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The Photoreaction of Benzyl 1-Cycloalkenyl Ketone in Acidic or Protic Media*

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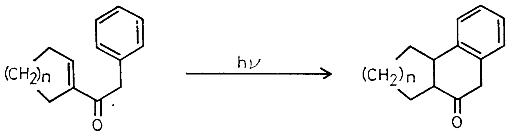
Three benzyl 1-cycloalkenyl ketones, I—III, were irradiated in the presence of boron trifluoride-diethyl ether (0.05 mol/l) in benzene to give the products V—VII, formed by the bonding between the β-position of $\alpha\beta$-unsaturated ketone and the *ortho* position of the benzene ring. Benzyl 1-cyclooctenyl ketone (IV) was inactive to the photocyclization because of the preferential geometrical isomerization of the olefin moiety. Trifluoroacetic acid promotes the reaction exceedingly, but the reaction takes place also in methanol. The reaction in methanol was deduced from quenching experiments to be a triplet process. The reaction takes both singlet and triplet processes when irradiation is carried out in the presence of boron trifluoride-diethyl ether. The participation of the complex between benzyl 1-cycloalkenyl ketone and boron trifluoride is proposed for the singlet process.

It has been reported that a photochemical Friedel-Crafts reaction takes place upon the irradiation of cycloalkene and benzene derivatives in the presence of a catalytic amount of Lewis acid.[1] A strained *trans*-cycloalkene has been considered to be an active intermediate which gives a carbonium ion in the presence of an acid catalyst. In this paper we will report the photochemical cyclization of benzyl 1-cycloalkenyl ketones (I—III) under various reaction conditions.

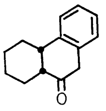
The external irradiation (a 450-W medium pressure Hg lamp) of solutions of I, II, and III in benzene containing boron trifluoride–diethyl ether (0.05 mol/l) through a Pyrex tube for 3 h gave the reaction products of V, VI, and VII in 79, 87, and 90% yields respectively. However, the starting material was recovered when benzyl 1-cyclooctenyl ketone (IV) was irradiated. These experimental results are in sharp contrast with the fact that an attempted thermal cyclization of benzyl 1-cyclohexenyl ketone (II) with Lewis acid recovered the starting material.[2—4] Elemental analyses and the molecular peaks of mass spectra due to the products V (m/e=186), VI (m/e=200), and VII (m/e=214) show the products to be the isomers of the starting ketones. All the products show the infrared absorption for the saturated ketone at 1720 (V), 1710 (VI), and 1717 cm^{-1} (VII) and the absorptions for *ortho*-disubstituted benzene ring at 750 (V), 755 and 765 (VI), and 753 cm^{-1} (VII). NMR spectra of the products V, VI, and VII show signals (singlet) due to the methylene adjacent to the carbonyl group at δ= 3.62 (V), 3.48 (VI), and 3.50 ppm (VII). These spectral data define unequivocally the structures of the products except for the stereochemistry of the ring junction. The V and VII products were found to be homogeneous by GLC analyses (SE-30 and OV-17 on Chromosorb W), but the VI product consisted of two isomers, VIa and VIb. VIa was deduced to be *cis*-1,2,3,4,4a,10a-hexahydro-10-phenanthrone by the transformation of VIa into *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene.[1,5] The thioketal obtained by the action of 1,2-ethanedithiol–borontrifluoride–diethyl ether to VIa was reduced by Raney-Ni, and the reduced product was identified with the authentic octahydrophenanthrene by a comparison of their GLC and IR spectra. The formation of VIa and VIb was not due to the isomerization of the product under the present reaction conditions. The acid or base treatment of the VI product with varying ratios of the two isomers did not change the original ratio, and the base-catalyzed deuteration of the VI product by deuterium oxide gave only the dideuterated derivative, indicating that the enolization took place only in the direction of the benzylic position. The reaction occurs in reaction systems other than boron trifluoride–diethyl ether as will be described below, and the ratio of VIa and VIb is dependent on the solvent of the reaction, VIa : VIb=*ca.* 1 : 1 for boron trifluoride–diethyl ether/benzene, 4 : 1 for methanol, and 5 : 1 for acetonitrile. Base-catalyzed enolization takes place only in the direction of the benzylic position, and no epimerization can be expected for V and VII. The stereochemistry of these products, therefore, remains undetermined.



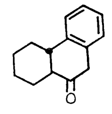
I: n=1 II: n=2
III: n=3 IV: n=4

V: n=1 VI: n=2
VII: n=3

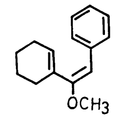
The benzyl 1-cyclohexenyl ketone (II) was subjected to a wide variety of the reaction conditions for the purpose of understanding the nature of the reaction. Trifluoroacetic acid is as effective a catalyst as boron trifluoride–diethyl ether for the photocyclization of II, and enol ethers of VIa and VIb were isolated from the reaction using methanol as the solvent. Polar solvents, such as methanol and acetonitrile, provide a good reaction system for the photo-cyclization even without



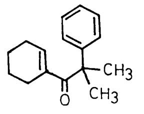
VIa



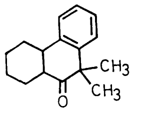
VIb



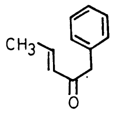
VIII



IX



X



XI

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* Part of this work was reported as a preliminary report: *J. Chem. Soc., Chem. Commun.*, **1975**, 55.

acid catalyst. The reactivity in various reaction systems decreases in the following sequence, judging by the time required for the completion of the reaction: 0.05 M boron trifluoride–diethyl ether/benzene$\approx$0.05 M trifluoroacetic acid/benzene$\approx$methanol$>$0.05 M boron trifluoride–diethyl ether/acetonitrile$\gg$acetonitrile$>$benzene.

One possible mechanism is an electrocyclization of the formal triene system in the enol form of the II ketone, however, this possibility was eliminated by the following observations. The enol ether VIII caused only geometrical isomerization upon irradiation, and the dimethyl derivative, IX, gave the cyclized product, X (molecular peak $m/e=228$, IR 1709 cm^{-1}), which was difficult to isolate in a practical yield due to its photo-lability.

The failure of the photocyclization of VI must be due to the rapid relaxation of the excited state by isomerization to the *trans*-cyclooctene system.[6] This was further supported by the irradiation of the benzyl 1-propenyl ketone (XI), which caused no cyclization, but only geometrical isomerization. In methanol, compound I, which has a cyclopentene moiety was converted smoothly into V (the conversion was completed within 120 min), while compound II, with a cyclohexene moiety, reacted more slowly to give VI. Compound III, with a cycloheptene moiety, was not, however, converted into VII under the same reaction conditions. The cyclization of I in methanol was quenched effectively by 1,3-pentadiene to give linear Stern-Volmer plot, $k_q\tau=16$ M^{-1}. This quenching experiment shows that the photocyclization proceeds by means of a triplet process. In contrast to the reaction in methanol, all three compounds, I, II, and III, caused a facile cyclization to give V, VI, and VII in benzene containing boron trifluoride–diethyl ether (0.05 mol/l). The Stern-Volmer plots of the quenching experiments of the reaction in the boron trifluoride–diethyl ether/benzene system using 1,3-pentadiene as the quencher are shown in Fig. 1. The curvatures of the plots and plateaus at $\Phi_0/\Phi=1.8$ for I and $\Phi_0/\Phi=1.3$ for II show that both singlet and triplet processes are encountered in the reaction of I and II. In the region showing the plateaus, the triplet process is almost completely quenched, and the following relation exists: $\Phi_0=(\Phi_S+\Phi_T)$ and $\Phi=\Phi_S$, where Φ_S and Φ_T denote the quantum yield of the reaction by the use of a singlet and a triplet process respectively. This analysis reveals that 56% and 77% of the reactions of I and II respectively proceed through a singlet process.[7] On the contrary, the reaction of compound III is essentially not quenched by 1,3-pentadiene and gives a linear Stern-Volmer plot with a small negative slope. This means that the cyclization of III takes place *via* only a singlet process. The negative slope is accounted for by the quenching of the triplet decay of the cyclized product, VII, which was substantiated by the irradiation of the isolated product.

Carbonyl compounds form complexes with boron trifluoride–diethyl ether,[8] and the UV absorption of II in hexane containing boron trifluoride–diethyl ether (0.05 mol/l) shows a new absorption around 270 nm, with concomitant decrease in the intensity of the π-π^* absorption at 224 nm (Fig. 2); the absorption in benzene containing boron trifluoride–diethyl ether (0.05 mol/l) is very different from the absorption in the absence of the acid in n-π^* region (Fig. 3). This spectroscopic behavior, in conjunction with the quenching experiments, suggest that the excitation of the complex between the corbonyl compound and boron trifluoride is reponsible for the photochemical cyclization by a singlet process. This conclusion is supported by the facts that compound III reacts in the presence

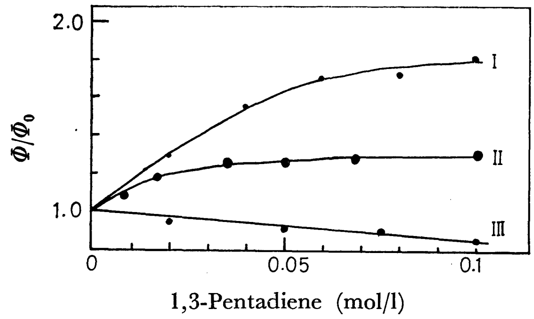


Fig. 1. Quenching of photocyclization of I, II, and III (0.1 mol/l) in benzene containing BF$_3$-etherate (0.05 mol/l).

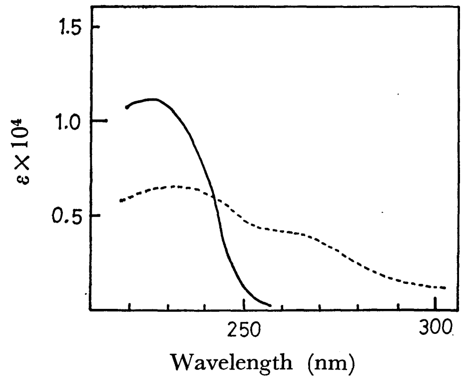


Fig. 2. UV spectra of benzyl 1-cyclohexenyl ketone (II) in hexane (——) and in hexane containing BF$_3$-etherate (0.05 mol/l) (----).

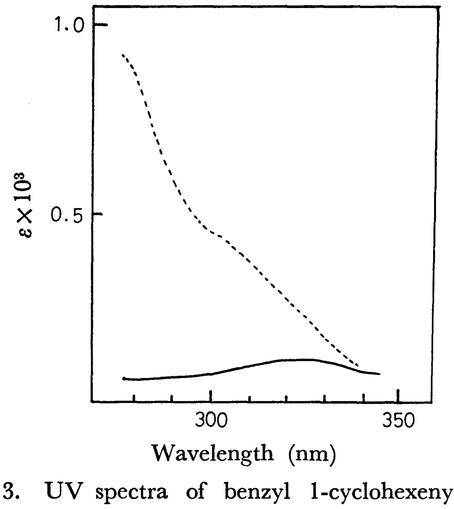
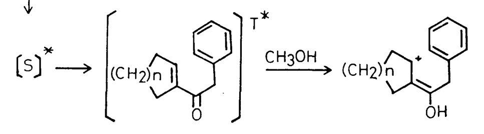


Fig. 3. UV spectra of benzyl 1-cyclohexenyl ketone (II) in benzene (——) and in benzene containing BF$_3$-etherate (0.05 mol/l) (----).

of boron trifluoride–diethyl ether, but no reaction takes place in methanol, and that the importance of the singlet process decreases with the decrease in the ring size of the cycloalkene moiety of compounds III (100%), II (77%), and I (56%).

The most important process in the energy dissipation of the triplet excited state is a geometrical isomerization of the double bond in the cycloalkene moiety. With compound I, with a cyclopentene moiety, in which the geometrical isomerization is impossible, the triplet cyclization in methanol is an effective process, whereas compound III, with a cycloheptene moiety, preferentially deactivates to the *trans* isomer of III and no cyclization takes place in methanol. On the same ground, the relative importance of the triplet process for the cyclization in benzene containing boron trifluoride–diethyl ether increases in the order of compound III (0%), compound II (23%), and compound I (44%). As has been described earlier, the benzyl 1-cyclooctenyl ketone (IV) and the benzyl 1-propenyl ketone (IX) do not undergo the photocyclization in either methanol or benzene containing boron trifluoride–diethyl ether. This means that the energy dissipation by the geometrical isomerization of the cycloalkene moiety is also important in the singlet excited state of the complex. The geometrical isomerization from the excited state of the complex is an important competitive process with photocyclization in the cases of compounds IV and XI.

The importance of the acidic function in the photocyclization is demonstrated by the fact that the reaction proceeds more rapidly in methanol than in acetonitrile, which is a more polar solvent than methanol. These facts prompt us to propose the reaction mechanism depicted in Scheme 1, where S* and T* denote a singlet and a triplet excited state respectively. The reaction in an aprotic solvent such as acetonitrile must proceed in a fassion similar to the reaction in methanol, but without a protonated intermediate.

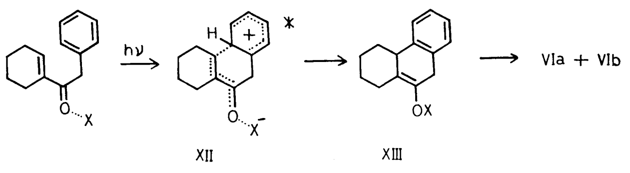


Scheme 1.

The excitation of the complex between the carbonyl compound and boron trifluoride may be expected to produce a more polar state which accumulates a more positive charge on the β-position of the unsaturated carbonyl compound.[9] On the other hand, the carbonyl compound can be expected to acquire an intensified basicity in its triplet excited state and to abstract a proton from a protic solvent, and the increase in the positive charge on β-position can also be expected.[10] Thus, the β-carbons of compounds I, II, and III must become more electrophilic by excitation to attack the benzene ring intramolecularly.

The irradiation of a mixture of 1-acetylcyclohexene and toluene in the presence of boron trifluoride–diethyl ether does not bring about an intermolecular reaction of a type similar to that of the benzyl 1-cycloalkenyl ketone. This implies an interaction between the enone system and the benzene ring in the excited state. The participation of the benzene ring in the excited state and the oriented structure of this intramolecular exciplex, XII, may be essential factors in making possible the facile intramolecular cyclization (Scheme 2).

The stereochemistry of the product must be governed by the mode of protonation to the intermediate enol derivative, XIII, and must be dependent on the polarity of the solvent in the case of the reaction of the benzyl 1-cyclohexenyl ketone (II).



Scheme 2.

Experimental

Syntheses of Starting Materials. *A) Benzyl 1-Cycloalkenyl Ketones (I—IV)*: Ketones I—IV were synthesized by the method of Cook and Hawett for the synthesis of the II ketone,[2] using carbon disulfide as the solvent. The benzyl 1-cyclopentenyl ketone (I), the benzyl 1-cyclohexenyl ketone (II), the benzyl 1-cycloheptenyl ketone (III), and benzyl 1-cyclooctenyl ketone (IV) were obtained in 16, 54, 21, and 35% yields respectively. The αα-dimethylbenzyl 1-cyclohexenyl ketone (IX) was synthesized by a similar method, but using dichloromethane as the solvent and at a reaction temperature of −60 °C. The crude product (IX) obtained by distillation contained three isomeric impurities; the material for the photoreaction was purified by succesive chromatography on silica gel eluted by benzene and preparative GLC (8% Carbowax 20 M on Chromosorb P, He). I: mp 64 °C. Mass: $M^+=186$. IR(CCl_4): 1660 cm^{-1}. Found: C, 83.63; H, 7.64%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%. II: mp 46 °C.[2] Mass: $M^+=200$. IR(CCl_4): 1655 cm^{-1}. III: bp 120 °C/0.9 mmHg. Mass: $M^+=214$. IR(neat): 1650 cm^{-1}. Semicarbazone; mp 171—172 °C. Found: C, 71.10; H, 7.92; N, 15.75%. Calcd for $C_{16}H_{21}ON_3$: C, 70.82; H, 7.80; N, 15.49%. IV: bp 170—172 °C/0.65 mmHg. Mass: $M^+=228$. IR(neat): 1560 cm^{-1}. Semicarbazone; mp 170—172 °C. Found: C, 71.46; H, 8.33; N, 14.73%. Calcd for $C_{17}H_{23}ON_3$: C, 71.54; H, 8.12; N, 14.73%. IX: bp 170—172 °C/0.35 mmHg. Mass: $M^+=228.1499$. Calcd for $C_{16}H_{20}O$: 228.1513. IR(neat): 1650 cm^{-1}

B) Benzyl 1-Propenyl Ketone (XI): Benzylmagnesium chloride prepared from benzyl chloride (12.6 g, 0.1 mol) and magnesium (2.4 g, 0.1 mol) in 60 ml of ether was added to crotonaldehyde (7.0 g, 0.1 mol) diluted with ether (60 ml) over a 1-h period under cooling in an ice-bath. The *reaction* mixture was then agitated for a further hour at the ambient temperature. The reaction mixture was then treated with a saturated solution of ammonium chloride (22 ml), and the organic layer was condensed after drying over sodium sulfate to give crude 1-phenyl-3-penten-2-ol. This alcohol was oxidized by means of the Saret reagent (CrO_3 10 g/pyridine 100 ml) at room temperature for 24 h. Ether was added to the reaction mixture, and it was filtered; the filtrate was then washed with water and a saturated solution of cupric sulfate. The condensate of the solution, after drying over sodium sulfate, gave a rather complex mixture. The Benzyl 1-propenyl ketone (200 mg) was isolated from the mixture by repeated chromatography on silica gel eluted with a mixed solvent of chloroform and hexane. Mass: $M^+=$ 160.0886. Calcd for $C_{11}H_{12}O$: 160.0888. IR(neat): 1660 and 1680 cm^{-1}. NMR(CCl_4): 1.40 (3H, double doublet, $J=6$ and 2 Hz), 3.63 (2H, singlet), 6.05 (1H, double doublet, $J=13$ and 2 Hz), and 6.80 ppm (δ) (1H, double quartet, $J=13$ and 6 Hz).

General Procedure of Photocyclization. The solvents and reagents used in the photochemical reaction were purified in the following ways. The methanol was refluxed over magnesium methoxide and distilled. The benzene was washed with concd H_2SO_4 and distilled after refluxing over sodium. The acetonitrile was purified by distillation after drying over phosphorus pentoxide. Boron trifluoride–diethyl ether was distilled under a nitrogen atomosphere and stored in a sealed tube in a cold and dark place. The trifluoroacetic acid was a commercially available reagent, and used without purification. The irradiation of the starting ketones, placed in a Pyrex tube, was carried out using a 450-W USHIO medium-pressure Hg lamp mounted in an imersion jacket and using a RIKOSHA merry-go-round-type irradiation apparatus—the distance between lamp and reaction tube was *ca.* 5 cm. The progress of the reaction was monitored by means of an IR spectrum of the aliquot; we observed the disappearance of the absorptions due to unsaturated carbonyl groups.

Photochemical Reaction in the Presence of Boron Trifluoride–Diethyl Ether. The starting ketones, I—IV, IX, and XI (1—1.5 mmol), in 10 ml of benzene containing boron trifluoride–diethyl ether (0.05 mol/l) were placed in Pyrex tubes, and the air was replaced by nitrogen or argon. Irradiation was then continued until the starting materials had completely disappeared. The reaction mixtures were then passed through an alumina column (10 × 100 mm, Merck activity II—III) to remove the boron trifluoride; the benzene eluate was condensed under reduced pressure to give the cyclized ketones in yields of 79% (V), 87% (VI), and 90% (VII). The yield of the X ketone was poor due to its photo-lability, which was proved by the irradiation of the isolated X ketone. Some improvement in the yield was, however, achieved by using a soft glass filter instead of a Pyrex filter. The irradiation of the benzyl 1-cyclooctenyl ketone (IV) and the benzyl 1-propenyl ketone (IX) recovered the starting materials even after a prolonged reaction period (8 h). V: bp 105—110 °C (bath)/1.0 mmHg. Mass: $M^+=$ 186.1034. Calcd for $C_{13}H_{14}O$, 186.1045. IR(CCl_4): 1720 cm^{-1}. NMR (CCl_4): 3.62 ppm(δ) (2H, singlet). VI: bp 145—155 °C (bath)/0.9 mmHg. Mass: $M^+=200$. IR (CCl_4): 1710 cm^{-1}. NMR(CCl_4): 3.48 ppm (δ) (2H, singlet). Found: C, 84.16; H, 8.32%. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05%. VII: bp 145—150 °C (bath)/0.2 mmHg. Mass: $M^+=214$. IR(neat): 1717 cm^{-1}. NMR (CCl_4): 3.50 ppm (δ) (2H, singlet). Found: C, 84.31; H, 8.58%. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%. X: bp 100 °C (bath)/0.2 mmHg. Mass: $M^+=228$. IR(neat): 1709 cm^{-1}. NMR(CCl_4): 1.40 (6H, singlet), 3.00 (1H, multiplet), and 2.40 ppm (δ) (1H, multiplet). Found: C, 84.18; H, 8.94%. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83%.

GLC analyses (5% OV-17 and Carbowax 20 M on Chromosorb W, N_2) showed the V and VII ketone to consist essentially of one stereoisomer. VI ketone, however, showed two peaks due to the isomers (VIa and VIb) *cis* and *trans* with respect to the ring junction, and the IR and NMR spectra of VI were identical with those of 1,2,3,4,4a,10a-hexahydro-10-phenanthrone obtained by Parham *et al.*[11] The two isomers were separated by preparative GLC and have similar spectroscopic properties in every respect. The faster moving isomer, VIa, was deduced to be *cis*-1,2,3,4,4a,10a-hexahydro-10-phenanthrone.

Photochemical Reaction in Methanol. Irradiations were carried out in the manner described above except for the use of methanol instead of boron trifluoride–diethyl ether/benzene as the solvent system. The benzyl 1-cyclopentenyl ketone (I) and the benzyl 1-cyclohexenyl ketone (II) were consumed within 2 and 3 h respectively, and they gave the cyclized products, V and VI, in 90 and 80% yields respectively. The benzyl 1-cycloheptenyl ketone (III), however, does not cyclize to VII under those reaction conditions.

Photochemical Reactions in Other Solvent Systems. The irradiation of II ketone was carried out in acetonitrile, in acetonitrile containing boron trifluoride–diethyl ether (0.05 mol/l), in benzene, and in benzene containing trifluoroacetic acid (0.05 mol/l). The ratio of VIa to VIb was dependent upon the solvent used, VIa : VIb were 1 : 1 in the boron trifluoride–diethyl ether/benzene, 5 : 1 in the acetonitrile, and 8 : 1 in the methanol.

Transformation of VIa into cis-*1,2,3,4,4a,9,10,10a-Octahydrophenanthrene.* The VI ketone (VIa : VIb = 8 : 1), dissolved in 3 ml of 1,2-ethanedithiol, was treated with 2 ml of boron trifluoride–diethyl ether, after which the reaction mixture was stirred for 15 min at room temperature. An excess amount of saturated aqueous sodium hydrogencarbonate was then added to the mixture and it was extracted with hexane. The hexane extract was condensed after drying over sodium sulfate to give a yellow residue. The residue was dissolved in 10 ml of ethanol containing 1.5 g of Raney-Ni, and the mixture was stirred for 15 h at the ambient temperature. The subsequent evaporation of the ethanol after filtration gave 55 mg of the product (62%). GLC and NMR analyses of the product identified it as *cis*-1,2,3,4,4a,-9,10,10a-octahydrophenanthrene[1] containing a small amount of the *trans* isomer.

Attempted Equilibration of VI. The VI ketone (VIa : VIb = 1 : 1 and 8 : 1, 50 mg) was dissolved in 10 ml of methanolic potassium hydroxide (1 mol/l), after which the solution was stirred for 24 h at room temperature under nitrogen. The reaction mixture was then neutralized with dil H_2SO_4, diluted with water, and extracted with ether. The evaporation of ether after drying over sodium sulfate recovered the starting material. GLC analysis of the recovered material showed an identical peak ratio due to the two components of the starting ketones. The attempted equilibration of the VI ketone using H_2SO_4 instead of the base catalyst gave the same result.

Deuteration of the VI Ketone. The VI ketone (5 mg) was dissolved in 1 ml of a mixed solvent of deuterium oxide and tetrahydrofuran (1 : 4) and 20 μl of pyridine was added to it, after which the mixture was kept at the ambient temperature for 45 h. After the evaporation of tetrahydrofuran under reduced pressure, the aqueous mixture was extracted with hexane. The mass spectrum of the ketone, VI, recoverd from the hexane extract showed intensified ($M+1$) and

$(M+2)$ peaks, $(M+1)/M=2.07$ and $(M+2)/M=1.50$, whereas the ratio of $(M+3)$ to $(M+2)$ was the one expected from the natural abundance of ^{13}C, $(M+3)/(M+2)=0.15$.

Irradiation of Enol Ether, VIII. The Z and E-forms of enol ether, VIII, were isolated in pure forms from a mixture of enol ether prepared from the II ketone and trimethyl orthoformate by the catalysis of H_2SO_4. The Z or E-form of the enol ether in 2 ml of benzene was placed in a Pyrex tube and was externally irradiated. GLC analysis (5% OV-17 on Chromosorb W, N_2) of either solution showed only a geometrical isomerization of the enol ether at the double bond, and a photo-equilibrated mixture of the same composition resulted from the irradiation of either isomer for 2 h, 58% Z and 42% E.

Quenching of the Photoreaction in Boron Trifluoride-Diethyl Ether/Benzene by 1,3-Pentadiene. The I, II, and III ketones (0.5 mmol each) were dissolved in 5 ml of benzene containing boron trifluoride-diethyl ether (0.05 mol/l) and 1,3-pentadiene (0.01—0.1 mol/l). Pyrex tubes containing the reaction mixture with varying amounts of 1,3-pentadiene were placed in a merry-go-round-type irradiation apparatus and irradiated in the same manner as in the preparative experiments for 5—15 min when more than 70% of the starting materials persisted. After irradiation, the same quantity of the internal standard was added to each reaction tube for the measurement of the peak intensity of the product by GLC analysis (5% OV-17 on Chromosorb W, N_2). In the case of the reaction of II, the GLC peak due to one of the products (VIa) was not well separated from that of the starting material, and so the peak due to VIb was employed for the quenching experiments. The experimental results are shown in Fig. 1. 1,3-Pentadiene was not consumed in the presence of boron trifluoride-diethyl ether to an extent detectable by the NMR analysis of the reaction mixture under the present reaction conditions.

Quenching of the Photoreaction in Methanol-Benzene by 1,3-Pentadiene. The I ketone (20 mg) was dissolved in 40 ml of a mixed solvent of methanol and benzene (1 : 4) containing varying amounts of 1,3-pentadiene (0.01—0.1 mol/l); an experiment similar to that described above was then performed. Benzene was added to the solvent system to get a homogeneous solution of 1,3-pentadiene. Stern-Volmer plot of this experiment showed a straight line with the slope of $k_q\tau=16\ M^{-1}$.

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