.003.

Run II-07. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (104.1 mg, 419.3 μmol), activity 11.76 μCi/mmol, and 1.047 g of propiophenone (0.0078 mol, 0.205 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 313 mμ, 286.4 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (432.1 mg, 1740 μmol) added to ^{14}C-photolysate (16.7 mg, 67.1 μmol): 4, 116 mg, 94.0–95.0°, 426.1 $\pm$ 1.5; 396.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (406.8 mg, 1638 μmol) added to ^{14}C-photolysate (20.8 mg, 83.9 μmol): 5, 132 mg, 76.0–77.0°, 16.66 $\pm$ 0.11; 11.3 μmol produced; ϕ = 0.0394 $\pm$ 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (301.2 mg, 1213 μmol) added to ^{14}C-photolysate (33.3 mg, 134.2 μmol): 10, 61 mg, 116.0–118.0°, 0.285 $\pm$ 0.060; 0.089 μmol produced; ϕ = 3.1 ($\pm$2.0) $\times$ 10^{-4}.

3,4-Diphenylcyclohex-2-en-1-one (313.7 mg, 1263 μmol) added to ^{14}C-photolysate (33.3 mg, 134.2 μmol): 6, 46 mg, 99.0–100.0°, 0.168 $\pm$ 0.060; 0.055 μmol produced; ϕ = 1.9 ($\pm$1.0) $\times$ 10^{-4}.

Run II-08. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (100.9 mg, 406.4 μmol), activity 12.12 μCi/mmol, and 1.380 g of propiophenone (0.0103 mol, 0.271 *M*) in 38.0 ml of *t*-butyl alcohol at 27.0° irradiated through monochromator B (band width 22 mμ) at 313 mμ, 242.5 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (583.3 mg, 2349 μmol) added to ^{14}C-photolysate (12.1 mg, 48.8 μmol): 4, 165 mg, 94.0–95.0°, 248.3 $\pm$ 0.8; 409.3 μmol recovered.[56]

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (477.8 mg, 1924 μmol) added to ^{14}C-photolysate (12.1 mg, 48.8 μmol): 4, 63 mg, 76.0–77.0°, 14.19 $\pm$ 0.08; 18.8 μmol produced; ϕ = 0.0774 $\pm$ 0.003.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (418.4 mg, 1685 μmol) added to ^{14}C-photolysate (44.4 mg, 178.8 μmol): 12, 40 mg, 116.0–117.5°, 2.68 $\pm$ 0.011; 0.85 μmol produced; ϕ = 3.5 ($\pm$ 0.5) $\times$ 10^{-3}.

3,4-Diphenylcyclohex-2-en-1-one (480.6 mg, 1936 μmol) added to ^{14}C-photolysate (32.3 mg, 130.0 μmol): 5, 69 mg, 99.0–100.0°, 3.218 $\pm$ 0.012; 1.60 μmol produced; ϕ = 6.6 ($\pm$ 0.5) $\times$ 10^{-3}.

Run III-01. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (1108 mg, 4,463 μmol), activity 11.76 μCi/mol, and 20.48 g of naphthalene (0.160 mol, 0.213 *M*) in 750 ml of benzene at 25.0° irradiated in the macroappartus (filter D) at 335–400 mμ, 5,513 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (1000 mg, 4029 μmol) added to ^{14}C-photolysate (110.8 mg, 446.3 μmol): 4, 610 mg, 94.0–95.0°, 1116.0 $\pm$ 3.0; 4,225 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (445.6 mg, 1795 μmol) added to ^{14}C-photolysate (55.4 mg, 223.2 μmol): 4, 281 mg, 76.0–77.0°, 54.50 $\pm$ 0.23; 167.0 μmol produced; ϕ = 0.0303 $\pm$ 0.0015.

Run III-02. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (103.6 mg, 417.2 μmol), activity 11.76 μCi/mmol, and 2.434 g of naphthalene (0.0190 mol, 0.500 *M*) in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 366 mμ, 137.6 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (687.7 mg, 2770 μmol) added to ^{14}C-photolysate (41.4 mg, 166.9 μmol): 4, 463 mg, 94.0–95.0°, 659.4 $\pm$ 2.0; 411.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (602.3 mg, 2426 μmol) added to ^{14}C-photolysate (41.4 mg, 166.9 μmol): 4, 311 mg, 76.0–77.0°, 6.03 $\pm$ 0.13; 3.11 μmol produced; ϕ = 0.0226 $\pm$ 0.0011.

cis-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (230.4 mg, 927.9 μmol) added to ^{14}C-photolysate (10.4 mg, 41.7 μmol): 11, 50 mg, 116.0–118.0°, 0.000 $\pm$ 0.06; product formation below limits of detection.

3,4-Diphenylcyclohex-2-en-1-one (187.6 mg, 755.5 μmol) added to ^{14}C-photolysate (10.4 mg, 41.7 μmol): 6, 47 mg, 99.0–100.0°, 0.000 $\pm$ 0.06; product formation below limits of detection.

Run III-03. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (184.6 mg, 743.5 μmol), activity 11.76 μCi/mmol, and 3.887 g of naphthalene (0.0303 mol, 0.798 *M*) in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 366 mμ, 90.3 μEinstein; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (923.4 mg, 3719 μmol) added to ^{14}C-photolysate (73.8 mg, 297.4 μmol): 4, 510 mg, 94.0–95.0° 847.4 $\pm$ 2.4; 720.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (645.3 mg, 2599 μmol) added to ^{14}C-photolysate (73.8 mg, 297.4 μmol): 4, 209 mg, 76.0–77.0°, 2.90 $\pm$ 0.10; 1.60 μmol produced; ϕ = 0.0177 $\pm$ 0.0009.

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(56) Mass balance unexplainably high by *ca.* 6%.

Run III-04. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (204.0 mg, 821.6 μmol), activity 11.76 μCi/mmol, and 4.949 g of naphthalene (0.0386 mol, 1.017 *M*) in 38.0 ml of benzene irradiated through monochromator A (band width 17 mμ) at 366 mμ, 173.9 μEinstein; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (763.9 mg, 3077 μmol) added to ^{14}C-photolysate (81.6 mg, 328.6 μmol): 5, 529 mg, 94.0–95.0°, 1115.0 ± 3.0, 804.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (804.0 mg, 3238 μmol) added to ^{14}C-photolysate (81.6 mg, 328.6 μmol): 5, 264 mg, 76.0–77.0°, 3.943 ± 0.080; 2.71 μmol produced; $\phi = 0.0156 \pm 0.0008$.

Run III-05. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (209.6 mg, 844.1 μmol), activity 11.76 μCi/mmol, and 6.522 g of naphthalene (0.0509 mol, 1.34 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 495.0 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (954.0 mg, 3842 μmol) added to ^{14}C-photolysate (83.8 mg, 337.7 μmol): 5, 482 mg, 94.0–95.0°, 932.4 ± 3.3; 827.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (556.6 mg, 2242 μmol) added to ^{14}C-photolysate (83.4 mg, 337.7 μmol): 5, 170 mg, 76.0–77.0°, 11.37 ± 0.15; 5.42 μmol produced; $\phi = 0.0110 \pm 0.0005$.

Run III-06. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (202.3 mg, 814.7 μmol), activity 11.76 μCi/mmol, and 8.187 g of naphthalene (0.0639 mol, 1.68 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 527.0 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (828.1 mg, 3335 μmol) added to ^{14}C-photolysate (80.9 mg, 325.9 μmol): 4, 428 mg, 94.0–95.0°, 1041.0 ± 4.0; 809.8 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (567.1 mg, 2284 μmol) added to ^{14}C-photolysate (80.9 mg, 325.9 μmol): 4, 211 mg, 76.0–77.0°, 10.84 ± 0.15; 5.26 μmol produced; $\phi = 0.0100 \pm 0.0005$.

Run III-07. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (198.8 mg, 800.6 μmol), activity 11.76 μCi/mmol, and 9.807 g of naphthalene (0.0766 mol, 2.01 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 621.2 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (787.0 mg, 3170 μmol) added to ^{14}C-photolysate (74.7 mg,[57] 320.3 μmol): 4, 277 mg, 94.0–95.0°, 1014.0 ± 4.0; 795.5 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (457.5 mg, 1843 μmol) added to ^{14}C-photolysate (74.7 mg,[57] 320.3 μmol): 5, 136 mg, 76.0–77.0°, 12.29 ± 0.16; 5.13 μmol produced; $\phi = 0.0083 \pm 0.0004$.

Run IV-01. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (101.4 mg, 408.4 μmol), activity 11.76 μCi/mmol, and 1.013 g of piperylene (0.0149 mol, 0.392 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 191.8 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (572.1 mg, 2304 μmol) added to ^{14}C-photolysate (40.6 mg, 163.4 μmol): 4, 182 mg, 94.0–95.0°, 713.4 ± 2.6; 372.0 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (470.8 mg, 1896 μmol) added to ^{14}C-photolysate (40.6 mg, 163.4 μmol): 4, 188 mg, 76.0–77.0°, 10.49 ± 0.15; 4.23 μmol produced; $\phi = 0.0221 \pm 0.0011$.

Run IV-02. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (97.7 mg, 393.5 μmol), activity 11.76 μCi/mmol, and 3.477 g of piperylene (0.0511 mol, 1.34 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 276.2 μEinsteins; analysis by Van Slyke method.

4,4-Diphenylcyclohex-2-en-1-one (746.3 mg, 3,006 μmol) added to ^{14}C-photolysate (39.1 mg, 157.4 μmol): 4, 298 mg, 94.0–95.0°, 532.9 ± 2.0; 356.7 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (390.2 mg, 1571 μmol) added to ^{14}C-photolysate (39.1 mg, 157.4 μmol): 4, 142 mg, 76.0–77.0°, 7.92 ± 0.13; 2.65 μmol produced; $\phi = 0.0096 \pm 0.0005$.

Run IV-03. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (99.1 mg, 399.1 μmol), activity 12.12 μCi/mmol, and 1.640 g of 2,5-dimethyl-2,4-hexadiene (0.0149 mol, 0.392 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 636.0 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (524.6 mg, 2113 μmol) added to ^{14}C-photolysate (39.6 mg, 159.6 μmol): 4, 165 mg, 94.0–95.0°, 856.1 ± 2.7; 401.4 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (460.8 mg, 1856 μmol) added to ^{14}C-photolysate (59.5 mg, 239.5 μmol): 5, 20 mg, 76.0–77.0°, 20.88 ± 0.10; 5.32 μmol produced; $\phi = 0.0084 \pm 0.0004$.

Run IV-04. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (120.4 mg, 484.9 μmol), activity 12.12 μCi/mmol, and 2.925 g of 2,5-dimethyl-2,4-hexadiene (0.0265 mol, 0.698 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 393.1 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (599.0 mg, 2,412 μmol) added to ^{14}C-photolysate (48.2 mg, 194.0 μmol): 4, 240 mg, 94.0–95.0°, 927.6 ± 3.1; 499.2 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (450.2 mg, 1813 μmol) added to ^{14}C-photolysate (72.2 mg, 290.9 μmol): 4, 59 mg, 76.0–77.0°, 9.890 ± 0.047; 2.47 μmol produced; $\phi = 0.0063 \pm 0.0003$.

Run IV-05. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (91.6 mg, 368.9 μmol), activity 12.12 μCi/mmol, and 5.011 g of 2,5-dimethyl-2,4-hexadiene (0.0456 mol, 1.20 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 624.2 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (639.1 mg, 2574 μmol) added to ^{14}C-photolysate (36.6 mg, 147.6 μmol): 4, 167 mg, 94.0–95.0°, 641.3 ± 2.0; 359.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (458.8 mg, 1848 μmol) added to ^{14}C-photolysate (55.0 mg, 221.3 μmol): 4, 37 mg, 76.0–77.0°, 9.026 ± 0.056; 2.29 μmol produced; $\phi = 0.0037 \pm 0.0002$.

Run IV-06. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (99.5 mg, 400.7 μmol), activity 12.12 μCi/mmol, and 1.199 g of 1,3-cyclohexadiene (0.0150 mol, 0.394 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 482.0 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (557.3 mg, 2244 μmol) added to ^{14}C-photolysate (39.8 mg, 160.3 μmol): 4, 161 mg, 94.0–95.0°, 804.5 ± 2.6; 399.1 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (409.1 mg, 1648 μmol) added to ^{14}C-photolysate (59.7 mg, 240.4 μmol): 4, 26 mg, 76.0–77.0°, 16.41 ± 0.08; 3.72 μmol produced; $\phi = 0.0077 \pm 0.0004$.

Run IV-07. 4,4-Diphenylcyclohex-2-en-1-one-4-^{14}C (97.3 mg, 391.9 μmol), activity 12.12 μCi/mmol, and 3.098 g of 1,3-cyclohexadiene (0.0386 mol, 1.02 *M*) in 38.0 ml of benzene irradiated through monochromator B (band width 22 mμ) at 366 mμ, 639.0 μEinsteins; analysis by liquid scintillation counting.

4,4-Diphenylcyclohex-2-en-1-one (624.9 mg, 2517 μmol) added to ^{14}C-photolysate (38.9 mg, 156.7 μmol): 4, 112 mg, 94.0–95.0°, 688.8 ± 2.2; 379.3 μmol recovered.

trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-one (455.3 mg, 1834 μmol) added to ^{14}C-photolysate (58.4 mg, 235.1 μmol): 4, 75 mg, 76.0–77.0°, 8.656 ± 0.054; 2.19 μmol produced; $\phi = 0.0034 \pm 0.0002$.

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[57] A small amount of the condensed photolysate was lost prior to dilution. Product to starting material ratios are unaffected by the loss, and amounts of photolysate given have been corrected for this loss by consideration of original and observed total activities.