were such that both the sample and actinometer solutions had an optical density of >2 for a 1-cm path length. Since the "merry-go-round" is designed so that light is incident only upon a 2-cm^2 area of the sample tube at its widest point, greater than 99% of the incident light was absorbed by both the sample and actinometer.

Sample tubes were removed at various times during the initial 2–12% of reaction. The disappearance of **1** was measured by the decrease in optical density at 4680 Å. The quantum yield for camphorquinone disappearance was calculated for each tube and the product of quantum yield times for each tube was plotted against time to give a straight line whose slope, the quantum yield, was determined by a least-squares analysis. This treatment of the data corrects for possible errors in determination of the initial optical density of the solution and is equivalent to a plot of moles of reaction *via* Einsteins of light added.

In the determination of the quantum yield for the disappearance of **1** in methanol all operations were carried out under a red light due to the ease with which **1** undergoes photooxidation in methanol.

Photosensitized Quantum Yield Determinations. The following general procedure was used for the photosensitized quantum yield determinations. A weighed amount of **1** was added to a volumetric flask, a volume of a stock solution of sensitizer added, and the flask filled to the mark with solvent. The initial optical density was measured at 4680 Å. If necessary the sample was diluted to obtain an optical density of less than 0.8. Three or four milliliter aliquots were transferred to 13-mm o.d. Pyrex test tubes whose upper portions had been constructed. These were degassed and sealed as above.

The sample tubes were irradiated on a "merry-go-round" apparatus using a 450-W Hanovia medium-pressure mercury vapor arc lamp as a light source. At the concentration of sensitizer used $>99\%$ of the light was absorbed by the sample. In the benzophenone-sensitized experiments the 313-mμ region of the spectrum was isolated by a two-compartment filter consisting of a 1.5-cm path length of an aqueous solution of 26 g of cobaltous sulfate heptahydrate per 100 ml and a 0.6-cm path length of 0.132 g of potassium chromate in 250 ml of 1% aqueous sodium carbonate. In the *m*-methoxyacetophenone-sensitized experiments this region was isolated by a two-part filter consisting of the potassium chromate filter solution which was recirculated through the quartz immersion well and a Corning 7-54 glass filter. The 366-mμ region of the spectrum was isolated by a filter made up of a Corning 0-52 and a Corning 7-37 glass filter. Sample tubes were removed over the first 2–20% of reaction and analyzed as above. The determinations with 3130-Å light were corrected for camphorquinone absorption and for the amount of reaction occurring from this absorption.

Electron Paramagnetic Resonance. Sample tubes were degassed by three freeze–pump–thaw cycles with a forepump followed by two such cycles with a diffusion pump with pumping 3×10^{-6} mm Hg on the final cycle and sealed off. Irradiation was carried out by a Hanovia 2500-W mercury–xenon high-pressure mercury vapor lamp. The light was filtered through 10 cm of 2% cobalt chloride solution and focused on a $^3/_8$-in. hole in a copper plate which was used as the cover plate for the esr cavity. To isolate the 3660-Å region of the spectrum a Corning 7-37 filter immersed in a Pyrex beaker of water was also placed in the light path. Steady-state radical concentrations and decay constants were obtained by methods that have previously been described.[31]

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Photochemical Transformations of Small Ring Carbonyl Compounds. XIX. The Photochemistry of Benzoylcyclobutanes[1-3]

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Abstract: The photolysis in benzene of cyclobutyl phenyl ketone has been found to afford four products. The structures have been assigned as 1-phenyl-4-penten-1-one, 2-hydroxy-2-phenylbicyclo[1.1.1]pentane, cyclobutylphenylcarbinol, and the pinacol of starting material. The formation of the keto olefin and the bicyclopentanol is considered to proceed through a diradical intermediate formed by transannular hydrogen abstraction by the excited $n-\pi^*$ triplet. The inefficiency of the photoreaction, both in terms of quantum yield and rate, is attributed to the unfavorable geometry required for internal hydrogen transfer. *cis*- and *trans*-2-phenylcyclobutyl phenyl ketones undergo rapid photointerconversion followed by a further intramolecular reaction to produce 1,5-diphenyl-4-penten-1-one. The photoisomerization has been rationalized by homolytic ring cleavage of the cyclobutyl ring.

The photochemical behavior of three-ring carbonyl compounds has been the subject of extensive study.[6] Although much remains to be learned about the electronic configuration of the excited state, there has emerged a fair understanding of the potential reactivity of this class of compounds.[7] In the case of conjugated cyclopropyl ketones, the primary photochemical process often involves ring opening by breakage of the cyclopropyl bond that conjugates best

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(1) For part XVIII, see A. Padwa and R. Gruber, *J. Am. Chem. Soc.*, **90**, 4456 (1968).

(2) Support of this work by a grant from the National Science Foundation (Grant GP-9385) is acknowledged with appreciation.

(3) This work was presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstract P88.

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

(5) National Science Foundation Undergraduate Research Participant, summer 1967.

(6) For a review see A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

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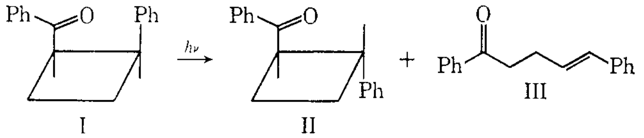
with the carbonyl group.[8–14] In larger rings of similar construction, bond reorganization of this type might be precluded and alternate modes of reaction could be expected. In fact, the products obtained from the irradiation of the homologous four-ring ketone are best described as involving a preliminary Norrish type I bond cleavage.[15] The drastic difference in photochemical behavior between these small rings was attributed either to the difference in unsaturation characteristics and/or the C–C bond strengths of the two rings.

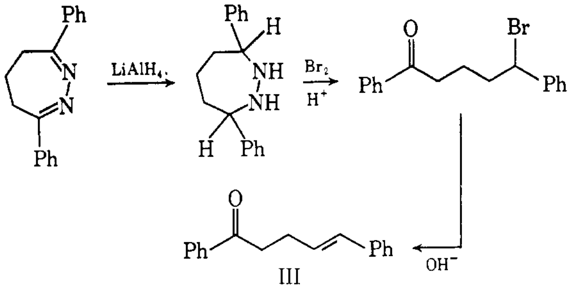
Despite the extensiveness of our knowledge regarding the photochemistry of conjugated cyclopropyl ketones, relatively little is known about the photochemistry of the homologous four-membered carbocyclic ring. As part of our continuing interest in small-membered rings and in connection with a study on the photochemical transformations of carbonyl compounds, we recently reported on a transannular hydrogen abstraction in the benzoylcyclobutane system.[16] It was our intent in this work to investigate more fully the scope of this novel transannular reaction and to examine some of the factors which could lead to other types of reactions.

Results and Discussion

cis- and *trans*-2-phenylcyclobutyl phenyl ketones (I and II) were prepared in good yield by treatment of the corresponding carboxylic acids with phenyllithium. The configurations of the aryl ketones follow from their preparation from acids of known stereochemistry.[17] The *cis* ketone I, mp 67–68°, and similarly the *trans* ketone II, mp 42–43°, were obtained as crystalline solids. The spectral data and elemental analyses were consistent with these structures and are summarized in the Experimental Section. Isomerization of I to the thermodynamically more stable *trans* form (II) may be readily effected with ethanolic sodium hydroxide. Photolysis of *cis*-2-phenylcyclobutyl phenyl ketone (I) in benzene with a Pyrex filter gave a mixture of products which were separated by preparative vapor phase chromatography. In addition to unreacted starting material (I), two new compounds were obtained and subsequently identified as *trans*-2-phenylcyclobutyl phenyl ketone (II) and 1,5-diphenyl-4-penten-1-one (III).

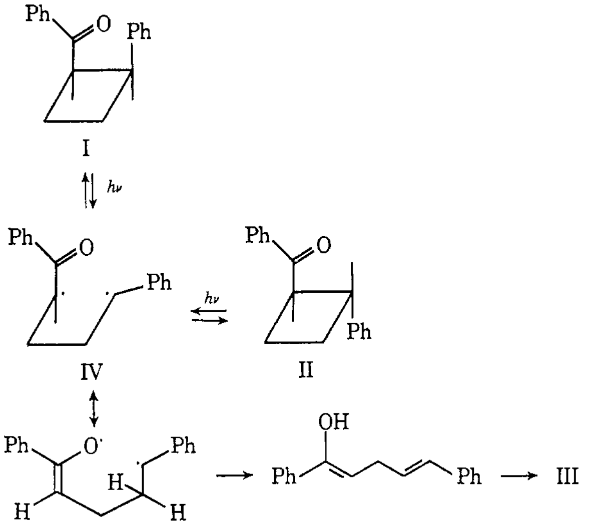


The structure of the keto olefin III was elucidated by its elemental analysis and spectral data (see Experimental Section). Structure III was further confirmed by its unequivocal synthesis from dibenzoylpropane azine as outlined below.



When the *cis* ketone I is irradiated in benzene and the reaction is monitored by glpc analysis, one sees first the conversion of the *cis* isomer I to the *trans* isomer II. A solution of I and II reached an apparent photostationary state (I/II = 2.0) after 15 hr. The photoisomerization of *cis*-2-phenylcyclobutyl phenyl ketone ($\Phi = 0.09$) was shown to be reversible. Irradiation of a pure sample of the *trans* isomer II affords I and III. By stopping the irradiation of II after 15 hr, the same photostationary state was obtained. As the irradiation of I and II is continued, another product (III) begins to appear. In time, I and II disappear leaving mostly III. These observations indicate that a rapid photointerconversion of I and II occurs and is followed by further intramolecular reaction to form III.

The isomerization and the formation of compound III may be rationalized on the assumption that the reaction proceeds *via* diradical IV, a species derived by homolysis of the C–C bond β to the carbonyl group.



Such a process is not without analogy. Griffin and coworkers, for example, have observed that arylaroylcyclopropanes undergo reversible photoisomerization. Initial homolysis of the cyclopropyl bond β to the carbonyl group was advanced to explain the photoisomerization.[18,19] Further analogy is provided by the work of Crandall, Arrington, and Watkins, wherein cyclooct-4-enone is photoisomerized to 3-vinylcyclohexanone.[20] The isolation of III in addition to the

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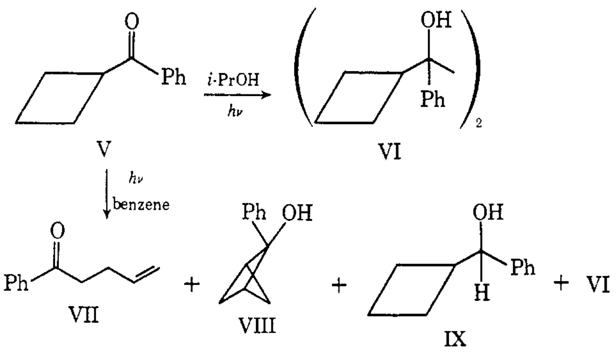
trans isomer II makes the intermediacy of a 1,4 biradical, from which both types of product could result, especially appealing. Internal hydrogen abstraction followed by rearrangement of the enol to a carbonyl group readily explains the formation of III from IV. Alternatively, it may be argued that III arises by a Norrish type II cleavage similar to that observed for cyclobutyl phenyl ketone (see discussion below).

Isomerization of I and II through reversible photodissociation of the benzoyl group seems improbable, particularly in view of the conspicuous absence of major by-products derived from secondary reactions of either the benzoyl or cyclobutyl radicals. The low-energy n–π* band is undoubtedly the significant absorption band, since light above 280 mμ was employed. The light absorbed by the 2-phenylcyclobutyl phenyl ketones possesses sufficient energy to effect a bond cleavage. The energy corresponding to 316-mμ radiation (90.8 kcal/mol) is substantially greater than the maximum energy required for bond dissociation in cyclobutane itself (58 kcal/mol),[21] which in turn is higher than that required for bond rupture in I and II. The photoisomerization and rearrangement could be quenched by the addition of piperylene in agreement with a n–π* triplet as the reactive excited state.

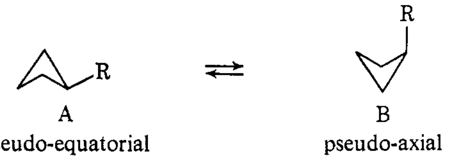
With the above results in hand, we considered it relevant to explore the photochemistry of the simpler cyclobutyl phenyl ketone system. Irradiation of cyclobutyl phenyl ketone (V) in isopropyl alcohol afforded the pinacol VI as the virtually exclusive photoproduct. The pinacol VI was found to be a mixture of *dl* and *meso* forms as evidenced by nmr analysis. Lead tetraacetate cleavage of the pinacol VI regenerated the reactant V, not only providing a structure proof but also a method for assaying pinacol. Further evidence for the structure of VI was obtained by synthesis from I by reductive dimerization with aluminum amalgam–ethyl alcohol. When the irradiation of V was carried out in benzene as solvent, 1-phenyl-4-penten-1-one (VII, 24%), 2-hydroxy-2-phenylbicyclo[1.1.1]pentane (VIII, 38%), cyclobutylphenylcarbinol (IX, 8%), and the pinacol of I (VI, 10%) were the major products.

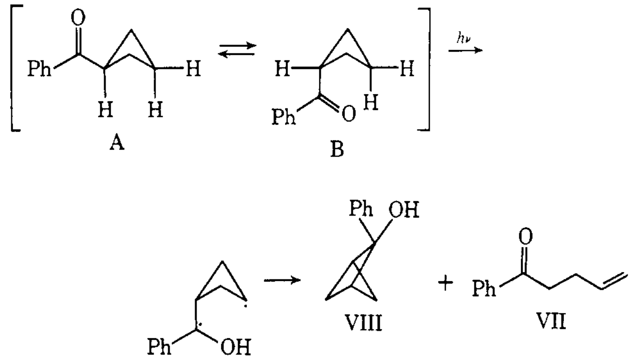


The structure of VII follows from inspection of its spectral data and by comparison of its semicarbazone derivative with an authentic sample synthesized by the method of Vavon and Conia.[22] The structure of the bicyclopentanol (VIII) was elucidated on the basis of an X-ray single-crystal structure analysis of its urethan derivative.[23] Cyclobutylphenylcarbinol (IX) was identified by comparison of infrared and retention time with that of an authentic sample.[24]

Mechanistic Results and Discussion

Chart I. Conformational Equilibrium in Substituted Nonplanar Cyclobutanes





During the past several years, a good deal of physical information has accumulated which supports a nonplanar structure for cyclobutane.[25–32] The nonplanar conformations lead to axial and equatorial positions similar to those of cyclohexane and are indicated in Chart I. The cyclobutyl ring is quite flexible and exhibits a dynamic ring-bending equilibrium which has been termed pseudorotation and allows for conformational equilibration of monosubstituted cyclobutanes.[33] In one of the two possible conformations of V (conformer B), hydrogen abstraction by the n–π* excited state can proceed *via* a six-membered transition state. Once formed, the biradical intermediate undergoes spin inversion prior to ring closure (VIII) or elimination (VII). These processes may be considered to be analogous to the Norrish type II cleavage and cyclobutanol formation observed with the irradiation of aliphatic ketones containing γ-hydrogens.[34] It is noteworthy that the biradical intermediate prefers ring closure to β elimination. This is in marked contrast to the results obtained in the acyclic system, where photoelimination predominates.[35] 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

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at the radical centers. With cyclobutyl phenyl ketone, where such overlap is very difficult to attain, photoelimination becomes the minor route.

The quantum yield for disappearance of V with direct irradiation was found to be 0.03. The quantum yield for appearance of bicyclopentanol VIII is 0.019 and for keto olefin VII is 0.006. These reactions thus contrast with the photochemistry of the related valerophenone system where virtually every quantum of light is utilized in product formation.[35]

Evidence on the multiplicity of the reacting species was gained from quenching experiments. In order to demonstrate conclusively that a triplet n–π* state was involved in reactions of V, quenching experiments were run using naphthalene as the quencher. Energy transfer from the triplet state of the carbonyl compound to naphthalene is sufficiently exothermic to ensure diffusion control of triplet destruction.[36] The photolysis was readily quenched by naphthalene, thus indicating that formation of all products occurs exclusively from the triplet state of the ketone. With the same objective in mind, that of determining multiplicity, we have examined the phosphorescence of V at 77°K. The 0–0 band of V in an ethanol–methanol glass corresponds to a triplet energy of 74.3 kcal. The vibrational spacing between the 0–0 and 0–1 band is 1730 cm^{-1}. These results provide strong evidence for the emission coming from an n–π* triplet.

In an attempt to correlate the observed inefficiency of the photoreaction to some molecular feature, we have studied the variation of quantum yield *vs.* quencher concentration. Figure 1 is a plot of the reciprocal of the quantum yield of bicyclopentanol (VIII) photoproduct against naphthalene concentration. The Stern–Volmer formulation for quenching a unimolecular reaction of an excited state (rate constant = k_r) results in the following expression

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

The slope of the plot gives k_q/k_r and the intercept gives $(k_r + k_d)/k_r$. Quenching by naphthalene (E_T = 61 kcal/mol) will be diffusion controlled since the triplet energy of V is 74.3 kcal/mol. From the observed slope of 9.1×10^5 for the Stern–Volmer plot, and using $k_q = 5 \times 10^9$ l. mol^{-1} sec^{-1},[37] the value for the unimolecular rate constant for bicyclopentanol formation from the triplet state, k_r, is found to be 5.5×10^3 sec^{-1}. Knowing k_r and the intercept we obtain k_d (unimolecular rate of triplet decay to ground state) as 6.6×10^5 sec^{-1}. The constant, k_d, for decay of triplet cyclobutyl phenyl ketone is of the same magnitude as that observed for benzophenone.[38] Thus the inefficiency of the photoreaction cannot be attributed to an unusually rapid triplet degradation. The unimolecular rate of reaction, k_r, is remarkably low when compared to other acyclic carbonyl compounds. Other rate constants for unimolecular reaction are 5.0×10^7 sec^{-1} for *n*-valerophenone and 2.7×10^6 sec^{-1} for *n*-butyrophenone.[38] We can readily see that the rate of rearrangement is of the order of 10,000-fold smaller for V than for the related acyclic aromatic ketones.

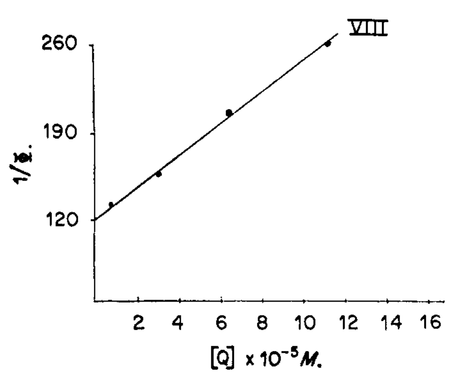

Figure 1. Reciprocal of quantum yield *vs.* quencher concentration.

Having established the dramatic inefficiency of internal hydrogen abstraction both in terms of quantum yields and rearrangement rates, we felt it worthwhile to explore the reactivity of V toward external hydrogen abstraction. Photoreduction of cyclobutyl phenyl ketone in isopropyl alcohol afforded the pinacol in high yield. The quantum yield for pinacol formation is 0.2 at 3130 Å. From a Stern–Volmer plot of $1/\phi$ *vs.* naphthalene, the rate of hydrogen abstraction from isopropyl alcohol by the triplet state, k_a, is found to be 1.3×10^5 l. mol^{-1} sec^{-1}. This bimolecular rate of hydrogen abstraction compares favorably to the $k_a = 4 \times 10^5$ l. mol^{-1} sec^{-1} reported for acetophenone triplet in isopropyl alcohol[39] and the $k_a = 6 \times 10^5$ l. mol^{-1} sec^{-1} found for benzophenone triplet in the same solvent.[39] These results indicate that the excited n–π* triplet of V has the same order of reactivity as that observed for aromatic ketones in intermolecular hydrogen abstraction but differs substantially for internal abstraction.

One clear-cut conclusion from our results is that the formation of VII and VIII proceeds from a common biradical intermediate. The low quantum yield observed must be related to some molecular feature of V which retards formation of the biradical. We suspect that the inefficiency of the photoprocess is due to the unfavorable geometry required for internal hydrogen transfer. With regard to the geometrical features of the abstraction step, it would appear that the preferred transition state is one in which carbon, hydrogen, and the nonbonding electron on oxygen can approximate a linear configuration. This linearity factor has long been recognized as an important factor in the Hofmann–Loeffler–Freitag reaction[40] and for intramolecular hydrogen abstraction in long chain hypohalites.[41] Similarly, the striking contrast in the photochemistry of *cis*- and *trans*-2-*n*-propyl-4-*t*-butylcyclohexanones has been attributed to the stereoelectronic requirements of the hydrogen transfer step.[42] The slowness and inefficiency of formation of VII and VIII from V can be readily attributed to the nonlinearity of the hydrogen abstraction step. Alternatively, it may be argued that the inefficiency of the photoreaction is related to the low concentration of conformer B in

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the excited state of V. This interpretation is consistent with the formation of products VI and IX in benzene; both products are presumably derived by external hydrogen abstraction by conformer A in its excited state. While irradiation of I in benzene afforded a mixture of products, photolysis in a hydrogen donor solvent afforded the pinacol. Thus, the least stable configuration would be expected to undergo internal hydrogen transfer under conditions which suppress photoreduction of the more stable conformation. The available evidence does not decisively distinguish among the preceding possibilities. In fact, it is quite probable that both explanations account for the observed inefficiency.

It is interesting, at this point, to compare the irradiation of V with that of methyl cyclobutyl ketone (X). Since X has available γ-hydrogens, we would anticipate photoreaction by a route comparable to that observed with V. Actually, irradiation of X has been reported to yield products derived from a Norrish type I cleavage.[15] The failure of X to undergo internal hydrogen transfer may, in part, be attributed to the greater excited (π^*) electron localization in the carbonyl group of X and hence greater probability for bond cleavage. In the excited benzoyl group of V the excited electron is distributed throughout the phenyl group and is less available for scission. A related situation has been noted by Zimmerman for the $n-\pi^*$ photochemical transformations of α,β-epoxy ketones.[43] Alternatively, the unique difference in photochemical behavior of X *vs.* V may be attributed to the possible difference in the multiplicity of the excited state. The dependence of a photochemical reaction on the multiplicity of the excited state has been amply demonstrated in the literature.[34] In this case, the reactive state of X may actually be a $n-\pi^*$ singlet whereas photoreaction of V proceeds from a $n-\pi^*$ triplet. Still another consideration which may account for the difference between V and X is the fact that the irradiation of X was carried out in the vapor phase. In the condensed medium, the rapid loss of vibrational energy by collisional deactivation with solvent molecules would be expected to diminish the propensity for Norrish type I cleavage. Whether this factor is sufficient to allow for internal hydrogen abstraction of X in the condensed phase awaits further experimentation.

Experimental Section[44]

cis- **and** *trans-***2-Phenylcyclobutanecarboxylic Acids.** A 15.0-g sample of 2-phenylcyclobutane-1,1-dicarboxylic acid[17] was refluxed in 150 ml of mesitylene for 2 hr. The cooled solution was extracted with 150 ml of a 15% sodium hydroxide solution. After being washed twice with ether, the alkaline solution was acidified at a temperature below 10°, and the oil which separated was chromatographed on a 90 × 2.5 cm column of silica gel (Davison, Grade 950, 60–200 mesh) slurry packed in 15% ether–hexane. Fractions 4–12 consisted of a mixture of oil and crystals from which, by trituration with pentane, 5.5 g of *cis*-2-phenylcyclobutanecarboxylic acid, mp 82–84° (lit.[17] 84–85°), was obtained. Rechromatography of the oily portion from fractions 4–12 on silica gel gave another 1.2 g of the *cis* isomer. The last fractions eluted with 30% ether–hexane yielded 2.5 g of an oily acid, which from its infrared spectrum (700, 753 cm^{-1} as a smeared film) was judged to be pure *trans*-2-phenylcyclobutanecarboxylic acid.

*cis***-2-Phenylcyclobutyl Phenyl Ketone.** *cis*-2-Phenylcyclobutanecarboxylic acid (2.0 g) was dissolved in 50 ml of anhydrous ether in a three-necked flask equipped with a magnetic stirrer, reflux condenser, and pressure-compensated dropping funnel. Phenyllithium (10.8 ml of a 2.08 *M* solution) was added over a period of 0.5 hr at a rate so as to maintain a steady reflux. The mixture was stirred for an additional 0.5 hr and then hydrolyzed by the addition of 10% sulfuric acid solution. When two clear layers had formed, the ether layer was separated, washed with saturated sodium carbonate solution and twice with water, and dried over anhydrous magnesium sulfate. Removal of the solvent *in vacuo* left a colorless liquid which solidified on standing. Recrystallization from methanol gave *cis*-2-phenylcyclobutyl phenyl ketone (540 mg) as a white solid, mp 67–68°.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.63; H, 6.93.

The infrared spectrum shows a strong carbonyl band at 6.02 μ and a series of sharp bands at 9.12, 8.20, 13.02, 13.47, 14.04, and 14.41 μ. The ultraviolet spectrum in 95% ethanol has maxima at 247 mμ (ϵ 10,800) and 318 mμ (ϵ 78). The nmr is in excellent agreement with the structure and has multiplets centered at τ 7.58 5.78, 2.91, and 2.43. The peak areas are in the ratio of 4:2:8:2.

*trans***-2-Phenylcyclobutyl Phenyl Ketone.** The conversion of 2.0 g of *trans*-2-phenylcyclobutanecarboxylic acid to the phenyl ketone using phenyllithium (10.6 ml of a 2.08 *M* solution) in 50 ml of anhydrous ether was carried out exactly as described above for the *cis* stereoisomer. The product, 560 mg, was obtained as a colorless liquid which on crystallization from methanol gave a white, crystalline solid, mp 42–43°.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.70; H, 6.77.

This material possessed an infrared spectrum which was decidedly different from that of the stereoisomer. The infrared spectrum shows a carbonyl band at 5.98 μ and a series of sharp bands at 8.08, 8.20, 9.78, 10.00, 13.60, and 14.51 μ. The ultraviolet spectrum in 95% ethanol has maxima at 245 mμ (ϵ 14,700) and 318 mμ (ϵ 114). The nmr spectrum has multiplets centered at τ 7.76, 6.07, 2.65, and 2.22. The peak areas are in the ratio of 4:2:8:2.

trans-2-Phenylcyclobutyl phenyl ketone was also prepared by the base-catalyzed epimerization of the *cis* stereoisomer. A 0.58-g sample of the *cis* isomer and 0.07 g of sodium methoxide in 10 ml of methanol was refluxed for 36 hr. After evaporation of the solvent the oily residue was triturated with pentane to afford a colorless solid (490 mg), which melted at 42–43°. The infrared spectrum of this material was identical in every detail with that of *trans*-2-phenylcyclobutyl phenyl ketone prepared from the phenyllithium reaction. The mixture melting point of these two materials was undepressed at 41–43°.

The *trans* stereoisomer could also be prepared from the thermal isomerization of the *cis* ketone. A 20-mg sample of *cis*-2-phenylcyclobutyl phenyl ketone was heated in a sealed tube at 180° for 2 hr. The crude residue was analyzed by vapor phase chromatography on a F & M Model 5720 instrument. The two major components were separated on a column of SE-30 silicone oil (10% Chromosorb W) at 183° at a flow rate of 52 cc/min. Comparison of retention times and infrared spectra with those of known samples of *cis*- and *trans*-2-phenylcyclobutyl phenyl ketones established the identity of the major components present in the residue.

Irradiation of *cis***-2-Phenylcyclobutyl Phenyl Ketone.** The photolysis was carried out on a solution of 0.5 g of *cis*-2-phenylcyclobutyl phenyl ketone in 1 l. of anhydrous benzene for 20 hr. Purified nitrogen[45] was bubbled through the solution for 45 min before and then during the photolysis. The light sources was a 550-W Hanovia medium-pressure lamp with a Pyrex filter, all in a water-cooled immersion well. The photolysis was monitored by removing aliquots for glpc analysis. Two new components were easily observable after 5 hr. The concentration of one of these increased steadily while the other reached a maximum concentration and then gradually decreased along with the starting ketone as irradiation proceeded. Concentration of the solution left an oil which was

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(43) H. E. Zimmerman, B. R. Cowley, C. Y. Tseng, and J. W. Wilson, *J. Am. Chem. Soc.*, **86**, 947 (1964).

(44) All melting points are corrected and boiling points uncorrected. Elemental analyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, and Alfred Bernhardt Laboratories, Hohenweg, Germany. The infrared absorption spectra were determined on a Perkin-Elmer Infracord spectrophotometer, Model 137. The ultraviolet absorption spectra were measured with a Cary recording spectrophotometer, using 1-cm matched cells. The nuclear magnetic resonance spectra were determined at 60 Mc with the Varian Associates high-resolution spectrometer. Tetramethylsilane was used as an internal standard.

(45) L. Meites and T. Meites, *Anal. Chem.*, **20**, 984 (1948).

subjected to preparative gas chromatography. The first two peaks collected corresponded to *cis*- and *trans*-2-phenylcyclobutyl phenyl ketones (ratio 2:1). The third product, mp 58–59°, was identified as 1,5-diphenyl-4-penten-1-one on the basis of the following observations.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.29; H, 6.80.

The infrared spectrum shows a strong carbonyl band at 5.96 μ and strong bands at 8.32, 10.46, 13.52, 14.47, and 14.61 μ. The nmr (deuteriochloroform) showed a triplet at τ 7.49, a triplet at 7.14, a multiplet at 3.82, a multiplet at 2.84, and a multiplet at 2.26. The peak areas are in the ratio of 2:2:2:8:2. The structure of this material was further verified by comparison with a sample independently synthesized as described below.

Preparation of 1,5-Diphenyl-4-penten-1-one. The procedure of Overberger and Monagle was adopted to the present case.[46] In 1 l. of absolute alcohol containing 50 g of dibenzoylpropane were heated 10 ml of hydrazine hydrate and 2 ml of concentrated hydrochloric acid at reflux for 8 hr. While still hot the solution was poured into a mixture of ice and water. The white solid was collected by suction filtration and dried overnight in air to give 46 g of dibenzoylpropane azine, mp 159–611° (lit.[46] mp 163–164°).

The above dibenzoylpropane azine (31 g) in 500 ml of anhydrous tetrahydrofuran was added over a period of 5 hr, to a suspension of 15.2 g of lithium aluminum hydride in 800 ml of anhydrous ether. After the addition was completed the solution was stirred for about 2 hr. The excess lithium aluminum hydride was decomposed by the dropwise addition of water. The mixture was filtered, and the filtrate was dried over sodium sulfate. Removal of the solvent gave a yellow oil which was distilled to give 19 g of a clear yellow oil, bp 202–205° (2.0 mm).

The freshly distilled hydrazine (10 g) was dissolved in 100 ml of ethanol; 60 ml of water was then added and the mixture cooled to 5°. A solution of 50 ml of concentrated hydrochloric acid in 90 ml of water was added and the solution was cooled to 0°. To this cold solution was added 13.1 g of bromine over a period of 10 hr. After the addition was completed, the stirring was stopped and the solution filtered to remove the solid formed. The wet solid was dissolved in 300 ml of methylene chloride and dried over sodium sulfate. Evaporation of the solvent left a yellow solid that was recrystallized from chloroform–pentane, mp 108–112°.

A suspension of the above 5-bromo-1,5-diphenyl-1-pentanone (2.8 g) and 1.1 g of potassium hydroxide in 75 ml of absolute ethanol was refluxed for 1 hr. The cooled, yellow solution was neutralized by the addition of concentrated hydrochloric acid. The solids were filtered and washed with several portions of ethanol. The combined filtrate and washings were evaporated, and the residue was chromatographed on a silica gel column prepared in 2% ethyl acetate–benzene. The eluent, in 50-ml fractions, was concentrated and dried *in vacuo*. Fractions 4–9 contained 1.4 g of a solid, mp 46–54°. Recrystallization from 95% ethanol gave colorless prisms, mp 58–59°. The infrared and nmr spectra of this material were identical in every detail with those of 1,5-diphenyl-4-penten-1-one isolated from the photolysis of *cis*-2-phenylcyclobutyl phenyl ketone. The mixture melting point of these two materials was undepressed at 57–58°.

Irradiation of *trans*-2-Phenylcyclobutyl Phenyl Ketone. A solution of 630 mg of *trans*-2-phenylcyclobutyl phenyl ketone in 500 ml of anhydrous benzene was photolyzed for 18 hr in the same manner as described above for the *cis* ketone. Gas chromatographic analysis of the product mixture indicated the presence of starting ketone (30%), the *cis* stereoisomer (60%), and 1,5-diphenyl-4-penten-1-one (10%). A photostationary state (*cis*:*trans* 2:1) between the cyclobutyl ketones was established after 7 hr.

Photolysis of Cyclobutyl Phenyl Ketone in Isopropyl Alcohol. A solution of 1.0 g of cyclobutyl phenyl ketone in 400 ml of isopropyl alcohol was irradiated for 8 hr through a Pyrex filter using a Hanovia Type L 550-W mercury lamp and a positive pressure of oxygen-free nitrogen. The photolysis was readily monitored by removing aliquots and checking the infrared spectrum. The 5.96-μ carbonyl band characteristic of the starting material disappeared after 8 hr. Evaporation of the solvent left 1.1 g of a pale yellow residue, which rapidly crystallized on addition of ethanol to give a colorless solid, mp 131–133°. Repeated recrystallization from 95% ethanol gave a solid, mp 150–151°, that analyzed for the pinacol of cyclobutyl phenyl ketone.

Anal. Calcd for $C_{22}H_{26}O_2$: C, 81.88; H, 8.06. Found: C, 81.72; H, 8.14.

The infrared spectrum shows a hydroxyl band at 2.87 μ and sharp bands at 3.45, 6.96, 8.61, and 10.09 μ. The nmr spectrum (hexadeuterioacetone) has a broad envelope centered at τ 8.50 and a multiplet at 2.85.

Pinacol of Cyclobutyl Phenyl Ketone. To 1.1 g of cyclobutyl phenyl ketone dissolved in 6 ml of absolute ethanol was added 4 ml of benzene, 0.12 g of mercuric chloride, and 0.16 g of aluminum foil. The mixture was heated to reflux for 8 hr. It was then diluted with an equal volume of 10% hydrochloric acid solution and thoroughly extracted with ether. Drying and evaporation of the ether gave 980 mg (94%) of a white solid, mp 127–132°. Recrystallization from 95% ethanol brought the melting point to 150–151°. The infrared spectrum of this material was identical in every detail with that of the pinacol from photolysis. The mixture melting point of these two materials was undepressed at 150–151°.

Lead Tetraacetate Cleavage of the Pinacol. A solution of 0.15 g of lead tetraacetate in 2 ml of glacial acetic acid was added to a solution of the pinacol (0.49 g) in 5 ml of benzene. After allowing the solution to stir for 15 min, 0.3 ml of 4 *N* sulfuric acid solution was added. The solids were filtered and washed with anhydrous ether. The combined filtrate and washings were dried over sodium sulfate. The residue after concentration weighed 27 mg and had an infrared almost identical with that of cyclobutyl phenyl ketone. Gas chromatographic analysis of the crude reaction mixture showed one major peak which was subsequently isolated by preparative gc and identified as cyclobutyl phenyl ketone by comparison of infrared and glpc behavior.

Photolysis of Cyclobutyl Phenyl Ketone in Benzene. A solution of 1.0 g of cyclobutyl phenyl ketone in 400 ml of benzene was irradiated at room temperature in a nitrogen atmosphere with a Hanovia 550-W mercury arc lamp using a Pyrex filter to eliminate wavelengths below 280 mμ. The progress of the reaction was followed by vapor phase chromatography with a 5 ft × 0.25 in. aluminum column packed with 5% DEGS on Chromosorb W at a flow rate of 60 cc/min and at a temperature of 120°; after 60 hr the reaction was 85% complete. The solvent was removed on a rotary evaporator, and the remaining oil was subjected to preparative vpc. The chromatogram showed four peaks with retention times of 4.5, 5.6, 8.0, and 11.0 min. The second material to be eluted was identified as recovered starting material (14%). The last peak in the gas chromatogram was cyclobutylphenylcarbinol (3%), bp 121–123° (10 mm). Definite identification was made by comparison of infrared and retention time with an authentic sample.[24] A portion of the crude reaction mixture (500 mg) was chromatographed on a Florisil column packed in 2% ethyl acetate in benzene; 50-ml fractions were collected. Fractions 6–10 contained the pinacol, mp 131–133° (54 mg, 10%), identified by infrared.[47] Repeated crystallization from 95% ethanol raised the melting point to 150–151°.

1-Phenyl-4-penten-1-one. The first material to be eluted was identified as 1-phenyl-4-penten-1-one (25%), bp 140° (9 mm); infrared spectrum 5.98, 6.11, and 10.92 μ; ultraviolet spectrum (95% ethanol) λ_{max} 243 mμ (ε 10,000); nmr three overlapping triplets (J = 16.0, 9.0, and 6.0 Hz) centered at τ 4.20, two overlapping doublets centered at 5.07 and 5.16, a triplet (J = 7.0 Hz) at 7.11, and a quartet (J = 7.0, 6.0 Hz) at 7.69; mass spectrum (m/e): 160 (M^+), 105 (base peak), 91, 77, 51, 41, and 39.

The structure of this material was further confirmed by its unequivocal synthesis from acetophenone and allyl bromide. To a solution of 150 g of acetophenone and 60 g of allyl bromide dissolved in 600 ml of benzene was added slowly with stirring 50 g of potassium *t*-butoxide. The solution was maintained at 20–25°. After all the potassium *t*-butoxide had been added, the reaction mixture was stirred for 1 hr. The solution was then washed with water and the organic layer separated. Removal of the solvent *in vacuo* and distillation of the crude oil at 140° (9.5 mm) afforded 1-phenyl-4-buten-1-one. The infrared and nmr spectra of this material were identical in every detail with those of 1-phenyl-4-buten-1-one isolated from the photolysis of cyclobutyl phenyl ketone. The structure of the unsaturated ketone was further confirmed by comparison of its semicarbazone derivative, mp 151–152°, with an authentic sample synthesized by the method of Vavan and Conia.[22]

2-Hydroxy-2-phenylbicyclo[1.1.1]pentane. The third product collected from preparative vpc was a colorless solid (38%), mp

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(46) C. G. Overberger and J. J. Monagle, *J. Am. Chem. Soc.*, **78**, 4470 (1956).

(47) The material melting at 131–133° was shown to be a *meso–dl* mixture by nmr analysis.

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-phenylbicyclo[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.

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

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

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(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.

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