prisms: mp 53–55°; $\lambda_{max}^{isooctane}$ 243 nm ($\epsilon$ 15,000); $\delta_{TMS}^{CDCl_3}$ 7.2 (s, 10, aryl), 6.0 (t, $|J|$ = 6 Hz, 2, vinyl), 3.6–4.0 (m, 2, bridgehead), 3.1 (t of d, $J_t$ = 6 Hz, $J_d$ = 1 Hz, 2, *gem*-allyl), 1.1–2.3 (m, 4, $-CH_2CH_2-$); ir (neat) 2985, 2899, 2825, 1942, 1678, 1639, 1597, 1572, 1488, 1439, 1227, 1074, 1030, 911, 840, 758, 697 $cm^{-1}$.

*Anal.* Calcd for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.41; H, 7.58

**B. At Low Temperature.** A solution of 25 mg of **21** in $CDCl_3$ contained in an nmr tube was photolyzed (200-W Hanovia lamp through Pyrex) for 30 min and examined by nmr, all below −55°; the spectrum was that of **22**.

**Pyrolysis of 21.** A solution of 25 mg of **21** and 100 mg of tetrachloroethylene was sealed under vacuum in a thick-walled nmr tube. During 90 min in an nmr probe at 135°, the spectrum of the solution changed cleanly from that of **21** to that of **22**. The half-life of the reaction was estimated to be approximately 20 min.

**Acknowledgment.** Financial support for this research was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also express appreciation to Dr. Paul Demarco for assistance with the NOE and LIS studies, to Dr. Louis Leichter for his help with the low-temperature nmr experiments, and to Dr. Stanley Wilson for his part in the kinetic determinations.

# Cyclopropane in Photochemistry. II. Photochemistry of 4-Cyclopropyl-4-phenylcyclohexenone[1]

**Roger C. Hahn* and David W. Kurtz[2]**

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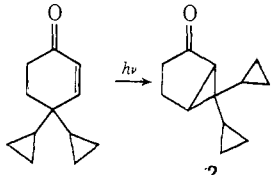
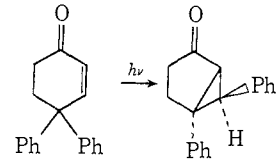
**Abstract:** Irradiation of 4-cyclopropyl-4-phenylcyclohexenone (**5**) in heptane and benzene gave 5-cyclopropyl-*trans*-6-phenylbicyclo[3.1.0]hexan-2-one (**7**), 5-cyclopropyl-*cis*-6-phenylbicyclo[3.1.0]hexan-2-one (**8**), and 3-phenyl-4-cyclopropylcyclohex-2-enone (**9**). Irradiation of **5** in methanol yielded, in addition to **7–9**, ~20% of *endo*-6-phenyl-*exo*-6-cyclopropylbicyclo[3.1.0]hexan-2-one (**10**). The results are consistent with a narrowing of the gap between n,$\pi^*$ and $\pi,\pi^*$ triplet energy levels on going from nonpolar to polar solvents. Comparisons of the behavior of several analogous 4,4-disubstituted cyclohexenones indicate that C-4 substituent stabilization of $\pi,\pi^*$ triplets relative to n,$\pi^*$ triplets increases in the order phenyl < cyclopropyl < methyl.

Recently[1] we reported the photorearrangement of 4,4-dicyclopropylcyclohexenone (**1**) to give exclusively products derived from the enone "type A" reaction[3] (*e.g.*, **2**). In contrast, 4,4-diarylcyclohexenones rearrange exclusively *via* 1,2-aryl migration.[4] These divergent photoreactions of 4,4-dialkyl- and 4,4-diarylcyclohexenones have been attributed to $\pi,\pi^*$ and n,$\pi^*$ triplet excited states, respectively.[4,5]




1 2

However, spectroscopic studies[5] have shown that the energy levels of $\pi,\pi^*$ and n,$\pi^*$ triplets lie close together in cyclohexenones; it therefore seemed possible, through the effects of selected substituents, that 4,4-disubstituted cyclohexenones could be constructed which would undergo both types of photochemical reaction. Such behavior would afford an opportunity to explore the influence of medium polarity on the choice of reaction pathways, since solvent changes are known to alter energy differences between n,$\pi^*$ and $\pi,\pi^*$ triplet states.[6] Given the divergence in photochemical behavior of **1** and 4,4-diphenylcyclohexenone (**3**),[4] we

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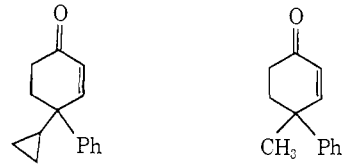
chose to look for borderline behavior in 4-cyclopropyl-4-phenylcyclohexenone (**5**). This compound also would test the suggestion[7] that stabilization by a non-migrating C-4 aryl substituent is necessary for aryl migration to take precedence over type A rearrangement. Recently Dauben, Spitzer, and Kellogg,[8] for reasons similar to those enumerated above, reported a study of the photochemistry of 4-methyl-4-phenylcyclohexenone (**6**); comparison of their results with those

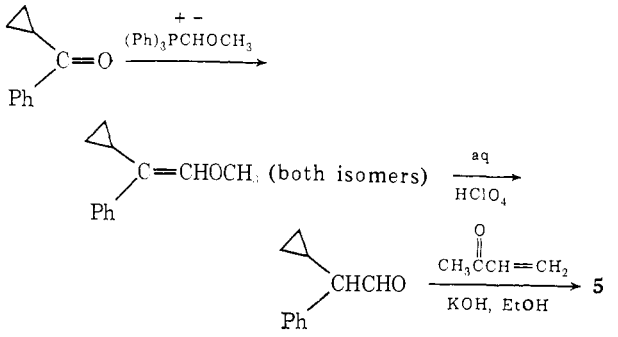



5 6

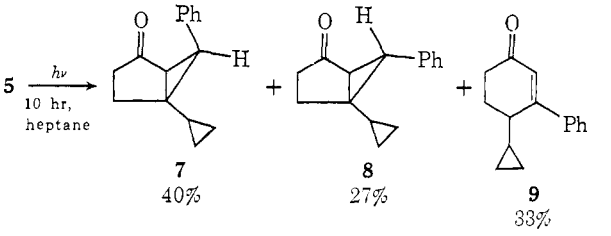
(1) Part I: R. C. Hahn and G. W. Jones, *J. Amer. Chem. Soc.*, **93**, 4232 (1971).
(2) N.D.E.A. Predoctoral Fellow, 1966–1969.
(3) H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **88**, 1965 (1966).
(4) H. E. Zimmerman and W. R. Elser, *J. Amer. Chem. Soc.*, **91**, 887 (1969), and references therein.
(5) G. Marsh, D. R. Kearns, and K. Schaffner, *J. Amer. Chem. Soc.*, **93**, 3129 (1971), and references therein.
(6) A. A. Lamola, *J. Chem. Phys.*, 47, 4810 (1967).
(7) (a) H. E. Zimmerman and R. L. Morse, *J. Amer. Chem. Soc.*, **90**, 954 (1968); (b) H. E. Zimmerman, *Angew. Chem.*, **81**, 45 (1969); *Angew. Chem., Int. Ed. Engl.*, **8**, 1 (1969).
(8) W. G. Dauben, W. A. Spitzer, and M. S. Kellogg, *J. Amer. Chem. Soc.*, **93**, 3674 (1971).

from irradiation of **5** provided a further opportunity to define the role of a 4-cyclopropyl substituent in affecting cyclohexenone photochemistry. Synthesis of **5** is outlined in Scheme I.

**Scheme I**



**Photolyses.** Irradiation of enone **5** in heptane through a Pyrex filter ($\lambda > 280$ nm) provided three volatile photoproducts (vpc analysis) accounting for 80–85% of the consumed starting material. These were isolated by Florisil chromatography and/or preparative vpc and identified as 5-cyclopropyl-*trans*-6-phenylbicyclo[3.1.0]hexan-2-one (**7**), 5-cyclopropyl-*cis*-6-phenylbicyclo[3.1.0]hexan-2-one (**8**), and 4-cyclopropyl-3-phenylcyclohex-2-enone (**9**).



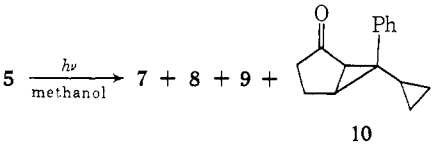
The product distribution was not significantly different when benzene was the photolysis medium, but briefer irradiation of **5** in either solvent yielded a smaller proportion of "cis-bicyclic" **8**. Direct irradiation of "trans-bicyclic" **7** revealed secondary photorearrangements of this compound to both **8** and **9**, with **7** → **8** conversion much faster (Table I). These results,

**Table I.** Irradiation of **7** ($\lambda > 280$ nm)

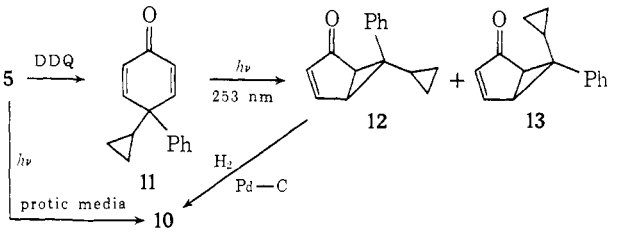
| Time, hr | 7, % | 8, % | 9, % |
|---|---|---|---|
| 1[a] | 90 | 10 | |
| 2.25[a] | 85 | 13 | 2.4 |
| 3[a] | 82 | 14 | 3.5 |
| 4[a] | 80 | 16 | 4.2 |
| 5[a] | 77 | 18 | 5.2 |
| 6[a] | 72 | 20 | 7.7 |
| 6[b] | 78 | 15 | 7.2 |
| 8.5[b] | 69 | 21 | 10 |
| 14.25[b] | 63 | 23 | 14 |
| 19.75[b] | 56 | 29 | 15 |

[a] In heptane. [b] In *tert*-butyl alcohol.

precedents,[9,10] and theory[9] suggest that the **7**–**8** ratio from primary photoreaction of **5** is much higher than in the briefest (1 hr) irradiations presently performed, but the relatively large experimental error in measurement of **8** (~3%) makes data from shorter irradiations unreliable; it also remains undetermined whether **8** is converted photochemically to **7** and **9**. Irradiation of enone **5** in *tert*-butyl alcohol or 90% dioxane–water (other conditions unchanged) gave four detectable monomeric photoproducts. In addition to **7**–**9**, which appeared in only slightly different proportions from those found in aprotic media, a new photoproduct was isolated as 3–5% of the monomeric product mixture. Spectral data allowed identification of this compound as the type A rearrangement product *endo*-6-phenyl-*exo*-6-cyclopropylbicyclo[3.1.0]hexan-2-one (**10**); an independent synthesis was performed as outlined in Scheme II. The stereochemistry of the phenyl and

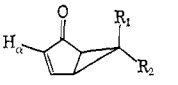


**Scheme II**



cyclopropyl groups in **12** and **13** (and hence in **10**) was assigned by comparison of the $\alpha$-vinyl nmr shift values with those of suitable reference compounds (Table II).

**Table II.** $H_\alpha$ Shifts ($CDCl_3$) for **12**, **13**, and Reference Compounds



| Substituents | $H_\alpha$, $\tau$ |
|---|---|
| $R_1 = R_2 =$ Ph | 4.49[a] |
| $R_1 =$ Ph, $R_2 = \nabla$ (**12**) | 4.62 |
| $R_1 = \nabla$, $R_2 =$ Ph (**13**) | 3.98 |
| $R_1 = R_2 = \nabla$ | 4.08[b] |

[a] H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, **91**, 434 (1969). [b] G. W. Jones, Ph.D. Dissertation, Syracuse University, 1970.

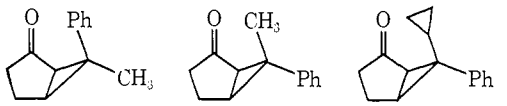
Replacement of an *endo*-cyclopropyl group by an *endo*-phenyl group can be seen to result in $H_\alpha$ upfield shifts of 0.51 and 0.54 ppm; these shifts are consistent with a preferred conformation of the phenyl group in which this moiety is roughly coplanar with the cyclopentenone ring and thus in a position to exert a shielding anisotropy effect on $H_\alpha$.

When **5** was irradiated in methanol, the proportion of type A rearrangement product **10** rose to 22%; as discussed elsewhere,[8] this result is attributable to the increased dielectric constant of methanol relative to those of previously used solvents and is consistent with a further solvent-related narrowing of the energy gap between the $n,\pi^*$ and $\pi,\pi^*$ triplet energy levels.

At this point, noting that Dauben and coworkers[8] isolated both *endo*-6-phenyl-*exo*-6-methylbicyclo[3.1.0]-

(9) H. E. Zimmerman and K. G. Hancock, *J. Amer. Chem. Soc.*, **90**, 3749 (1968).
(10) H. E. Zimmerman, R. D. Rieke and J. R. Scheffer, *J. Amer. Chem. Soc.*, **89**, 2033 (1967).

hexan-2-one (**14**) and its C-6 epimer (**15**) from irradiation of **6**, with a **14**–**15** ratio of 1:2, we became con-



**14** **15** **16**

cerned with the apparent absence of **16** (the epimer of **10**) in the mixtures from irradiation of **5**. An impure sample of **16** was prepared by hydrogenation of 85% pure **13** and was found to have the same vpc retention time as trans-bicyclic ketone.[7] However, nmr and ir spectra of **7** collected by preparative vpc from irradiations of **5** in polar or nonpolar media contained no detectable features characteristic of the missing epimer; it must be present only in very small amounts. Molecular models indicate that the *endo*-phenyl in **10** can readily assume a conformation which causes minimal interaction with the *endo*-C-3 and -C-4 hydrogens. In contrast, there appears to be no conformation of an *endo*-cyclopropyl group which does not result in severe crowding of these hydrogens. Assuming that the transition states of the type A rearrangements leading to these epimers are affected by these factors, the dominant formation of **10** can be rationalized. Similar considerations can account for the preference for *endo*-methyl epimer in the type A rearrangement of 4-methyl-4-phenylcyclohexenone;[8] an overall endo preference order methyl > phenyl > cyclopropyl is indicated.[11]

Fractions of **7**–**9** formed in polar solvents were searched by vpc, tlc, and spectroscopic methods for products of cyclopropyl migration, without success.

Acetophenone sensitization of **5** in benzene or *tert*-butyl alcohol caused a threefold acceleration of the reaction (similar to the effect reported for **6**),[8] a slight increase in **8**, and a slight decrease in **9**; the absence of **10** in nonpolar media and its presence in polar media were unaffected. The changes in product composition probably are due to acceleration of secondary reactions by triplet sensitization; 3-phenyl-4-cyclopropylcyclohexenone (**9**) was shown to be stable to prolonged direct irradiation in benzene or *tert*-butyl alcohol but on sensitization was converted slowly to higher molecular weight material. These results clearly indicate that both the type A product (**10**) and the products of phenyl migration (**7**–**9**) arise from triplet excited states and that the nature of the solvent is the only factor influencing the partitioning of **5** into type A and phenyl migration reaction pathways.

The high percentage of rearranged enone **9** (43% in benzene) from photolysis of **5** contrasts sharply with the small amounts of comparable products from the 4,4-diphenylenone **3** (<1%)[9] and 4,4,5-triphenylcyclohexenone (13%).[7] Monitored photolyses of **5** showed that net rates of formation of **7** and **9** are nearly equal; data summarized in Figure 1 establish that secondary conversion of **7** to **9** accounts for less than 25% of the latter formed in the first 6 hr of reaction. According to Dauben, Spitzer, and Kellogg, 4-methyl-3-phenylcyclohex-2-enone represents 48% of the monomeric products from photoreaction of **6** (in benzene);[8] there appears to be only a small difference between a 4-

(11) The endo preference order is not the same for the corresponding, superficially similar dienone type A rearrangements; *cf.* H. E. Zimmerman and G. Jones II, *J. Amer. Chem. Soc.*, **92**, 2753 (1970).

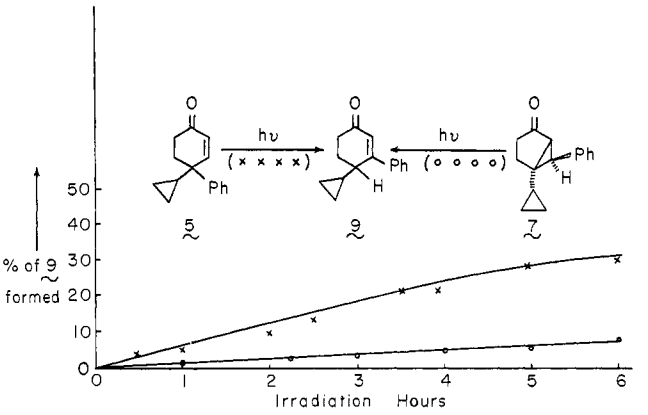
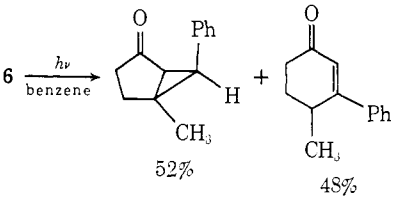
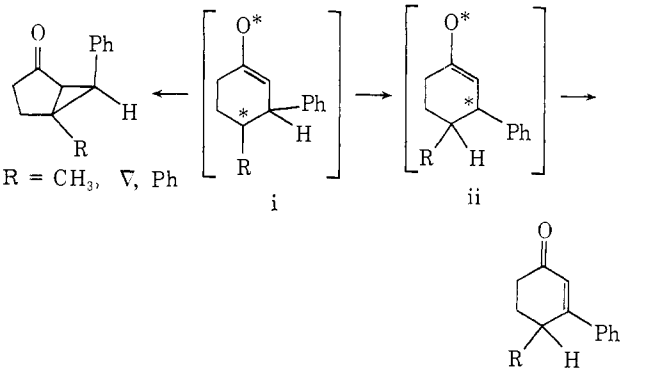



Figure 1. Photochemical formation of **9** from **5** or **7** in heptane.



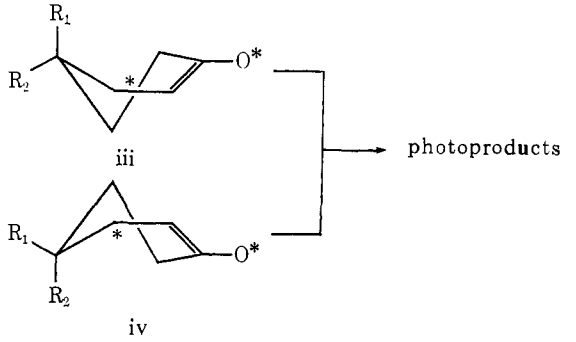

methyl and a 4-cyclopropyl group in affecting the fate of species engendered subsequent to aryl migration. That difference, however, is in the direction anticipated for the behavior of the previously proposed[9] and discussed[8] intermediate i; hydrogen migration to form ii should become increasingly favorable in the order R = Ph < ▽ < $CH_3$.




Taken together, substituent and solvent effects on the photochemistry of 4,4-diphenyl-,[4] 4-cyclopropyl-4-phenyl-, and 4-methyl-4-phenylcyclohexenone[8] (**3**, **5**, and **6**, respectively) form a pattern which supports the previously noted hypotheses[4,5,8] relating to photochemical reactivity of such enones. In nonpolar solvents, all of these enones react exclusively *via* phenyl migration, while in polar media the type A reaction emerges to the extent of 0% for **3**, ~20% for **5**, and ~70% for **6**. Assuming that phenyl migration involves n,π* triplet states and type A reaction involves π,π* triplet states, it can be concluded from the above data that successive replacement of a 4-phenyl substituent in **3** by cyclopropyl and methyl causes successive reductions in the π,π* triplet energy level, relative to the n,π* triplet. This trend correlates nicely with an increase in substituent electron-donating ability as carbon orbital hybridization changes from $sp^2$ to $sp^3$; such an effect would be expected to preferentially

stabilize the excited state ($\pi,\pi^*$) having the greater electron deficiency at C-3.[12]

The observed trend can be correlated also with steric effects on the population of excited triplet conformers capable of phenyl migration. As represented by iii and iv, such triplets can be assumed to have either $R_1$ or $R_2$ in a pseudoaxial geometry, from which orbital




overlap with and subsequent migration to C-3 should be most facile. If both $R_1$ and $R_2$ are phenyl groups, one is always in a pseudoaxial position (*i.e.*, ready to migrate). However, if $R_1$ is phenyl and $R_2$ is cyclopropyl or methyl, only iii can readily initiate phenyl migration, and (in a medium which can impose the proper $n,\pi^*-\pi,\pi^*$ energy relationship) population of a state capable of type A rearrangement is more likely to occur. The relative populations of iii and iv should be a function of the steric bulk of $R_2$; all indications are that cyclopropyl is a larger group than methyl, so that the probability of generating a conformer with *no* axial phenyl increases in the order $R_2$ = phenyl < cyclopropyl < methyl. The available data appear to provide no choice between the electronic and steric explanations; this problem is under further study.

Our data also do not rule out the possibility that in **5** either triplet may be reacting by both the phenyl migration and type A pathways; however, the absence of type A product on irradiation in benzene or heptane establishes that the lowest triplet (presumably $n,\pi^*$) is incapable of type A rearrangement in these media.

## Experimental Section

Infrared spectra were obtained with a Perkin-Elmer 137 Infracord and ultraviolet spectra with a Perkin-Elmer 202 spectrometer. Nmr spectra were obtained with a Varian A-60 using tetramethylsilane or dichloromethane as an internal standard. Melting points were taken on a Fisher-Johns apparatus and are corrected; boiling points are uncorrected. Elemental analyses were performed by Micro Analytical Laboratories, Herlev, Denmark.

***cis*-and *trans*-1-Cyclopropyl-1-phenyl-2-methoxyethylene.** Triphenylmethoxymethylphosphonium chloride[13] (172 g, 0.505 mol) was slurried in ether (1.5 l.) under nitrogen, and *n*-butyllithium (0.505 mol in ether–hexane solution) was added dropwise with rapid stirring. The mixture became orange, then red. After 0.5 hr more, phenyl cyclopropyl ketone (73.0 g, 0.500 mol) in dry ether (150 ml) was added in 45 min. Brisk refluxing ensued and triphenylphosphine oxide precipitated. After 1 hr more of stirring and refluxing, the mixture was cooled and filtered and the filtrate washed and dried. Solvent removal, simple distillation, and then spinning band fractionation of the mixture gave three fractions, bp 67–71°, 85–89°, and 92–96° (1.4 mm). The latter two fractions totaled 43 g (49.4%) and were identified as *cis*- and *trans*-1-cyclopropyl-1-phenyl-2-methoxyethylene. They are separable in silica gel chromatography. The low-boiling isomer has: ir (neat, NaCl) 3000, 1640 (s), 1220 (s), 1135, 1100, 1025, 950, 760, and 696 $cm^{-1}$; pmr (neat) $\tau$ 2.40–3.00 (m, 5 H), 3.87 (s, 1 H), 6.59 (s, 3 H), 8.00–8.52 (m, 1 H), and 9.15–9.60 (m, 4 H). The higher boiling isomer has: ir (neat, NaCl) 3000, 1648, 1590, 1540, 1258, 1208, 1155, 1090, 1030, 978, 868, 768, and 695 $cm^{-1}$; pmr (neat) $\tau$ 2.10–2.35 (2 H, m) 2.50–3.00 (3 H, m), 4.00 (1 H, d, $J$ = 2 Hz), 6.69 (3 H, s), 8.33–8.8 (1 H, m), and 9.25–9.76 (4 H, m).

**Phenylcyclopropylacetaldehyde.** A mixture of *cis*- and *trans*-1-phenyl-1-cyclopropyl-2-methoxyethylene (43.9 g, 0.247 mol), ether (750 ml), and 70% aqueous perchloric acid (20 ml) was refluxed 24 hr. The cooled mixture was neutralized, washed, and dried. Solvent was stripped and the residue distilled to afford 36.1 g (91%) of phenylcyclopropylacetaldehyde: bp 94–98° (1.5 mm); ir (neat, NaCl) 3050, 2990, 2798, 2680, 1725 (s), 1600, 1490, 1445, 1020, 910, 855, 822, 760, and 700 $cm^{-1}$; pmr (neat) $\tau$ 0.33 (d, 1 H, $J$ = 2.8 Hz), 2.78 (s, 5 H), 7.28 (dd, 1 H, $J$ = 2.8, 9.6 Hz), 8.50–9.05 (m, 1 H), and 9.33–9.90 (m, 4 H). The 2,4-dinitrophenylhydrazone had mp 139–140°. *Anal.* Calcd for $C_{17}H_{16}N_4O_4$: C, 60.00; H, 4.74; N, 16.46. Found: C, 59.75; H, 4.81; N, 16.79.

**4-Cyclopropyl-4-phenylcyclohexenone (5).**[14] Phenylcyclopropylacetaldehyde (32.05 g, 0.201 mol) and freshly distilled methyl vinyl ketone (14.40 g, 0.248 mol) were stirred in dry ether (500 ml) at 0° during addition (1 hr) of 26.5 ml of 2 *N* ethanolic potassium hydroxide. The reaction mixture was stirred at 0–10° for 3 hr more and at 25° for 1.5 hr. After acidification with 25 ml of 2.5 *N* sulfuric acid, the separated ether phase was washed with water and dried over sodium sulfate. The residue from the removal of solvent was chromatographed on 1 kg of silica gel (elution with hexane/ether) to give 25.65 g (60.2%) of **5** as a pale yellow oil; distillation gave material with no detectable impurities: bp 116–121 (0.1 mm); ir (neat, NaCl) 3040, 2980, 1675 (s, C=O), 1485, 1438, 1019, 930, 870, 762 (s), and 700 $cm^{-1}$ (s); uv $\lambda_{max}^{EtOH}$ 208 m$\mu$ ($\epsilon$ 15,000), sh 220 (12,300), sh 262 (1350), and sh 320 (52); $\lambda_{max}^{heptane}$ 346 ($\epsilon$ 66); pmr ($CCl_4$) $\tau$ 2.43–2.83 (m, 5 H), 3.55 (AB quartet, $J$ = 10 Hz, 2 H), 7.57–8.00 (m, 4 H), 8.78 (m, 1 H), and 9.25–9.90 (m, 4 H), mass spectrum *m/e* 212 ($M\cdot^+$) and 184 ($M - C_2H_4$; 100%).

**Preparative Irradiation of 5.** Cyclohexenone **5** (2.05 g, 9.68 mmol) in 1090 ml of *tert*-butyl alcohol was irradiated through Pyrex with a medium pressure mercury lamp in a centerwell apparatus for 60 hr. After removal of solvent, gc analysis of the residue (10% QF-1 on Chromosorb W, 5 ft × 1/8 in. 215°) showed four peaks (in order of increasing retention time) corresponding to **10**, 3.0%; **7**, 34%; **5** + **8**, 20%; and **9**, 43%. Chromatography on 120 g of Florisil monitored at 270 m$\mu$ in a Hitachi Perkin-Elmer flow-through cell gave the following fractions: 1 l. hexane–nil; 1 l. 2% ethyl acetate/hexane–nil; 1.5 l. 2.5% ethyl acetate/hexane–0.578 g of pure **7**; 2 l. 2.5% ethyl acetate/hexane–0.451 g of mixture of 12% **10**, 12% **7**, and 76% **5** + **8**; 3.5 l. of 3% ethyl acetate/hexane–0.794 g of pure **9**. The overlap fraction was subjected to preparative gc on a 20% QF-1 DMCS Chromosorb W column, 3/8 in. × 10 ft. Compounds **10** (35 mg) and **8** (270 mg) were collected.

**Characterization of 5-Cyclopropyl-*trans*-6-phenylbicyclo[3.1.0]-hexan-2-one (7).** A second pass of the above photolysis mixture through the Florisil column or preparative gc on QF-1 gave pure **7** as a colorless oil: bp 105° (0.1 mm); ir (NaCl) 1723 (s, typical of the bicyclo[3.1.0]hexan-2-one framework), 772 (s), and 728 $cm^{-1}$ (s); uv $\lambda_{max}^{EtOH}$ 253.5 ($\epsilon$ 357), 259 (349), 264.5 (271), and 284 m$\mu$ (120) (sh); pmr ($CCl_4$) $\tau$ 2.73 (s, 5 H), 7.38 (d, $J$ = 9.3 Hz, 1 H), 7.78–8.11 (m, 3 H), 8.15–8.47 (m, 1 H), 8.52–8.80 (m, 1 H), 8.93–9.14 (m, 1 H), and 9.26–10.0 (m, 4 H); mass spectrum (70 eV) *m/e* 212 ($M\cdot^+$).

Stirring 80 mg of **7** in 95% EtOD/5% $D_2O$ at 23° with 50 mg of potassium carbonate cleanly exchanged one proton (*exo*-H-3), erasing the multiplet at $\tau$ 8.15–8.47, collapsing the three-proton multiplet to two overlapping doublets ($\tau$ 7.89, $J$ = 8.5 Hz; 8.03, $J$ = 9.4 Hz), and reducing fine structure in the multiplet at 8.93–9.14.

Refluxing the monodeuterated material in 10 ml of 95% EtOD/5% $D_2O$ with 50 mg of potassium carbonate further collapsed the three-proton multiplet to a singlet at $\tau$ 7.90 and a doublet at 8.03 ($J$ = 9.4 Hz) and removed the multiplet at 8.93–9.14 (*endo*-H-3).

The pmr spectrum of 62 mg of **7** and 74 mg of $Eu(fod)_3$ in 200 $\mu$l of $CCl_4$ showed peaks at $\tau$ 1.52 (m, 2 H, aromatic), 2.18–2.67 (m, 3 H, aromatic), 3.87, 4.21 (dm, 1 H, *exo*-H-3), 4.81 (d, $J$ = 9.5 Hz, 1 H, H-1), 5.19 (dd, $J$'s = 9, 19 Hz, 1 H, *endo*-H-3), 6.18 (d, $J$ = 9.5 Hz, 1 H, H-6), 6.63 (m, 2 H, C-4 methylene), 7.91–8.30 (m, 1 H, cyclopropyl methine), and 9.00–9.34 (m, cyclopropyl $CH_2$'s).

(12) H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **89**, 6589 (1967).

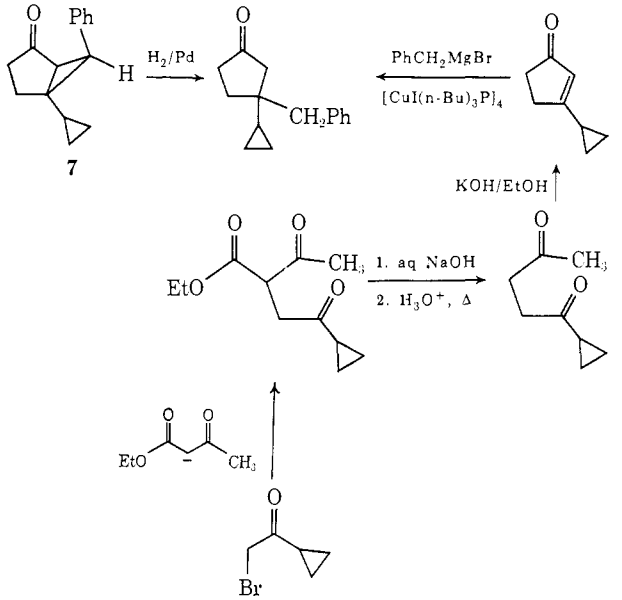
(13) R. P. Mariella and R. R. Raube, *J. Amer. Chem. Soc.*, **74**, 521 (1952).

(14) The method described was adapted from that of H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *J. Amer. Chem. Soc.*, **88**, 4895 (1966).

The $J_{1,6}$ coupling constant (9.5 Hz) is consistent with vicinal *cis*-cyclopropyl protons.[10] *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.90; H, 7.67.

Catalytic hydrogenation of **7** gave 3-benzyl-3-cyclopropylcyclopentanone, identical with material independently synthesized as shown in Scheme III.[15]

**Scheme III**




**Characterization of 5-Cyclopropyl-*cis*-6-phenylbicyclo[3.1.0]hexan-2-one (8).** The third peak collected by pregarative gc of the photolysis mixture was found by pmr analysis to contain 10–12% of unreacted enone **5**. Alumina, silica gel, and Florisil chromatography failed to separate the two isomers; the amount of **5** could be reduced to less than 5% by irradiation of the mixture in *tert*-butyl alcohol for 5 hr, then preparative gc on QF-1. Spectral properties of **8** include: ir (NaCl) 1725 (s, again indicating a bicyclo[3.2.1]hexan-2-one), 752, and 736 $cm^{-1}$; pmr ($CCl_4$) $\tau$ 2.71 (s, 5 H), 7.27 (d, $J$ = 3.2 Hz, 1 H), 7.75–8.00 (m, 4 H), 8.50–9.00 (m, 1 H), and 9.00–9.90 (m, 5 H). A mixture of 21 mg of $Eu(fod)_3$ and 21 mg of **7** ($CCl_4$) showed pmr peaks at $\tau$ 2.08 (m, 2 H, aromatic), 2.40–2.71 (m, 3 H, aromatic), 4.26–4.65 (m, 2 H, C-3 methylene), 4.69 (d, $J$ = 3.2 Hz, 1 H, H-1), 5.64 (d, $J$ = 3.2 Hz, 1 H, H-6), 6.87 (t, $J$ = 7.8 Hz, 2 H, C-4 $CH_2$), and 8.33–9.27 (m, 5 H, cyclopropyl).

The $J_{1,6}$ coupling constant (3.2 Hz) is diagnostic for trans hydrogens on a cyclopropane;[10] thus **8** cannot be a type A product. The cis geometry of the cyclopropyl and phenyl in **8** is further indicated by the absence of phenyl anisotropic shielding of the *endo*-H-3. This hydrogen in **7** appears at ~0.7 ppm higher field than does the exo proton (see above); in **8**, both C-3 hydrogens appear at nearly the same field. *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.40; H, 7.55.

**Characterization of 3-Phenyl-4-cyclopropylcyclohex-2-enone (9).** The last fraction from Florisil chromatography of the photolysis mixture was distilled to give pure **9** as a colorless oil: bp 128° (0.05 mm); ir (NaCl) 3020, 2950, 2900, 1668 (s, C=O), 1600, 1560, 1490, 1436, 1333, 1221, 1020, 887, 772, 755, and 697 $cm^{-1}$; uv $\lambda_{max}^{EtOH}$ 203 ($\epsilon$ 34,100), 221 (20,800), and 282 m$\mu$ (19,600); pmr ($CCl_4$) $\tau$ 2.57 (s, 5 H), 3.91 (s, 1 H), 7.48–7.95 (m, 5 H), and 8.68–10.00 (m, 5 H). The ir carbonyl frequency (1668 $cm^{-1}$) and the pmr vinyl singlet at $\tau$ 3.91 are consistent with a 3-substituted cyclohex-2-enone; the uv maxima are similar to those of 3-phenylcyclohex-2-enone: 221 (10,000) and 283 m$\mu$ (19,500).[16]

The product derivable from cyclopropyl migration in **5**, 3-cyclopropyl-4-phenylcyclohex-2-enone, was independently prepared by condensation of benzyl cyclopropyl ketone with methyl vinyl ketone. Its uv spectrum consisted of a single maximum at 255 m$\mu$ ($\epsilon$ ~18,000); other spectral properties were quite distinct from those of **9**. These data unambiguously establish **9** as 3-phenyl-4-cyclopropylcyclohex-2-enone.

The semicarbazone of **9** has mp 194–195°. *Anal.* Calcd for $C_{16}H_{19}N_3O$: C, 71.35; H, 7.11; N, 15.60. Found: C, 71.23; H, 7.22; N, 15.42.

**Characterization of *endo*-6-Phenyl-*exo*-6-cyclopropylbicyclo[3.1.0]hexan-2-one (10).** After one more pass through the QF-1 preparative column, **10** crystallized from hexane as colorless needles: mp 78–79°; ir (KBr) 1728 (s), 1020 (s), and 765 $cm^{-1}$ (s); pmr ($CCl_4$) $\tau$ 2.70 (s, 5 H), 7.97 (m, 4 H), 8.25–9.18 (m, 3 H), and 9.25–9.96 (m, 4 H); uv $\lambda_{max}^{EtOH}$ 252 ($\epsilon$ 308), 258 (317), 364.5 (268), and 280 m$\mu$ (116, sh). *Anal.* Calcd for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.52; H, 7.84.

Independent synthesis of **10** was accomplished as shown in Scheme II.[15]

**Analytical (Direct) Photolysis of 5.** Irradiations in heptane, benzene, *tert*-butyl alcohol, 10% aqueous dioxane, or methanol were carried out using a 450-W Hanovia medium pressure mercury lamp cooled by circulating water; the temperature of the solution was 45 ± 2°.

In a typical experiment 320 mg of **5** was dissolved in 155 ml of solvent, degassed for 0.5 hr with oxygen-free nitrogen, and irradiated for 10 hr. A positive nitrogen pressure was maintained throughout the reaction. Rates of formation of **7**, **9**, and **10** were monitored by gc analysis of aliquots withdrawn at intervals throughout the experiment. The percentage of starting material was determined by pmr at the end of the irradiation and the amount of bicyclic ketone **8** calculated by difference.

**Sensitized Photolysis of 5.** A typical experiment is described. A solution of acetophenone (4.110 g, 34.3 mmol) and **5** (355 mg, 1.68 mmol) in 155 ml of *tert*-butyl alcohol was degassed and irradiated as previously described. The acetophenone was calculated to absorb more than 96% of the incident light. Product formation was monitored as in direct photolysis.

**Acknowledgment.** The authors are grateful to Dr. Gary R. Elling for performing the irradiation experiments in methanol.

(15) For synthesis details, see D. W. Kurtz, Ph.D. Dissertation, Syracuse University, 1971.

(16) C. N. Walker, *J. Amer. Chem. Soc.*, 77, 3664 (1955).