

Data for individual quantum yields are listed as follows: mass of starting material, added reagent if any, volume of *tert*-butyl alcohol solvent, apparatus, filter or wavelength, temperature, amount of light absorbed, mass of unreacted starting material, and per cent conversion. The mass, composition, and quantum yield for each product isolated are then given.

**Run II-01.** Starting material was 597.3 mg (2.447 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 3.91 mEinstein; 452.9 mg (1.856 mmol) of unreacted *trans*-bicyclic diene; conversion, 24.3%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (35.0 mg, 0.143 mmol), syn: anti ratio was 0.667,  $\Phi = 0.0366$ .

Diphenyltoluenes (5.3 mg, 0.022 mmol),  $\Phi = 0.0056$ .

**Run II-02.** Starting material was 598.3 mg (2.452 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 1.79 mEinstein; 524.0 mg (2.148 mmol) of unreacted *trans*-bicyclic diene; conversion, 12.3%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (17.5 mg, 0.0715 mmol), syn: anti ratio was 0.423,  $\Phi = 0.0401$ .

Diphenyltoluenes (2.7 mg, 0.011 mmol),  $\Phi = 0.0062$ .

**Run II-03.** Starting material was 1.028 g (4.213 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 1.96 mEinstein; 938.9 mg (3.848 mmol) of unreacted *trans*-bicyclic diene; conversion, 8.66%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (18.4 mg, 0.0754 mmol), syn: anti ratio was 0.394,  $\Phi = 0.0384$ .

Diphenyltoluenes (2.0 mg, 0.0082 mmol),  $\Phi = 0.0042$ .

**Run II-04.** Starting material was 38.0 mg (0.156 mmol) of 2-methylene-*trans*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 734.0 mg (4.033 mmol) of benzophenone; 40 ml; micro; 350 nm; 33°; 0.198 mEinstein; 26.5 mg (0.109 mmol) of unreacted *trans*-bicyclic diene; conversion, 28.9%.

2-Methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene (12.5 mg, 0.0512 mmol),  $\Phi = 0.259$ . After correction for energy transfer to product,  $\Phi = 0.28$ .

**Run III-01.** Starting material was 35.0 mg (0.143 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 40 ml; micro; 33°; 0.187 mEinstein; 24.9 mg (0.102 mmol) of unreacted *cis*-bicyclic diene; conversion, 28.9% (insoluble thermal product in this run makes this figure high).

1,5-Diphenylspiro[2.4]-4,6-heptadiene (3.0 mg, 0.0123 mmol), greater than 90% syn isomer,  $\Phi = 0.066$  (this figure is low due to light scatter caused by the insoluble thermal product mentioned above).

**Run III-02.** Starting material was 95.6 mg (0.392 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 750 ml; macro; filter D; 33°; 0.284 mEinstein; 83.3 mg (0.341 mmol) of unreacted *cis*-bicyclic diene; conversion, 12.9%.

1,5-Diphenylspiro[2.4]-4,6-heptadiene (5.8 mg, 0.024 mmol), greater than 98% syn,  $\Phi = 0.082$ .

**Run III-03.** Starting material was 12.0 mg (0.0492 mmol) of 2-methylene-*cis*-5,6-diphenylbicyclo[3.1.0]-3-hexene; 738.3 mg (4.057 mmol) of benzophenone; 40 ml, micro; 350 nm; 33°; 0.0709 mEinstein; 12.1 mg (0.053 mmol) of unreacted *cis*-bicyclic diene; 0%.

No photoproducts were observed.

**Acknowledgment.** Support of this research by the National Science Foundation, National Institutes of Health Grant No. GM07487, and the U. S. Army Research Office (Durham) is gratefully acknowledged, as are predoctoral NASA and NIH fellowships to D. F. J. and J. M. M.

## The Photochemistry of 4-Methyl-4-phenyl-2-cyclohexenone. The Effect of Solvent on the Excited State<sup>1</sup>

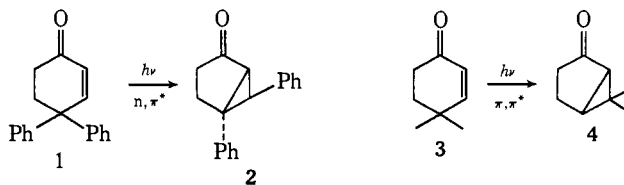
William G. Dauben,\* Wayne A. Spitzer,<sup>2a</sup> and Michael S. Kellogg<sup>2b</sup>

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720. Received June 25, 1970

**Abstract:** The photochemistry of 4-methyl-4-phenyl-2-cyclohexenone (**5**) was studied in a variety of solvents. In aprotic, nonpolar solvents, irradiations of **5** gave 5-methyl-*endo*-6-phenylbicyclo[3.1.0]hexan-2-one (**6**) and 4-methyl-3-phenyl-2-cyclohexenone (**7**), photoproducts of the type attributed to an  $n, \pi^*$  triplet reaction. In the protic polar solvents, irradiation of **5** gave **6** and **7**, as well as *exo*-6-methyl-*endo*-6-phenylbicyclo[3.1.0]hexan-2-one (**8**), 6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one (**9**), and *endo*-6-methyl-*exo*-6-phenylbicyclo[3.1.0]hexan-2-one (**10**), with **8-10** predominating. These latter products are of the type favored in  $\pi, \pi^*$  triplet reactions. The results are attributed to a bringing together (or perhaps an inversion) of the  $n, \pi^*$  and  $\pi, \pi^*$  triplet energy levels on going from nonpolar to polar solvents.

It is well established that 4,4-disubstituted 2-cyclohexenones can undergo a variety of reactions upon photoexcitation. The choice of reaction pathway followed by such compounds appears to be dependent upon the nature of the substituents at the 4 position and upon the character ( $n, \pi^*$  or  $\pi, \pi^*$ ) of the low-lying triplet. For example, the 1,2-phenyl migration and rearrangement of the disubstituted-cyclohexenone **1** to give the bicyclo[3.1.0]hexan-2-one (**2**) is thought to occur from the  $n, \pi^*$  triplet excited state,<sup>3,4</sup> whereas

skeletal rearrangements such as **3** to **4**<sup>5</sup> have been attributed to the  $\pi, \pi^*$  triplet excited state.<sup>6</sup>



In order to evaluate these suggestions, the photochemistry of 4-methyl-4-phenyl-2-cyclohexenone (**5**)

(1) This work was supported, in part, by Grant No. AM-00709, National Institute of Arthritis and Metabolic Diseases, U.S. Public Health Service, and the Hoffmann-LaRoche Foundation.

(2) (a) National Institutes of Health Predoctoral Fellow, 1967-1970; (b) National Institutes of Health Predoctoral Fellow, 1969-present.

(3) H. E. Zimmerman and J. W. Wilson, *J. Amer. Chem. Soc.*, **86**, 4036 (1964).

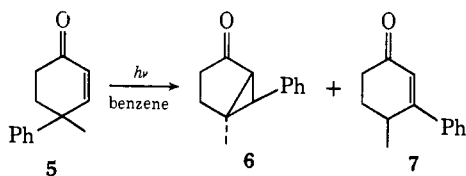
(4) H. E. Zimmerman and K. G. Hancock, *ibid.*, **90**, 3749 (1968).

(5) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Lett.*, 2049 (1963).

(6) D. Bellus, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **52**, 971 (1969).

was studied. In compound **5** both reaction pathways are potentially available. It is known that the  $n, \pi^*$  and  $\pi, \pi^*$  triplet levels of cyclohexenones are close together.<sup>6-8</sup> The difference between the photoreaction of the 4,4-diphenyl ketone (**1**) and the 4,4-dimethyl ketone (**3**) may arise by bringing together the two triplet energy levels sufficiently in one of the compounds so that thermal interconversion can occur between the triplet energy levels and thus get reaction from either triplet, or, indeed switching the low-lying triplets from what appears to be  $n, \pi^*$  in compound **1** to  $\pi, \pi^*$  in compound **3**. Thus in the 4-methyl-4-phenyl derivative **5**, a compound potentially capable of both reaction paths, a similar proximity of the triplet states would also be expected and with the known solvent effect on the relative energy differences between  $n, \pi^*$  and  $\pi, \pi^*$  triplet states,<sup>9</sup> it might be possible to guide the course of the reaction pathway followed by ketone **5** along the so-called  $n, \pi^*$  route or the  $\pi, \pi^*$  route.<sup>10</sup>

When the enone **5** was irradiated in a benzene solution with a Nonex filter ( $\lambda > 310$  nm), two photoproducts were formed in about equal amounts. The yields of these materials were low since they, in turn, gave polymeric products upon irradiation. The products were isolated by preparative glpc and identified as 5-methyl-*endo*-6-phenylbicyclo[3.1.0]hexan-2-one (**6**) and 4-methyl-3-phenyl-2-cyclohexenone (**7**). Thus, when the irradiation of **5** is conducted in benzene solution, the photoreaction follows the so-called  $n, \pi^*$  triplet pathway, as does compound **1**.



Effective sensitization by acetophenone ( $E_T = 74$ ) in a benzene solution of **5** to yield **6** and **7** in exactly the same ratio as observed on direct irradiation indicates the triplet nature of the excited state involved in the photoreaction. Furthermore, linear Stern-Volmer plots were obtained using naphthalene ( $E_T = 61$ ) as the quencher in benzene or cyclohexane solution.

In the earlier studies of the photoreaction of the diphenyl derivative **1**,<sup>4</sup> the rearranged unsaturated ketone was formed as a minor product (<1%). An intermediate **i** was proposed for the formation of the major product **2** and a hydride shift to form intermediate **ii** was suggested for the formation of **7a**.<sup>4</sup> This proposal is consistent with the photochemistry of **5** since when the R group is methyl rather than phenyl, hydrogen migration from **i** to **ii** should be a more favorable process, and such is what was observed.

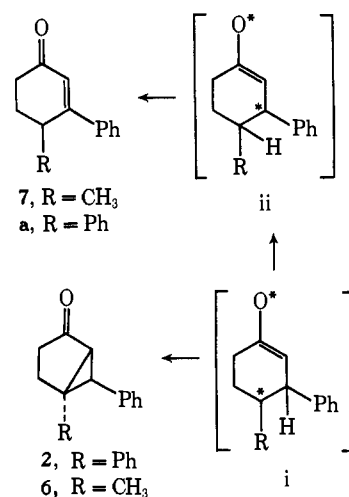
Since the irradiation in benzene, a nonpolar solvent, apparently proceeded by an  $n, \pi^*$  triplet, the photochemistry of **5** was investigated in a polar solvent which

(7) D. R. Kearns, G. Marsh, and K. Schaffner, *J. Chem. Phys.*, **49**, 3316 (1968).

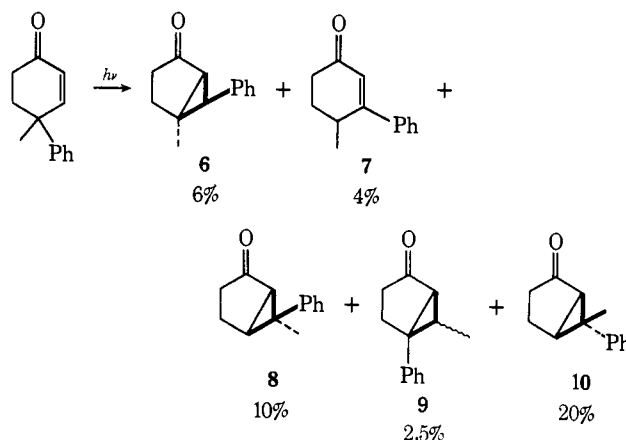
(8) G. Marsh, D. R. Kearns, and K. Schaffner, *Helv. Chim. Acta*, **51**, 1890 (1968).

(9) M. Weller, *Angew. Chem.*, **66**, 336 (1954); A. A. Lamola, *J. Chem. Phys.*, **47**, 4810 (1967).

(10) In the photochemistry of 2,4-cyclohexa- and -heptadienones, H. Hart [*Chem. Commun.*, 450 (1970) and earlier papers] has found solvent effects which appear to be related to the acidity of the solvent and the resulting effects on excited state.

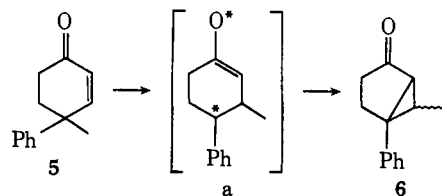


would lower the energy of the  $\pi, \pi^*$  triplet.<sup>9</sup> Thus, when **5** was irradiated in a 90% methanol-water solution under the same conditions as before, five photoproducts were formed. In addition to the compounds **6** and **7**, three new cyclopropyl-conjugated ketones, **8-10**, were formed. These products were identified by their spectral properties. The stereochemical assignments of **8** and **10** are based on the position of the methylene protons in the nmr spectra. In compound **8** the phenyl



group lies over the ring, while in **10** the phenyl group is extended out and away from the ring. Thus, the methylene groups are shielded in **8** but not in **10**.

The formation of photoproduct **9** is of special interest. While photoproducts **8** and **10** result from a migration of a methylene group from C-4 to C-3, the migration of an unsubstituted methyl group from C-4 to C-3 in compounds such as **3** has previously not been observed. The facility of methyl migration in this system probably results from the increased stability afforded by the C-4 phenyl group to the intermediate **a** which has been proposed for this type of rearrangement.<sup>11,12</sup>



(11) H. E. Zimmerman and D. J. Sam, *J. Amer. Chem. Soc.*, **88**, 4905 (1966).

(12) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *ibid.*, **88**, 158 (1966).

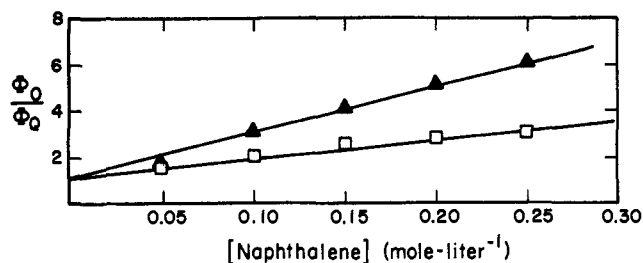


Figure 1. Stern-Volmer plot of triplet quenching of formation of 6 (□) and 8 (▲) in 95% ethanol.

As in the studies conducted in benzene, it was found that the formation of 8, 9, and 10 in the polar solvents also involved a triplet excited state of 5 since their formation in the same ratio as in the direct irradiation was achieved by sensitization by acetophenone in *tert*-butyl alcohol. Stern-Volmer type analyses for the products 6 and 8, products possibly representative of the reactions from different triplet states, were undertaken in 95% ethanol using naphthalene ( $E_T = 61$ ) as the quencher. The results are shown in Figure 1 and the difference observed in the slopes for the quenching of the production of these two compounds is indicative of the involvement of two excited states of different lifetimes.<sup>5,6</sup> It seems reasonable that there be a qualitative correlation between the lifetimes of reacting  $n, \pi^*$  and  $\pi, \pi^*$  triplets and the phosphorescence lifetimes of these same excited states, *i.e.*,  $n, \pi^*$  triplets have shorter lifetimes than  $\pi, \pi^*$  triplets. If this be the case, then these plots in Figure 1 further demonstrate the  $n, \pi^*$  character of the triplet involved in the phenyl group migration and the  $\pi, \pi^*$  character of the triplet involved in the skeletal rearrangement.

The foregoing results indicated that the photochemistry of 5 followed the  $n, \pi^*$  pathway in benzene while in 90% methanol-water the pathways predominantly involved the  $\pi, \pi^*$  triplet. This solvent effect was further evaluated by performing the irradiation of 5 in a variety of different solvents. (See Tables I and II.)

Table I. Photochemical Results in Aprotic Solvents

Solvent	Dielectric constant	Rel amounts	
		6, 7	8, 9, 10
Benzene	2.3	100	0
Ether	4.3	100	0
Acetonitrile	38.8	58	42
Formamide	109.0	38	62

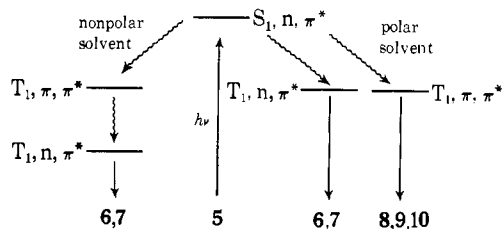
Table II. Photochemical Results in Protic Solvents

Solvent	Dielectric constant	Rel amounts	
		6, 7	8, 9, 10
<i>tert</i> -Butyl alcohol	10.9	67	33
Ethanol	25.0	39	61
2,2,2-Trifluoroethanol	26.5	30	70
Methanol	32.6	30	70
10% H <sub>2</sub> O-methanol	38.4	29	71
20% H <sub>2</sub> O-methanol	43.1	27	73
30% H <sub>2</sub> O-methanol	47.7	25	75

Two solvent properties, dielectric constant and hydrogen bonding, have been shown to be important in

regard to the blue shift of  $n, \pi^*$  excited states. Of these two properties, hydrogen bonding has been found to be the most important.<sup>13</sup> Examination of Tables I and II shows that the formation of photoproducts 8, 9, and 10 ( $\pi, \pi^*$  triplet reaction) increases both with increasing dielectric constant and with hydrogen bonding. The shift of the excited singlet state also is clearly evident in the uv spectra of 5 under these different solvent conditions. In ether, 5 shows a distinct  $n, \pi^*$  maximum at 340 nm ( $\epsilon$  30) while in methanol the  $n, \pi^*$  band is completely buried under the tail of the  $\pi, \pi^*$  band, the shift of the  $n, \pi^*$  and  $\pi, \pi^*$  transitions being about 20 nm in opposite directions. The solvent effect on the photochemistry of 5 can be summarized as shown in Scheme I.

Scheme I



As shown in Scheme I, the only definite conclusion which can be reached is that the change in solvent brings the two triplet states closer together in energy; no definite conclusion can be reached as to which triplet state is of lower energy in the different solvents. For example, while in polar, hydrogen-bonding solvents, the  $\pi, \pi^*$  triplet may be lower in energy than the  $n, \pi^*$  triplet; such a conclusion is not required by our results or the results of others.<sup>6-8</sup> It is clear, however, from our results that two triplets are involved in the photo-reaction in polar solvents. If, indeed, the two triplets are so spaced in energy that they may be in thermal equilibrium, then the  $n, \pi^*$  triplet might still be the lower in energy. However, since it is known that the quantum yield for phenyl migration is five times that for skeletal rearrangement,<sup>4</sup> it would seem more reasonable that, in fact, these solvent changes have made the  $\pi, \pi^*$  triplet lower in energy than the  $n, \pi^*$  triplet.

In some cases solvent polarity has been shown to be important in bringing about skeletal rearrangements of the type 3 to 4.<sup>5,6</sup> In other instances this rearrangement shows little or no dependence on solvent.<sup>13</sup> Undoubtedly, the solvent effect only becomes important when the  $n, \pi^*$  and  $\pi, \pi^*$  triplet states are very close in energy.

The photochemistry of compound 5 clearly supports the proposal that rearrangement of the type 1 to 2 results from  $n, \pi^*$  triplet reactions, while rearrangement of the type 3 to 4 results from  $\pi, \pi^*$  triplets. The results demonstrate the importance of knowing the path by which a photoreaction proceeds, because the course of the reaction can be determined by choice of solvent. Finally, the striking difference in the  $n, \pi^*$  and  $\pi, \pi^*$  reaction paths of compound 5 emphasizes the important role that electron distribution plays in photochemical processes.<sup>14</sup>

(13) G. J. Brealy and M. Kasha, *J. Amer. Chem. Soc.*, **7**, 4462 (1955).

(14) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *ibid.*, **89**, 6589 (1967).

## Experimental Section

**Irradiation of 4-Methyl-4-phenyl-2-cyclohexenone (5) in Benzene.** A solution of 1.3 g of 4-methyl-4-phenyl-2-cyclohexenone (5)<sup>15</sup> in 125 ml of benzene was irradiated with a 450-W Hanovia lamp using a Nonex filter ( $\lambda > 310$  nm). The progress of the irradiation was followed by glpc (5 ft, 3% Carbowax 20M).

After 42 hr, 78% of the starting cyclohexenone had reacted and the irradiation was halted. Two photoproducts (6, 11%, and 7, 10%) were formed and isolated in pure form by preparative glpc (10 ft, 5% SE-30). Photoproduct 7 was identified as 4-methyl-3-phenyl-2-cyclohexenone by comparison with the independently synthesized compound.<sup>16</sup> Photoproduct 6 was identified as 5-methyl-endo-6-phenylbicyclo[3.1.0]hexan-2-one on the basis of the following spectral properties: ir (CCl<sub>4</sub>) 1735 and 695 cm<sup>-1</sup>; nmr ( $\tau$ , CCl<sub>4</sub>) 2.81 (s, 5, phenyl), 7.42 (d, 1,  $J = 9$  Hz, cyclopropyl), 7.76–8.37 (m, 4, -CH<sub>2</sub>-), 8.54 (s, 3, -CH<sub>3</sub>), 8.98 (d, 1,  $J = 9$  Hz, cyclopropyl); mass spectrum  $m/e$  186, 158, 157, 145, 144, 143, 141, 130, 129, 128, and 115.

**Irradiation of 5-Methyl-endo-6-phenylbicyclo[3.1.0]hexan-2-one (6) in Benzene.** A solution of 15 mg of 6 in 125 ml of benzene was irradiated with a 450-W Hanovia lamp and Pyrex filter ( $\lambda > 280$  nm). The progress of the irradiation was followed by glpc (5 ft, 3% Carbowax 20M). Compound 6 was slowly consumed, but no monomeric photoproducts were formed.

**Irradiation of 4-Methyl-4-phenyl-2-cyclohexenone (5) in 90% Methanol-Water.** A solution of 1.2 g of 4-methyl-4-phenyl-2-cyclohexenone (5) in 90% methanol-water was irradiated with a 450-W Hanovia lamp and Nonex filter ( $\lambda > 310$  nm). The progress of the irradiation was followed by glpc (5 ft, 3% Carbowax 20M). After 60 hr of irradiation, 76% of the starting material had reacted and the irradiation was halted. Five photoproducts were formed: 6, 6%; 7, 4%; 8, 10%; 9, 2.5%; and 10, 20%. The products were isolated in pure form by preparative glpc (10 ft, 5% SE-30). Compound 8 was identified as *exo*-6-methyl-endo-6-phenylbicyclo[3.1.0]hexan-2-one, and has the following spectral properties: ir (CCl<sub>4</sub>) 1730 and 705 cm<sup>-1</sup>; nmr ( $\tau$ , CCl<sub>4</sub>) 2.80 (s, 5, phenyl), 7.68–8.23 (m, 4, -CH<sub>2</sub>-), 8.26–8.60 (m, 1, cyclopropyl), 8.66 (s, 3, -CH<sub>3</sub>), 8.93–9.43 (m, 1, cyclopropyl); mass spectrum  $m/e$  186, 145, 144, 143, 130, 129, 128, and 115.

Compound 9 was identified as 6-methyl-5-phenylbicyclo[3.1.0]hexan-2-one, and has the following spectral properties: ir (CCl<sub>4</sub>) 1730 and 695 cm<sup>-1</sup>; nmr ( $\tau$ , CCl<sub>4</sub>) 2.82 (s, 5, phenyl), 7.38–8.04 (m, 4, -CH<sub>2</sub>-), 8.04–8.84 (m, 2, cyclopropyl), 9.06 (d, 3,  $J = 6$  Hz, -CH<sub>3</sub>); mass spectrum  $m/e$  186, 145, 144, 143, 130, 129, 127, and 115.

(15) H. E. Zimmerman and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 2753 (1970).

(16) R. Chapurlat and J. Dreux, *Bull. Soc. Chim. Fr.*, 349 (1962).

Compound 10 was identified as *endo*-6-methyl-*exo*-6-phenylbicyclo[3.1.0]hexan-2-one, and has the following spectral properties: ir (CCl<sub>4</sub>) 1735 and 700 cm<sup>-1</sup>; nmr ( $\tau$ , CCl<sub>4</sub>) 2.95 (s, 5, phenyl), 7.43–8.06 (m, 5, -CH<sub>2</sub>- and 1 cyclopropyl), 8.06–8.44 (m, 1, cyclopropyl), 8.68 (s, 3, -CH<sub>3</sub>); mass spectrum  $m/e$  186, 145, 144, 143, 130, 129, 128, and 115.

**Solvent Study of the Irradiation of 4-Methyl-4-Phenyl-2-cyclohexenone (5).** The irradiation of compound 5 in several solvents was carried out in the following manner. Compound 5 (60 mg) was dissolved in 4 ml of the solvent and placed in a 5-ml quartz test tube. The quartz test tubes were placed in a "merry-go-round" apparatus, and irradiated with a 450-W Hanovia lamp and Pyrex filter ( $\lambda > 280$  nm). The photoproduct mixture was analyzed by glpc (10 ft, 3% Carbowax 20 M), and the ratio of photoproducts 6 and 7 and 8, 9, and 10 was compared. The ratio of these two groupings was determined early in the photoreaction when these compounds amounted to less than 15% of the remaining starting material (see Tables I and II).

**Sensitized Irradiations of 4-Methyl-4-phenyl-2-cyclohexenone (5).** Solutions containing 5 ( $1.0 \times 10^{-2}$  M) and acetophenone ( $3.42 \times 10^{-1}$  M) were prepared in *tert*-butyl alcohol, in *tert*-butyl alcohol containing 7% water, and in benzene. These solutions (2.5 ml) were placed in Pyrex irradiation vessels and degassed by helium purge, as were corresponding solutions containing no sensitizer. All vessels were capped with rubber septums and irradiated in a Rayonet Reactor merry-go-round apparatus using 350-nm lamps. The course of the photorearrangement was followed by glpc (6 ft, 10% SE-30 on 80–100 Chromosorb S, temperature programmed 135–180° at 4°/min). The same ratio of products was observed, respectively, in each solvent system with and without sensitizer, at comparable conversions. The rate of the sensitized reaction was at least three times more rapid as compared to direct irradiation.

At the concentration of acetophenone used, the sensitizer will absorb greater than 90% of the incident radiation. The concentration of sensitizer is too low for effective singlet transfer but large enough for triplet transfer.<sup>4,8</sup>

**Quenching Analysis of the Photorearrangement of 4-Methyl-4-phenyl-2-cyclohexenone (5).** Into Pyrex irradiation vessels were placed 2.5-ml portions of solutions which were  $1.0 \times 10^{-2}$  M in 5 and  $2 \times 10^{-3}$  M in *n*-undecanol (internal glpc standard). Naphthalene was present in five vessels in concentrations of 0.05, 0.10, 0.15, 0.20, and 0.25 M. The solutions were degassed by helium purge, capped with a rubber septum, and irradiated in a Rayonet Reactor merry-go-round apparatus using 350-nm lamps. The irradiations were halted when the vessels without quencher showed the presence of 6, amounting to about 3% of the remaining starting material. Analyses were performed as described in the sensitization experiment. The irradiation experiments were run in 95% ethanol, benzene, and cyclohexane solutions.