56–62°. Vacuum sublimation of the crude solid at 54° (0.1 mm) in a microsublimation apparatus gave crystals, mp 64–65°, which gave a satisfactory elemental analysis for 2-hydroxy-2-phenyl-bicyclo[1.1.1]pentane.

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.29; H, 7.46.

The infrared spectrum shows hydroxyl bands at 2.87 and 3.02 μ and a carbon–oxygen stretching band at 8.25 μ. The ultraviolet spectrum (95% ethanol) with maxima at 264, 258, 252, and 247 mμ (ϵ 160, 220, 195, and 155) is characteristic of an isolated benzene ring. The 100-MHz nmr spectrum is in excellent agreement with the proposed structure. The bicyclo[1.1.1]pentanol shows the aromatic hydrogens as a singlet at τ 2.73, the two bridgehead hydrogens as a singlet at 7.08, the hydroxyl proton as a singlet at 7.70, a doublet of doublets (J = 10.0 and 3.0 Hz) at 7.24, a doublet (J = 3.0 Hz) at 8.31, a doublet (J = 3.0 Hz) at 8.58, and a doublet of doublets (J = 10.0 and 3.0 Hz) at 8.73. The peak areas are in the ratio of 5:2:1:1:1:1:1. These assignments for the spin–spin coupling interactions were tested through double resonance experiments. When the signal at τ 7.24 was saturated with an external field, the doublet at 8.31 collapsed to a singlet and the signal at 8.73 collapsed to a doublet (J = 3.0 Hz). The mass spectrum of this material included peaks with m/e 160 (M^+), 159, 105 (base peak), 91, 77, 55, 51, and 39. The structure of this material was further confirmed on the basis of an X-ray single-crystal structure analysis of its urethan derivative.[23]

Quantum Yield Determinations. All quantitative measurements were made on a rotating assembly with a central light source (internal water-cooled mercury arc lamp, Hanovia Type L 450-W). Samples in 13-mm Pyrex ampoules were placed in holders on the assembly 5.5 cm from the immersion well. Corning 2 × 2 in. 7-39 filters (transmission 320–400 mm) were mounted in four filter holders flush against the well. The rest of the well was taped to eliminate stray light. All studies were made at room temperature. Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations.

An actinometer quantum yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[48] In the quantum yield determinations for the photoreduction of cyclobutyl phenyl ketone in isopropyl alcohol, actinometer tubes containing 0.1 M benzophenone and 1.0 M benzhydrol in benzene were used with a quantum yield of 0.97.[48] Reliably reproducible output rates of 5.0×10^{16} quanta/sec were recorded. After the irradiation the degree of reaction was determined by quantitative ultraviolet spectroscopy and vapor phase chromatography. The conversions in the cyclobutyl phenyl ketone system were run to 15% or less. The mass balance in the benzene runs were generally better than 95%.

Quenching Studies. Cyclobutyl phenyl ketone (98.4 mg) was dissolved in 10 ml of benzene. To each of five Pyrex tubes was added 1 ml of the above solution. To four of the tubes was added, respectively, 0.04, 0.02, 0.008, and 0.002 mg of naphthalene. One tube without any naphthalene was set aside as a control, and the four degassed, sealed tubes were placed in a turntable surrounding a 450-W Hanovia high-pressure Hg lamp in a quartz immersion well. The turntable was rotated slowly and the tubes were irradiated for 6 hr. At the end of this time, 1.47 mg of nitrobenzene was added to each of the tubes, and the solvent was removed at reduced pressure at room temperature until the residual volume was about 0.1 ml. The mixture was analyzed by glpc on a 5-ft 10% DEGS on 60–80 mesh Chromosorb W column at an oven temperature of 120° and a helium flow rate of 60 cc/min. The areas under the peaks due to the standard (nitrobenzene) and products were measured using a planimeter after triangulation. Each set of chromatograms was measured twice in this way, and the results were converted to per cent reaction based on starting ketone.

Transannular Hydrogen Abstraction in Small Ring Carbocyclic Systems[1,2]

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Abstract: On irradiation cyclopentyl phenyl ketone has been found to rearrange principally to 1-phenyl-5-hexen-1-one. Further irradiation affords 1-phenyl-4-hexen-1-one, 1-phenyl-1-hydroxy-2-vinylcyclobutane, 1-phenyl-3-cyclohexen-1-ol, and acetophenone. The photochemical transformations encountered in this work appear to be best described by a transannular hydrogen abstraction followed by subsequent reactions of the diradical thus formed. The photorearrangement was shown to proceed by way of a triplet n–π* state. In striking contrast to the extraordinarily slow and inefficient reaction in the cyclobutyl system, cyclopentyl phenyl ketone was found to rearrange with high quantum efficiency and of the order of three powers of ten faster.

The literature provides many examples of transannular hydrogen transfer in medium sized rings.[4] The isolation of N-methylgranatanine from the photolysis of a strongly acid solution of N-chloro-N-methylcyclooctylamine provided an important precedent for transannular hydrogen abstraction by a radical site.[5] It has been reported that the alkoxy radical rearrangement of cyclooctyl nitrite gives a product resulting from attack on a hydrogen atom in the 4 position.[6] A similar transannular free-radical reaction has also been observed in the photochemically induced rearrangement of 1-methylcyclooctyl hypochlorite.[7] The first example of a transannular hydrogen

(1) Photochemical Transformations of Small Ring Carbonyl Compounds. XX. For part XIX, see A. Padwa, E. Alexander, and M. Niemcyzk, *J. Am. Chem. Soc.*, 91, 456 (1969).

(2) Support of this research by a grant from the Air Force Office of Scientific Research (Grant No. AF-AFOSR-1213-67) is acknowledged with appreciation.

(3) Alfred P. Sloan Foundation Fellow, 1968–1970.

(4) For a review see, A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.* (London), 20, 119 (1966).

(5) S. Wawzonek and P. J. Thelen, *J. Am. Chem. Soc.*, 72, 2118 (1950).

(6) P. Kabasakalian and E. R. Townley, *J. Org. Chem.*, 27, 2918 (1962).

abstraction by an electronically excited state was reported by Barnard and Yang, who obtained a mixture of cis- and trans-9-decalols from the irradiation of cyclodecanone.[8] Similar transannular reactions have been observed in the photolysis of cyclododecanone[9] and 1,2-cyclodecanedione.[10] It seems clear from later mechanistic studies of the Norrish type II photo-elimination[11] that the reactive electronic state of cyclodecanone is of the n-π^* configuration and that it reacts by a transannular hydrogen abstraction.

In part XIX of this study of the photochemical transformations of small ring carbonyl compounds, it was shown that on irradiation of cyclobutyl phenyl ketone (I) in benzene the major products were compounds II and III.[12] The isolation of these compounds
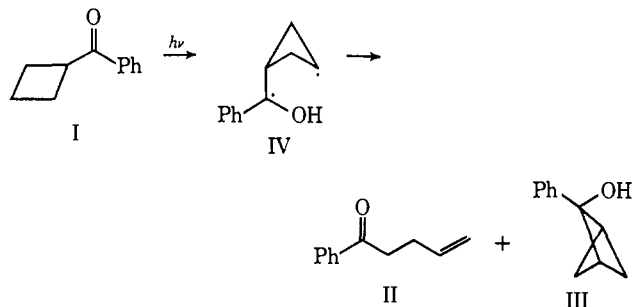
seemed most consistent with the intermediacy of the diradical IV which proceeds to products by ring closure or bond fragmentation. The formation of the diradical (IV) was proposed to occur by a novel transannular hydrogen abstraction by the excited n-π^* triplet. At the time this study was initiated, there were few examples of authenticated transannular hydrogen transfers in small-membered rings.[13,14] Documentation of this reaction pathway in related carbocyclic rings seemed worthwhile. To this end we undertook the study of the irradiation of cyclopentyl and substituted cyclohexyl phenyl ketones. It was also hoped that the transannular hydrogen abstractions in these carbocyclic systems could be put on a firm quantitative basis by examining both the quantum efficiency and rates of reaction.

Results and Discussion

Cyclopentyl phenyl ketone (V) was synthesized by a modification (see Experimental Section) of the procedure of Hey and Musgrave.[15] The irradiation of V was conducted in anhydrous benzene using an internal water-cooled mercury arc lamp (Hanovia, Type L, 450 W) fitted with a Pyrex filter. The photolysis was followed by withdrawal of small aliquots at various time intervals and examination of these by vapor phase chromatography. Careful monitoring of the photochemical rearrangement indicated that the rate of disappearance of V was relatively rapid at the outset but

(7) A. C. Cope, R. S. Bly, M. M. Martin, and R. C. Petterson, *J. Am. Chem. Soc.*, **87**, 3111 (1965).
(8) M. Barnard and N. C. Yang, *Proc. Chem Soc.*, 302 (1958).
(9) B. Camerino and B. Patelli, *Experientia*, **20**, 260 (1964).
(10) W. H. Urry, D. J. Trecker, and D. A. Winey, *Tetrahedron Letters*, 609 (1962).
(11) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 1245 (1966).
(12) See ref 1.
(13) A. Padwa and W. Eisenhardt, *J. Am. Chem. Soc.*, **90**, 2442 (1968).
(14) A. Padwa and R. Gruber, *ibid.*, **90**, 4456(1968).
(15) D. H. Hey and O. C. Musgrave, *J. Chem. Soc.*, 3156 (1949).

gradually diminished to a point where secondary photoreactions appeared to predominate. The data are summarized in Table I. Preparative vapor phase

Table I. Representative Time and Percentage Composition Values for the Photoreaction of Cyclopentyl Phenyl Ketone

Time,[b] hr	V	VI	VII	VIII	IX	X
0.5	80	2	18	..	...	..
4	15	22	14	15	2	9
8	..	32	..	12	3	12

[a] Percentage composition was calculated as described in the Experimental Section. [b] Pyrex filter in benzene as the solvent.

chromatography of photolysis mixtures permitted the purification and isolation of four components. An additional photoproduct whose average yield was approximately 3% was not present in quantities sufficient for isolation but was nevertheless assigned as 1-phenyl-1-hydroxy-2-vinylcyclobutane. Several small peaks attributed to butadiene dimers also appeared in the gas chromatogram. The products were identified in their order of elution from the gas chromatographic column as acetophenone (VI), 1-phenyl-5-hexen-1-one (VII), 1-phenyl-4-hexen-1-one (VIII), 1-phenyl-1-hydroxy-2-vinylcyclobutane (IX), and 1-phenyl-3-cyclohexen-1-ol (X). Spectral comparisons with authentic
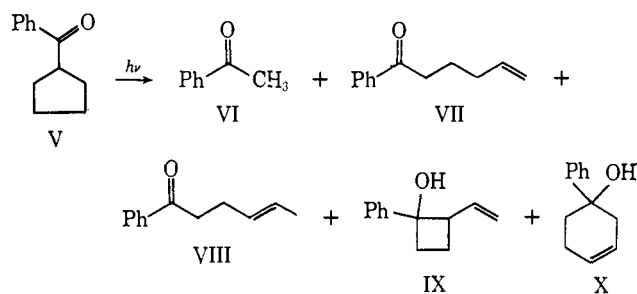

samples served to confirm the structures of VI and VIII. The major product initially formed was assigned structure VII on the basis of its analysis (2,4-DNPH derivative), spectral data, and chemical behavior. The infrared spectrum in CCl$_4$ shows a strong carbonyl band at 5.95 μ and a terminal vinyl group at 10.85 μ. Nmr studies in carbon tetrachloride indicated, *inter alia*, the presence in VII of three vinylic protons as multiplets centered at τ 5.20 (2 H) and 4.50 (1 H). Conclusive chemical evidence was derived from its catalytic hydrogenation to 1-phenylhexan-1-one. The other two materials present in the photolysis mixture were identified by their spectroscopic properties (see Experimental Section) and by chemical degradation. A photolysis of V was carried out in benzene and the crude reaction mixture was subjected to catalytic hydrogenation. The resulting mixture yielded 1-phenyl-2-ethylcyclobutanol and 1-phenylcyclohexanol, the expected reduction products of IX and X.

Consideration of the product distribution as a function of time in a number of photolyses showed an initial buildup of VII followed by a decrease in amount. This contrasted with a steady increase in the yields of the remaining products (Table I). With short exposures VII accounts for nearly all the products produced. At longer exposures, owing to secondary

reactions, the yield of VII gradually decreases. From the time studies, it is clear that VII is an intermediate in the formation of the remaining products. This was further confirmed by irradiation of VII in benzene under conditions comparable to those used for V. Photolysis of VII afforded compounds VI, VIII, IX, and X in about the same distribution as found in runs beginning with cyclopentyl phenyl ketone.
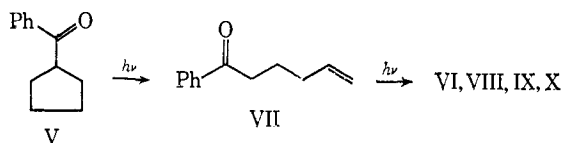
The Norrish type II photoelimination and cyclobutanol formation is undoubtedly the most common photoreaction of aliphatic and aromatic ketones that possess a hydrogen bearing γ-carbon.[16] The present evidence suggests that abstraction of the γ-hydrogen is reversible and can occur from either the first excited singlet state or from the triplet state.[17-19] The intermediate diradical formed in this process can either ring close or fragment. Chart I illustrates an adaption of this mechanism to describe the results of the present study.

Chart I
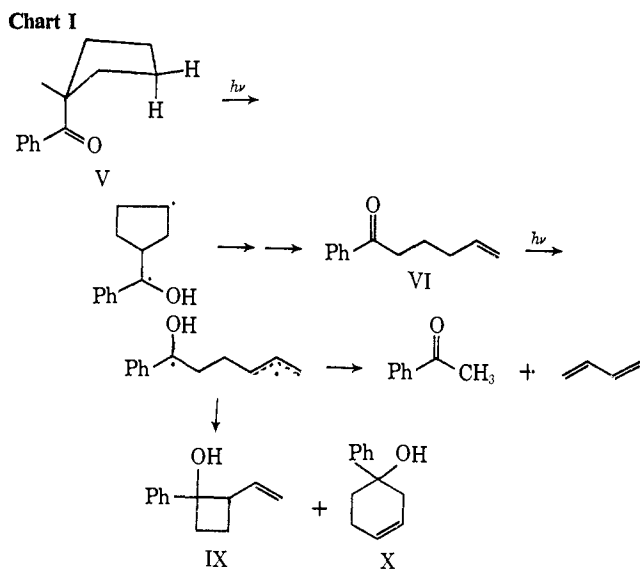
A priori, the possibility exists that VII could have arisen by ring scission in the manner described below.
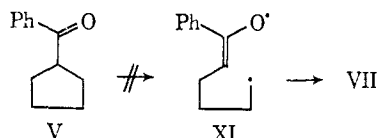
The problem as to whether an intermediate diradical depicted as XI is involved is not fully answered by the experimental results. However, for a species such as XI to lead to such a clean rearrangement is remarkable. One might qualitatively expect that this intermediate would afford a mixture of 2- and 5-hexen-1-ones.

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, pp 377–427.
(17) P. J. Wagner and G. S. Hammond, *J. Am. Chem. Soc.*, 87, 4009 (1965); 88, 1245 (1966).
(18) T. J. Dougherty, *ibid.*, 87, 4011 (1965).
(19) P. J. Wagner, *Tetrahedron Letters*, 1753 (1967); *J. Am. Chem. Soc.*, 89, 5988 (1967).

This is not the case. A more serious objection is that ring opening followed by disproportionation between the radical centers in XI would require an unfavorable 1,5- or 1,7-hydrogen shift. Furthermore, this path is inconsistent with the enhanced quantum efficiency and reaction rate (see below) of V when compared to cyclobutyl phenyl ketone. Photochemical ring opening to a diradical would be expected to be faster for the more highly strained four-membered ring. Therefore, it appears that ring opening by β scission is not a major reaction path of V and that a transannular hydrogen abstraction, similar to that invoked for the photochemistry of cyclobutyl phenyl ketone, adequately explains the formation of VII. It is noteworthy that no detectable quantities of 2-phenyl-2-hydroxybicyclo[2.1.1]hexane were found in the photolysis mixture. Thus it seems as though the diradical produced by transannular hydrogen abstraction prefers fragmentation to ring closure. This is in marked contrast to the results obtained in the cyclobutyl phenyl ketone system, where ring closure predominates. As stated earlier,[1] the preferred conformation for photoelimination requires that the four carbon atoms be coplanar for maximum overlap between the developing π orbitals and the π orbitals at the radical center. Such overlap is geometrically more feasible in the five-ring system and accounts for the preponderance of ring scission over ring closure.

On the basis of the spectral data for V the reaction may be formulated as occurring by means of n–π^* excitation. The question then arises whether singlet or triplet species are responsible for the subsequent rearrangement. The phosphorescence emission spectrum of V in an ethanol–methanol glass was determined at 77°K. From the location of the 0–0 band, the energy of the lowest triplet is found to be 74.1 kcal. The vibrational spacing between the 0–0 and 0–1 band is 1670 cm^{-1}. These results provide strong evidence for the emission coming from an n–π^* triplet, produced by intersystem crossing from the initially generated singlet. Quenching of the photolysis of V by naphthalene was observed with use of a Corning O-52 filter in addition to Pyrex, ensuring no light absorption by naphthalene (Table II). The observation of retardation of the

Table II. Quantum Yields in Quenched Irradiations of Cyclopentyl Phenyl Ketone (V) and 1-Phenyl-5-hexen-1-one (VII)

Run[a]	[V][b]	[VII][b]	Naphthalene, $10^3\ M$	Quantum yield[c]
1	0.019	...	...	0.40 ± 0.02
2	0.019	...	1.0	0.33 ± 0.03
3	0.019	...	6.5	0.14 ± 0.02
4	0.019	...	8.6	0.11 ± 0.01
5	0.019	...	10.0	0.091 ± 0.01
6	...	0.014	...	0.45 ± 0.03
7	...	0.015	8.3	0.35 ± 0.02
8	...	0.014	10.4	0.29 ± 0.02
9	...	0.015	16.6	0.20 ± 0.02
10	...	0.015	21.2	0.16 ± 0.01

[a] At 350 mμ in benzene at 25°. [b] Moles/liter. [c] Disappearance of V or VII.

reaction of V with naphthalene supports a n–π^* triplet as the reactive electronic state involved. Additionally, the reciprocal of the quantum yield was found

to vary linearly with quencher concentration [Q] in accordance with the Stern–Volmer expression (eq 1).

$$\frac{1}{\Phi} = \frac{k_r + k_d}{k_r} + \frac{k_q[Q]}{k_r} \qquad (1)$$

From the observed slope of 750 for the Stern–Volmer plot, and using $k_q = 5 \times 10^9$ l. mol^{-1} sec^{-1},[17] the value for the unimolecular rate constant for rearrangement from the triplet state, k_r, is found to be 6.7×10^6 sec^{-1}. This result indicates that the rate of rearrangement is of the order of 1200-fold larger for V than for the related cyclobutyl phenyl ketone system.

The course of the photochemical reaction of 1-phenyl-5-hexen-1-one (VII) in benzene may be considered analogous to the documented photochemical behavior of 6-hepten-2-one.[20] As indicated in Chart II, the formation of VI, IX, and X is readily rationalized by intramolecular hydrogen transfer from carbon to the p_y orbital of oxygen of the n–π^* excited state.

Chart II
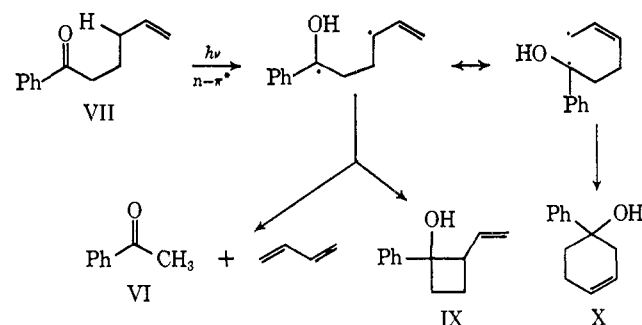
Photolysis of VII with naphthalene showed quenching of the rate of disappearance of VII (Table II). The data very clearly demonstrated that the formation of all products occur from the triplet state of the ketone. From the usual Stern–Volmer expression (eq 1) a value of $k_r = 3.6 \times 10^7$ sec^{-1} was calculated with the assumption that $k_q = 5 \times 10^9$ l. mol^{-1} sec^{-1}.[17] The value of k_r is approximately the same as that found for valerophenone[17] and is about sixfold more rapid than cyclopentyl phenyl ketone (V). This result demonstrates that the rates of formation of VI, VIII, IX, and X from VII are sufficiently rapid to account for their genesis in the photorearrangement of cyclopentyl phenyl ketone.

The formation of the disubstituted keto olefin VIII from the irradiation of VII is of considerable interest. This type of photoproduct has not been observed in the related 6-hepten-2-one system.[20] Several mechanisms may be advanced to explain its formation. The possibility that VIII results by internal hydrogen transfer followed by disproportionation between the
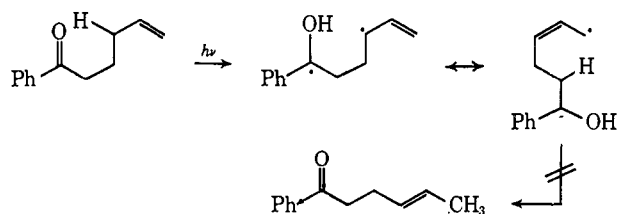
radical centers in the manner described above appeared attractive.

(20) N. C. Yang, A. Morduchowitz, and D. D. H. Yang, *J. Am. Chem. Soc.*, **85**, 1017 (1963).

In order to help elucidate the correct pathway, the photoisomerization of 1-phenyl-5-hexen-1-one-2,2-d_2 (XII) was examined. The deuterium-labeled ketone was prepared by the base-catalyzed exchange of VII in deuterated methanol. It was assayed for >95% d_2 by nmr analysis. Irradiation of XII afforded product VIII that was shown to have maintained both deuterium atoms α to the benzoyl group, as evidenced by nmr
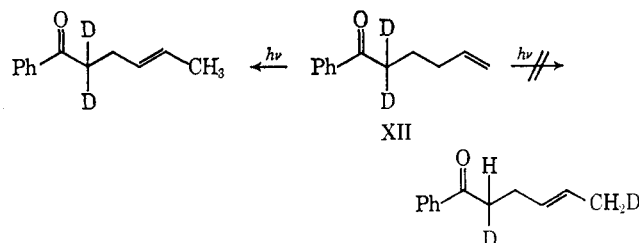
analysis. The absence of any significant amount of deuterium on the terminal carbon was clearly demonstrated from the nmr integration. The spectral evidence obtained clearly excludes the above mechanistic route.

It was also considered feasible that VIII could have arisen by intermolecular attack of an excited n–π^* ketone on the available allylic hydrogens of VII.
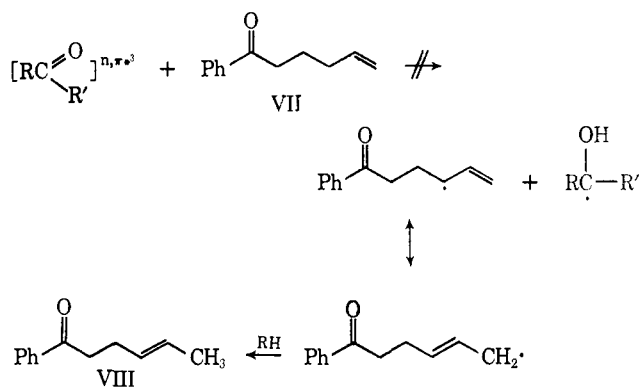
However, this mechanistic route is presently viewed as unlikely because the production of VIII is not dependent on the concentration of VII. Furthermore, this path is inconsistent with the observation that irradiation of VII in the presence of a fivefold excess of 1-octene (or methylenecyclohexane) caused no isomerization of the added olefin.

One can entertain at least two additional routes for the formation of VIII. One path may involve intramolecular energy transfer from the triplet state of the carbonyl group to the double bond with concomitant isomerization. Intramolecular photosensitization of this type is known to effect reaction at the olefinic site,[21,22] although a 1,3-hydrogen shift is without precedent. The formation of the isomerized ketone is probably not related to the double-bond isomerizations reported by Kropp[23] and Marshall[24] since those transformations occur only with cyclic ketones. Alternatively, the photoisomerization may proceed through a sequence involving γ-hydrogen abstraction, radical isomerization, and reverse transfer *via* an eight-mem-

(21) H. Morrison, *Tetrahedron Letters*, 3653 (1964); *J. Am. Chem. Soc.*, **87**, 932 (1965).
(22) R. L. Cargill, J. R. Damewood, and M. M. Cooper, *ibid.*, **88**, 1330 (1966).
(23) P. J. Kropp, *ibid.*, **88**, 4091 (1966).
(24) J. A. Marshall and R. D. Carroll, *ibid.*, **88**, 4092 (1966).

bered transition state. At the present time there is no basis for choosing one of these possibilities, although it may become possible to make more detailed statements in the future.

With the above results in hand, we considered it relevant to explore the photochemistry of the related six-membered cycloalkane.[25] Irradiation of cyclohexyl phenyl ketone (XIII) under conditions very similar to those used for V afforded only recovered starting material. Prolonged photolysis (20 hr) afforded small amounts of acetophenone (1%). Similarly, the irradiation of cis-4-t-butylcyclohexyl phenyl ketone (XIV) was very inefficient and afforded only acetophenone upon prolonged exposure. Examination of the photolysis mixture by infrared and nuclear magnetic resonance spectroscopy showed the absence of a terminal vinyl group but did indicate that reduction of the benzoyl group occurred. These results are entirely analogous to those reported by McIntosh.[26] The more stable conformers of the cyclohexane rings in XIII and XIV are the equatorial chair form of the cyclohexyl phenyl ketone and the diequatorial twist boat form of the cis-4-t-butylcyclohexyl phenyl ketone. Neither of these conformations readily permits the nonbonding electron on the oxygen of the n–π* state to come within the required distance for transannular abstraction.

Conclusion on Reaction Efficiency

The values found for the quantum yields and triplet reaction rates for the benzoylcycloalkanes studied are summarized in Table III. From the table, it can be

Table III. Quantum Yields and Reaction Rates of Benzoylcycloalkanes (RCOPh)

R	Φ	k_r, sec^{-1}
Cyclobutyl	0.03	5.5×10^3
Cyclopentyl	0.40	6.7×10^6
Cyclohexyl	<0.005	...
4-t-Butylcyclohexyl	~0.008	...

concluded that the ability of the n–π* state to undergo transannular hydrogen abstraction is markedly dependent on ring size. The higher efficiency of the cyclopentyl phenyl ketone system, when compared to the other benzoylcycloalkanes, can be attributed both to the preferred reactive conformation and the more favorable stereoelectronic features of the abstraction step.

Experimental Section

General. Nmr spectra were recorded on a Varian A-60 spectrometer using carbon tetrachloride as solvent. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark. Gas–liquid partition chromatographic analyses and preparative separations were carried out using a F & M Model 5720 instrument equipped with a 6 ft × 0.25 in. 20% Apiezon M on 60-80 mesh Chromosorb W column. Irradiations were carried out using Hanovia 450- and 550-W,

medium-pressure mercury lamps with water-cooled quartz immersion wells.

Cyclopentyl Phenyl Ketone. The procedure of Hey and Musgrave[15] was adopted to the present case. Cyclopentanecarboxyl chloride was prepared by the treatment of cyclopentanecarboxylic acid (11.4 g) with a solution of thionyl chloride (14 ml) in dry benzene (40 ml) and one drop of pyridine at 50° for 2 hr. The benzene and excess thionyl chloride were removed by distillation under reduced pressure. The residual acid chloride was used without further purification. A solution of the acid chloride (10.6 g) in anhydrous benzene (100 ml) was added to powdered anhydrous aluminum chloride (18 g). The mixture was heated on a steam bath for 1 hr, then poured into ice (300 g) and concentrated hydrochloric acid (200 ml). The aqueous solution was extracted with ether, which was washed with sodium bicarbonate and water, and dried over magnesium sulfate. The solution was concentrated and distilled to yield 8.6 g of clear colorless cyclopentyl phenyl ketone, bp 136-140° (16 mm).

1-Phenyl-5-hexen-1-one. To a solution of the Grignard reagent prepared from 0.81 g of magnesium and 5.0 g of 1-bromo-4-pentene in 100 ml of anhydrous ether was added slowly and with stirring 3.6 g of benzaldehyde in 50 ml of ether. The mixture was heated on a steam bath for 0.5 hr and then decomposed by ice and a 10% solution of hydrochloric acid. The ether layer was separated, washed once with water, then dried over anhydrous sodium carbonate, and fractionated through a 4-in. Vigreux column. The product (2.0 g) distilled at 76-92° (1.0 mm).

To 2.0 g of the above 1-phenyl-5-hexen-1-ol in 100 ml of pentane was added 10.0 g of activated manganese dioxide. The mixture was stirred for 24 hr at room temperature. At the end of this time, the mixture was filtered and the filtrate was concentrated under reduced pressure and distilled to yield 1.7 g of 1-phenyl-5-hexen-1-one, bp 77-78° (3 mm); infrared spectrum: 5.90, 6.05, and 10.85 μ; nmr: multiplet at τ 8.12, triplet at 7.27 (J = 6.5 Hz, 2 H), multiplets at 5.20 (2 H), 4.50 (1 H), 2.86 (3 H), and 2.40 (2 H). The 2,4-dinitrophenylhydrazone derivative had mp 161-162°.

Anal. Calcd for $C_{18}H_{18}N_4O_4$: C, 61.01; H, 5.12. Found: C, 60.97; H, 5.21.

1-Phenyl-4-hexen-1-one. A solution of 150 g of acetophenone and 68 g of crotyl bromide in 600 ml of benzene was cooled to 5°. To the mixture was added 56 g of potassium t-butoxide, taking care to keep the temperature below 25°. The solution was allowed to stir at room temperature for 2 hr and was then diluted with water. The aqueous solution was extracted with ether, and the combined extracts were dried over sodium sulfate. The solvent was removed under reduced pressure and the residue distilled to yield 135 g of 1-phenyl-4-hexen-1-one, bp 68-72° (0.7 mm); infrared spectrum: 5.95, 6.04, and 10.31 μ; nmr: distorted doublet at τ 8.43 (3 H), multiplets at 7.70 (2 H), 7.12 (2 H), 4.73 (2 H), 2.83 (3 H), and 2.35 (2 H). The semicarbazone derivative had mp 128-129° (lit.[27] 129-130°).[27]

cis-4-t-Butylcyclohexyl Phenyl Ketone. cis-4-t-Butylcyclohexylcarbonyl chloride[28] (10 g) was added dropwise in 100 ml of dry benzene to a mixture of aluminum chloride (10 g) in benzene (500 ml). After the mixture was stirred for an additional 3 hr, it was hydrolyzed with water (300 ml) and extracted twice with ether. The ethereal layer was washed with water, dried over sodium sulfate, and evaporated to dryness. Crystallization of the residue from pentane–chloroform gave cis-4-t-butylcyclohexyl phenyl ketone (53%), mp 108-109° (lit.[26] 108-109°); infrared spectrum 5.94 μ; ultraviolet spectrum (95% ethanol) λ_{max} 240 (4.08), 319 (1.96), and 275 mμ (log ε 2.31). The 2,4-dinitrophenylhydrazone derivative melted at 157-158°.

Irradiation of Cyclopentyl Phenyl Ketone. A. Preparative Scale. Cyclopentyl phenyl ketone (1 g) dissolved in 950 ml of anhydrous benzene was irradiated for 8 hr under a nitrogen atmosphere with a 450-W, medium-pressure Hanovia Type L mercury arc in an immersion well apparatus fitted with a Pyrex filter. The solvent was removed on a rotary evaporator and the residue (0.96 g) was subjected to preparative vpc separation [6 ft × 0.25 in copper column packed with 20% Apiezon M on Chromosorb W (60-80 mesh)] at 170°.

The first material to be eluted (1.2 min) was identified as acetophenone by comparison of retention time and infrared spectra with an authentic sample. The second product (5.8 min) was 1-phenyl-5-hexen-1-one, bp 77° (3 mm). The third peak (6.4 min)

(25) While this work was in progress a report on the photochemistry of the cyclohexyl phenyl ketone system appeared.[26]

(26) C. L. McIntosh, Can. J. Chem., 45, 2267 (1967).

(27) W. Kimel and A. C. Cope, J. Am. Chem. Soc., 65, 1992 (1943).

(28) H. H. Lau and H. Hart, ibid., 81, 4897 (1959).

corresponded to 1-phenyl-4-hexen-1-one, bp 68° (0.7 mm). The authenticity of these structures was derived by comparison of vpc retention times on two columns, infrared spectra, and nmr spectra. The fourth peak (8.2 min) consisted of a mixture of unreacted starting material and an unsaturated alcohol. This mixture could be resolved by glpc on a 5 ft × 0.25 in 10% DEGS on Chromosorb W (60–80 mesh) column at 170°. The unsaturated alcohol was identified as 1-phenyl-3-cyclohexen-1-ol on the basis of its infrared spectrum: 2.87, 8.51, 9.48, and 11.38 μ; nmr: multiplet at τ 7.84 (7 H), broad singlet at 4.24 (2 H), and a multiplet centered at 2.67 (5 H); and by the catalytic reduction to 1-phenylcyclohexanol.

B. Analytical Scale. A solution of 200 mg of cyclopentyl phenyl ketone in 100 ml of benzene was irradiated using a 450-W lamp through Pyrex. Aliquots were removed at 0.5-hr intervals (2-hr intervals after most of the starting material had disappeared) and were analyzed by glpc. After the first 0.5-hr period four components with retention times 1.2, 5.8, 6.4, and 8.4 min, respectively (retention time of cyclopentylphenyl ketone, 8.2 min), had appeared. The concentration of the second component passed through a maximum after 3 hr and decreased along with starting material as irradiation proceeded. Prolonged photolysis led to the disappearance of the second component and a slight shift in the retention time of the fourth peak. A similar irradiation through quartz produced the same components at a much faster rate.

Hydrogenation of Crude Photolysate Mixture. The crude photolysate mixture (500 mg) was hydrogenated in ethyl acetate at 15 psig in a Parr shaker over 10% palladium on charcoal at 30° for 24 hr. After filtration to remove the catalyst, the solution was concentrated and submitted to preparative glpc [6 ft × 0.25 in. 10% FS 1265 on Chromosorb W (60–80 mesh) column at 160°]. The four products present were characterized as acetophenone, 1-phenyl-1-hexanone, 1-phenylcyclohexanol, and 1-phenyl-2-ethylcyclobutanol. Comparison of retention times and infrared spectra with those of authentic samples established the identity of the four major products. 1-Phenyl-2-ethylcyclobutanol was prepared from the irradiation (8 hr) of 1.0 g of 1-phenyl-1-hexanone in 500 ml of dry benzene. Concentration of the photolysate and collection of the peak at retention time 1.6 min on a 6 ft × 0.25 in. 10% SF 1265 (Chromosorb W) column at 160° provided an authentic sample. 1-Phenylcyclohexanol was prepared by treating cyclohexanone (9.8 g in 100 ml of ether) with 50 ml of a 2.14 M solution of phenyllithium, followed by hydrolysis with a saturated ammonium chloride solution. The major component was collected by preparative glpc and was identical in all respects with the material isolated from the hydrogenation of the crude photolysate mixture.

Irradiation of 1-Phenyl-5-hexen-1-one-2,2-d_2. A 1.0-g sample of 1-phenyl-5-hexen-1-one and 0.1 g of sodium methoxide in 10 ml of methanol-d_1 was refluxed for 1 week. Removal of the solvent and distillation through a short-path distillation head gave 0.93 g

of 1-phenyl-5-hexen-1-one-2,2-d_2 that assayed for 97% d_2 by nmr analysis. A solution of 0.93 g of the deuterated ketone in 950 ml of benzene was irradiated for 3 hr using a 450-W lamp through Pyrex. Glpc analysis indicated that the content of starting ketone had decreased by more than 50%. The products isolated by preparative glpc were acetophenone, 1-phenyl-4-hexen-1-one-2,2-d_2 (all the deuterium appeared on the α carbon), and 1-phenyl-4-cyclohexen-1-ol-2,2-d_2.

Irradiation of cis-4-t-Butylcyclohexyl Phenyl Ketone. A solution of 1.0 g of cis-4-t-butylcyclohexyl phenyl ketone in 950 ml of benzene was photolyzed for 24 hr in the same manner as described above for the cyclopentyl phenyl ketone. Gas chromatographic analysis of the product mixture revealed the presence of acetophenone (11%) and starting material. The infrared and nuclear magnetic resonance spectra of the crude photolysate showed no terminal vinyl group, but did indicate partial reduction of the benzoyl group. Similar results were obtained when trans-4-t-butyl-cyclohexyl and cyclohexyl phenyl ketones were irradiated under comparable conditions. For these systems only trace amounts of acetophenone (ca. 1%) were detected.

Quantum Yield Determinations. In any given run degassed tubes containing different concentrations of naphthalene were irradiated in parallel with samples containing only ketone, all for the same length of time. Irradiations were performed in a "merry-go-round" apparatus which assured that each sample absorbed the same intensity of light.[29] Samples in 13-mm Pyrex test tubes were degassed to 5×10^{-3} mm in three freeze–thaw cycles and then sealed. Benzophenone–benzhydrol actinometry was used for quantum yield determinations. An actinometer yield of 0.69 was used when the concentration of benzophenone and benzhydrol in benzene was 0.1 M.[30] The tubes were irradiated with a Rayonet–Griffin–Srinivason photochemical reactor using a 3500-Å light source. Analyses were performed on a F & M Model 5720 gas chromatograph using a 6 ft × 0.25 in. column containing 20% Apiezon M on 60–80 Chromosorb W at 120°. The areas under the peaks due to the internal standard (nitrobenzene) and products were measured using a planimeter after triangulation. Each set of chromatograms was measured twice in this way and the results were converted to per cent reaction based on starting ketone.

(29) A. L. Lamola and G. S. Hammon, *J. Chem. Phys.*, **43**, 2129 (1965).

(30) W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).