Photoreaction of 1-(1-Cycloalkenyl)-4-phenyl-1-butanone under Neutral and Acidic Conditions

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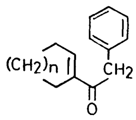
UV irradiation of 1-(1-cycloalkenyl)-4-phenyl-1-butanones gives differing products depending on the reaction conditions, neutral or acidic. In benzene 1-(1-cyclopentenyl)-4-phenyl-1-butanone gives 4-phenylspiro[4,4]-nonan-1-one, formed by the intramolecular abstraction of hydrogen, and 4-cyclopentylidene-4-phenylbutanal, formed by Norrish type I fission of the spiro ketone. 1-(1-Cyclohexenyl)-4-phenyl-1-butanone does not exibit this behavior. Both ketones give the reduction products, 1-cyclopentyl-4-phenyl-1-butanone and 1-cyclohexyl-4-phenyl-1-butanone, under the action of trifluoroacetic acid, and cyclized products, 7-phenylperhydro-4-indenone and 4-phenylperhydro-1-naphthelenone, under the action of boron trifluoride etherate. The reaction processes under acidic conditions have both an ionic and a free radical nature. The results have lead to the proposition of the mechanism involving electron transfer, proton transfer, and hydrogen abstraction.

Much attention has been paid to the intramolecular exciplex between two aromatic groups or between an aromatic moiety and a non-aromatic functional group.[1,2] It appears that the formation of the exciplex is dependent upon the length of the bridge connecting the two chromophores. Excited complexes have been postulated as the intermediates of intramolecular photochemical reactions.[3-5] Following the study on the photochemistry of 1-(1-cycloalkenyl)-2-phenyl-1-ethanones (Ia, Ib, and Ic)[6] and 1-(1-cycloalkenyl-3-phenyl-1-propanones (IIa and IIb),[7] the photoreactions of 1-(1-cycloalkenyl)-4-phenyl-1-butanones (IIIa and IIIb) having the trimethylene bridge between the enone and phenyl groups have been investigated. The UV irradiation of Ia, Ib, and Ic under acidic conditions or in protic media induces photo-coupling between the β-position of the enones and the ortho-position of the phenyl group.[6] Similarly the irradiation of IIb under acidic conditions gives the same type of photoproduct. Irradiation of IIa under neutral conditions, on the other hand, gives a product derived from the intramolecular abstraction of hydrogen by the β-carbon of the enone moiety.[7]



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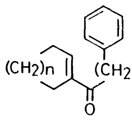
b: n=2
c: n=3



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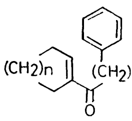

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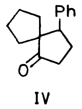
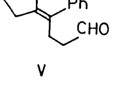
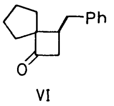


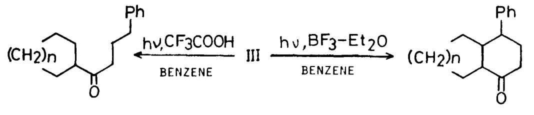
IV



V



VI



VII
a: n=1
b: n=2

VIII
a: n=1
b: n=2

The 1-(1-cycloalkenyl)-4-phenyl-1-butanones (IIIa and IIIb) have a trimethylene bridge by which the two chromophores may be expected to interact more effectively than I or II.[3-5] The present study demonstrates that the photochemical behavior of III is completely different from that of I and II.

Results and Discussion

Photoreaction under Neutral Conditions. Irradiation (10 h) of a solution of 1-(1-cyclopentenyl)-4-phenyl-1-butanone (IIIa) in benzene gave a spiro ketone IV and an aldehyde V in 24 and 17% yields, respectively. The structures of IV and V were deduced from spectral data. The IR absorptions of IV at 1735, 765, and 700 cm^{-1} show the presence of a five membered ketone and a monosubstituted benzene ring. The IR absorption at 2710 cm^{-1} and NMR signal at δ 9.85 (t, $J=2$ Hz) of V are due to an aldehyde group, and the IR absorptions at 775 and 700 cm^{-1} show the presence of a monosubstituted benzene ring. The IR absorption of the crude product from the irradiation of IIIa showed an absorption at 1774 cm^{-1} and this indicated the product VI having a cyclobutanone structure. This minor product, which was not isolated, appears to be formed by the intramolecular abstraction of the hydrogen at C_3-methylene by the β-carbon of the enone moiety of IIIa.[7] The product IV appears to be formed by the intramolecular abstraction of the benzylic hydrogen by the β-carbon of the enone moiety of IIIa. The formation of aldehyde V showed an induction period and hence V appears to be a secondary product from IIIa through the spiro ketone IV. This was ascertained by the direct irradiation of IV. Norrish type I fission of IV and hydrogen transfer account for the transformation of IV to V.

1-(1-Cyclohexenyl)-4-phenyl-1-butanone (IIIb) in benzene, in contrast, did not react even after prolonged irradiation (24 h). This may be explained in terms of the preferential dissipation of the excited energy due to the cis-trans isomerization of the cyclohexene moiety.[8]

Photoreaction under Acidic Conditions. A solution of 1-(1-cyclopentenyl)-4-phenyl-1-butanone (IIIa) or 1-(1-cyclohexenyl)-4-phenyl-1-butanone (IIIb) in benzene

Table 1. Yield of VIIa from IIIa (0.1 M in toluene) depending upon the amount of CF_3COOH

CF_3COOH (M)	Yield of VIIa (%)
0.03	trace
0.06	44
0.12	76
0.23	84

was irradiated for 32 or 70 h in the presence of 0.05 M trifluoroacetic acid, giving the dihydro derivatives VIIa and VIIb in yields of 63 and 40%, respectively. GLC analysis of the product mixture showed the formation of 1,2-diphenylethane and carbon dioxide when the reaction of IIIa was carried out in degassed toluene. The yield of VIIa was dependent on the amount of trifluoroacetic acid used and was improved up to 84% by using two equivalents of the acid in toluene (Table 1). These results demonstrate the involvement of free radical hydrogen abstraction and the degradation of trifluoroacetic acid. The photoreaction of IIIa in 2-propanol, however, did not give the reduction product, and this suggests that the reaction takes a mechanism other than a simple hydrogen abstraction from the solvent. Under the conditions in which essentially entire incident light was absorbed in the $n\pi^*$ region of IIIa, the relative rates of the photoreduction (relative quantum yield in the approximation) were dependent on the molar polarization of the solvent used as seen in Fig. 1. The figures in parentheses in Fig. 1 are the relative rates of hydrogen abstraction by an excited benzophenone.[9)] The retardation of the photo-reduction in benzene, an extremely poor hydrogen donor, explain this behavior. This suggests the polar nature of the photo-reduction and some dependence on the hydrogen donating ability of the solvent. The photo-reduction takes place only in the presence of a strong Brønsted acids such as trifluoroacetic acid (pK_a: 0.2). The weaker acids like benzoic acid (pK_a: 4.20), acetic acid (pK_a: 4.75), or phenol (pK_a: 10.00) can not induce the reaction.

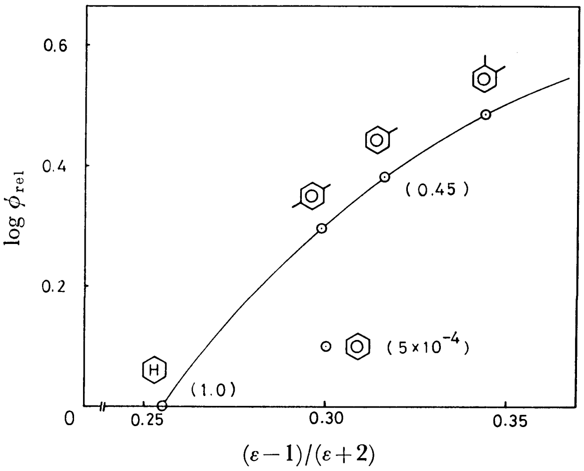


Fig. 1. Relation between the relative quantum yield of VIIa and the polarization of solvents. (The figures in parentheses are the relative rates of H-abstraction by an excited benzophenone.[9)])

A solution of 1-(1-cycloalkenyl)-4-phenyl-1-butanone (IIIa and IIIb) in benzene containing 0.05 M boron trifluoride etherate was irradiated for 20 h, the cyclized products VIIIa and VIIIb were obtained in 25 and 30% yields, respectively. The structures of products VIIIa and VIIIb were deduced from permanganate oxidation which gave banzoic acid and spectroscopic data (VIIIa, 1705, 760, and 700 cm^{-1}; VIIIb, 1710, 760, and 700 cm^{-1}). These data indicate the presence of a six-membered ketone and a monosubstituted benzene ring. Though the stereochemistry of the products VIIIa and VIIIb was not defined, only one of the possible stereoisomers was detected by GLC analysis. This type of ortho-cyclization also took place under catalysis of other Lewis acids such as tin(IV) chloride and titanium(IV) chloride (0.05 M). The reaction in hydrogen donating solvents such as toluene and xylene in the presence of boron trifluoride etherate did not give the products VIIIa and VIIIb in reasonable yields but gave the reduction products VIIa and VIIb predominantly (see next section).

Reaction Mechanism. The two types of reaction do not take place in the absence of trifluoroacetic acid or a Lewis acid and do not occur intermolecularly between 1-acetylcyclopentene (0.1 M) and tuluene under the same reaction conditions as for IIIa. This result indicates that an intramolecular interaction between the phenyl group and the enone moiety, at least in the excited state, is necessary for the photoreaction of IIIa and IIIb under acidic conditions, and that the existence of an acid must enhance the interaction. The UV-spectra of IIIa and IIIb are essentially the same as the spectrum of the 1:1 mixture of 1-acetylcyclopentene or 1-acetylcyclohexene and toluene, and therefore there is no evidence for the interaction between the two chromophores in the ground state. The enone moieties of IIIa and IIIb are nonemissive and only a weak fluorescence from the aromatic moieties may be observed. The intensity is much weaker than that of toluene and this is thought due to the efficient quenching of the excited state of the aromatic moiety by the intramolecular enone group. An α,β-unsaturated ketone has the intrinsic ability to quench the excited singlet state of an aromatic molecule. Thus 1-acetylcyclopentene quenched the fluorescence of toluene, 1-methylnaphthalene, and anthracene by diffusion controlled-rates (10^9—10^{10} M^{-1} s^{-1}). The quenching rates were obtained from the slopes of Stern-Volmer plots ($k_q\tau_0$) and the reported lifetimes (τ_0) of the aromatic compounds.[10)] The weak fluorescence of IIIa and IIIb is suggested due to the strong intramolecular interaction between the two chromophores in the singlet excited state. For the acid-coordinated species of IIIa and IIIb, the interaction between the two chromophores would be expected to be CT-type and the excitation of either a donor (aromatic moiety) or an acceptor (enone moiety) promotes the interaction. Though the excited state responsible for the photoreactions cannot be specified, the excitation of either chromophore must form an essentially similar CT-state. In addition it is highly possible that the photoreaction of IIIa and IIIb occurs from the new CT-excitation

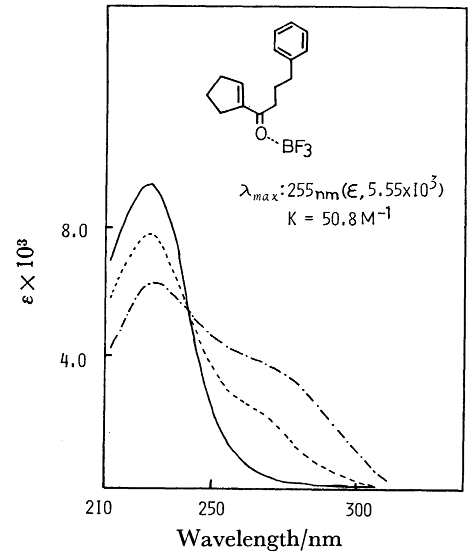
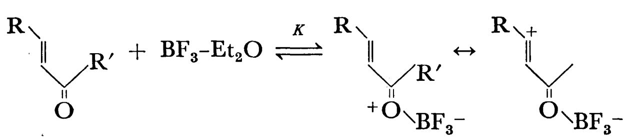


Fig. 2. UV absorption of IIIa (1.26×10^{-4} M in hexane) in the presence of BF_3-Et_2O: ——, 0 M; ----, 1.06×10^{-2} M; —·—·, 2.65×10^{-2} M.

indicated by the UV spectra of IIIa and IIIb in the presence of an acid.

In the presence of boron trifluoride etherate, the UV spectrum of IIIa in hexane (2.52×10^{-4} M) shows a broad band at around 260 nm with concomitant decrease in $\pi\pi^*$ absorption at 232 nm as shown in Fig. 2. The analysis of the spectrum having an isosbestic point at 242 nm by the Rose-Drago's method,[11] monitoring at 250, 260, 270, and 280 nm, gave $\lambda_{\max}^{\text{hexane}}$ 255 nm (ε 5550) and the stability constant $K=50.8$ M^{-1} for the complex X between IIIa and boron trifluoride. The complexing of boron trifluoride to α,β-unsaturated ketones has been reported by UV,[12] IR,[13] and NMR[14] spectra. A similar behavior was observed with trifluorocetic acid (10^{-3}—10^{-2} M) in the $n\pi^*$ region of IIIa in higher concentration (1.26×10^{-2} M), though the dilute solution of IIIa (1.26×10^{-4} M) showed only a slight bathochromic shift in $\pi\pi^*$ region. These results indicate that the enone IIIa is coordinated



$$\mathrm{RCH{=}CHC({=}O)R'} + \mathrm{BF_3\text{-}Et_2O} \overset{K}{\rightleftharpoons} \mathrm{RCH{=}CHC(R'){=}\overset{+}{O}{-}BF_3^-} \leftrightarrow \mathrm{R\overset{+}{C}H{-}CH{=}C(R'){-}O{-}BF_3^-}$$

X

effectively with a Lewis acid or a strong Brønsted acid under the reaction conditions—enone III 0.1 M and acid 0.05—0.06 M. The necessity for acid in the two types of photoreactions, suggests the direct involvement of the acid-coordinated form (X) of the starting ketone. The quenching of the photo-products VIIa and VIIIa by 1,3-pentadiene gave linear Stern-Volmer plots with $k_q\tau$ value of 88 M^{-1} for VIIa and 158 M^{-1} for VIIIa. If this quenching is due to the energy transfer from the triplet enone to the diene, the quenching rates would be expected to be diffusion-controlled (k_p=*ca.* 10^{10} M^{-1} s^{-1}), and the lifetime (τ) of the triplet enone would fall into 10^{-9}—10^{-8} s. These values are too small for the normal triplet species and hence the quenchable intermediate appears to be a singlet or triplet species with an unusually short lifetime.

Table 2. Solvent effect on the yield of VIIa and VIIIa from IIIa (0.1 M)

BF_3-Et_2O (0.05 M) solvent	Yield of VIIa (%)	Yield of VIIIa (%)	CF_3COOH (0.05 M) solvent	Yield of VIIa (%)	Yield of VIIIa (%)
Benzene	1.5	25	Benzene	43	7
Toluene	18	1.0	Toluene	80	2
o-Xylene	26	0	*o*-Xylene	80	0
Cyclohexane	8	1.3	Cyclohexane	29	4
			Hexane	16	3

The photoreactions in benzene were selective with the acid used. The reaction under boron trifluoride etherate gave the cyclized product VIII whereas the reaction under trifluoroacetic acid gave largly the reduction product VII. The variation in the yields are listed in the Table 2. The reaction in the hydrogen donating solvents such as toluene and *o*-xylene gave largly the reduction product found under both trifluoroacetic acid and boron trifluoride etherate. Thus the hydrogen donating ability of the solvent appears to be an important factor in the discrimination of the two types of photoreactions.

For the photoreaction of ketone IIIa and IIIb the mechanism shown in Fig. 3 is proposed on the basis of the experimental results; (a) the radical and ionic nature of the photochemical process, (b) the degradation of trifluoroacetic acid to carbon dioxide, (c) the necessity and reality of the intramolecular interaction in the excited state, (d) the existence of acid coordination to the enone and its enhancement of the intramolecular interaction between the two chromophores, (e) quenching, and (f) the solvent effect on the yield and distribution of products.

Excitation of the acid-coordinated enone—$n\pi^*$ excitation or direct CT-excitation of the complex X—forms an intramolecular singlet excited complex (X*) having CT-character, in which the phenyl group works as as an electron donor and the enone group works as an electron accepter. An electron transfer in this excited complex gives a radical ion pair XI. When the acid A is BF_3, the loss of BF_3 and the simultaneous proton transfer from the benzylic position to oxygen gives a

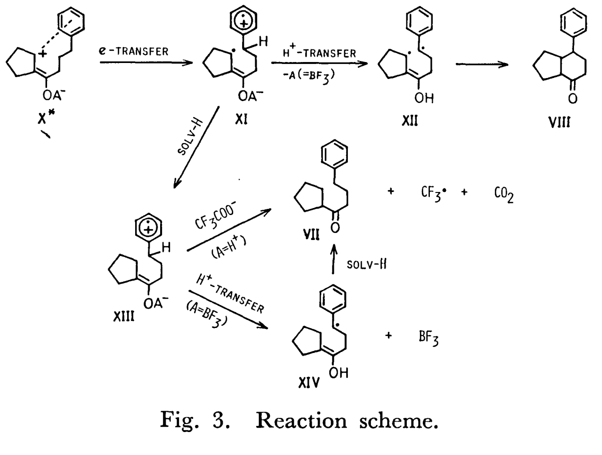


Fig. 3. Reaction scheme.

diradical XII, and the coupling of the diradical forms the photo-cyclization product VIII. In hydrogen donating solvents, the hydrogen abstraction by XI from the solvent gives a radical ion XIII. When the acid is CF_3COOH, another electron transfer from CF_3COO^- to XIII forms the reduction product VII and carbon dioxide. When the acid A in XIII is BF_3, the proton transfer from benzylic position to oxygen with simultaneous loss of BF_3 gives the benzyl radical XIV which forms the reduction product VII by another hydrogen abstraction from the solvent. This reaction mechanism accounts for solvent-polarity, the hydrogen donating ability of the solvent, and the acid—Brønsted or Lewis acid—on the product formation. The photoreactions observed for III were not observed in the case of I and II. The variation in the reactivity upon reaction conditions was again not observed with I and II. The interaction between the two chromophores in the excited state of III appeares to be stronger than that in I and II.[15] Evidently the trimethylene bridge combining the phenyl and the enone groups in III appeares to be an important factor for the different reactivity of III from those of I and II.

Experimental

Preparation of 1-(1-Cyclopentenyl)-4-phenyl-1-butanone (IIIa) and 1-(1-Cyclohexenyl)-4-phenyl-1-butanone (IIIb). Ketones IIIa and IIIb were synthesized from 4-phenylbutanoyl chloride and cycloalkene by the modified method of Cook and Hawett[16] for the synthesis of 1-(1-cyclohexenyl)-2-phenyl-1-ethanone (Ib). Dichloromethane was the solvent instead of carbon disulfide and $SnCl_4$ the acid catalyst. The reaction was carried out at a lower temperature (−80—−100 °C) under an atmosphere of nitrogen. Under these conditions clean 1-(2-chlorocycloalkyl)-4-phenyl-1-butanone was the product. 1-(2-Chlorocyclopentyl)-4-phenyl-1-butanone was dehydrochlorinated by refluxing the benzene solution in the presence of triethylamine. 1-(2-Chlorocyclohexyl)-4-phenyl-1-butanone was dehydrochlorinated in *N*,*N*-dimethylaniline at 180 °C. IIIa; bp 152 °C/0.3 mmHg. MS *m*/*e* 214 (M^+). IR(neat): 1655, 1613, 745, and 690 cm^{-1}. NMR(CCl_4): δ 7.20 (5H, m) and 6.80 (1H, br s). Semicarbazone; mp 123.5—125.0 °C. Found: C, 70.99; H, 7.85; N, 15.48%. Calcd for $C_{16}H_{21}N_3O$: C, 70.82; H, 7.80; N, 15.48%. IIIb; bp 115—120 °C/0.1 mmHg. MS *m*/*e* 228 (M^+). IR(neat): 1655, 1610, 750, and 700 cm^{-1}. NMR(CCl_4): δ 7.20 (5H, m), and 6.80 (1H, br s). Semicarbazone; mp 145 °C. Found: C, 71.73; H, 8.28; N, 14.96%. Calcd for $C_{17}H_{23}N_3O$: C, 71.54; H, 8.12; N, 14.73%.

Absorption and Emission Spectra of IIIa and IIIb. Hexane and cyclohexane were purified by passing over a long column of activated silica gel. The effect of BF_3-Et_2O on the absorption spectrum of IIIa was studied in hexane (IIIa, 2.52×10^{-4}M) containing 1.06—2.65×10^{-2} M BF_3-Et_2O in both sample and reference cells, and the results are shown in Fig. 2. The effect of CF_3COOH was studied in the same manner by using 1.26×10^{-4}M solution of IIIa and 1.44×10^{-3}—4.40×10^{-2}M CF_3COOH in hexane, and the $\pi\pi^*$ absorption shifted from 232 to 242 nm. The effect of CF_3COOH on $n\pi^*$ band was studied by using 1.26×10^{-2}M solution of IIIa and 2.63×10^{-3}—2.30×10^{-2}M CF_3COOH in hexane, and an isosbestic point was observed at 333 nm. Fluorescence spectra were measured by a Hitachi MPF-4 spectrophotometer using cyclohexane purged by argon as solvent. IIIa fluoresces weakly at 300—350 nm and it appeares in the same region to the $n\pi^*$ absorption of IIIa. The weakness of the fluorescence is not thought entirely due to the absorption by the enone at the concentrations for the measurement of fluorescence($<10^{-3}$ M). The concentrations of toluene and IIIa in hexane were adjusted to absorb the same quanta of light at 270nm for the measurement of the relative intensity of fluorescence. The intensity of fluorescence from IIIa under these conditions was much weaker than that of toluene, Φ(toluene)/Φ(IIIa)$>$200.

Fluorescence Quenching of Aromatic Compounds by 1-Acetylcyclopentene. The hexane solutions of (a) toluene (1.90×10^{-3} M), (b) 1-methylnaphthalene (1.45×10^{-3} M), and (c) anthracene (1.40×10^{-3}M), were used for the quenching experiments and were excited at 260nm (a), and 300 nm (b, c). The intensities of fluorescence were monitored at the emission maxima at 283 (a), 325 (b), and 400 nm (c). The concentration limits of the quencher, 1-acetylcyclopentene, were 3.64×10^{-4} to 5.82×10^{-3}M. The slopes of the Stern-Volmer plots ($k_q\tau_0$) were 427 (a), 265 (b), and 84 M^{-1} (c).

Irradiation of IIIa and IIIb under Neutral Conditions. The solution of IIIa (700 mg) in 150 ml of thiophene-free benzene was internally irradiated by a 450W high pressure mercury lamp mounted in a Pyrex cooling jacket. During the reaction the solution was stirred magnetically and kept in an atmosphere of argon. Reaction products were obtained by distillation, 100—120 °C/0.1mmHg, after evaporation of the solvent *in vacuo*. GLC analysis (5% PEG-20M on Chromosorb W, 200 °C) of the crude product showed two main peaks attributed to spiro ketone IV and aldehyde V beside small peaks attributed to the starting material IIIa and a minor product. The aldehyde V was collected by preparative GLC (120 mg, 17%). Since the spiro ketone IV was difficult to purify by preparative GLC, the aldehyde was destroyed by AgO treatment[17] of the crude product before GLC, IV (170 mg, 24%).

Irradiation of IIIb in the same manner did not give the product but recovered the starting material. IV, an oil. *MW* Found: *m*/*e* 214.1342. Calcd for $C_{15}H_{18}O$: *m*/*e* 214.1357. IR(neat): 1735, 765, and 700 cm^{-1}. NMR(CCl_4): 7.30 (5H, m). V, an oil, *MW* Found: *m*/*e* 214.1342. Calcd for $C_{15}H_{18}O$: *m*/*e* 214.1357. IR(neat): 2710, 1728, 775, and 700 cm^{-1}. NMR(CCl_4): δ 9.85 (1H, t, J=2 Hz), 7.20 (5H, m), and 2.68 (2H, t, J=7 Hz).

Photoreaction of IIIa and IIIb in the Presence of CF_3COOH.

a) Preparative Experiment: The solution of IIIa or IIIb (500 mg) in 140 ml of thiophene-free benzene was purged by argon and CF_3COOH added to make 0.05M CF_3COOH. Irradiation was carried out (32 h for IIIa and 70 h for IIIb) in the same manner as described for the photoreaction of IIIa in benzene. The reaction solution was passed through an alumina column to remove the acid and concentrated *in vacuo*. Distillation of the residue by a Kugelrohr apparatus gave product VIIa (*ca.* 110 °C/0.1 mmHg) in 63% yield and VIIb (*ca.* 120 °C/0.1 mmHg) in 40% yield. The products VIIa and VIIb were identified by IR, NMR, and GLC analyses with the authentic samples prepared by hydrogenation of IIIa and IIIb over Pd-C catalyst.

b) Detection of Carbon Dioxide: The solution of IIIa (50 mg) in toluene (4 ml) containing 0.05 M CF_3COOH was degassed by the freeze-thaw method and kept under an atomosphere of argon. After irradiation for 9 h, 3 ml of the gaseous layer was introduced into GLC (3 mm $\phi\times$

2.25 m silica gel 60/80 mesh, room temperature). The relative peak intensity of carbon dioxide from the irradiated sample and the sample kept in the dark was 16:1.

c) Solvent Effect: Enone IIIa was dissolved in cyclohexane, benzene, toluene, *p*-xylene and *o*-xylene to make the concentration of each solution to be 0.21M. This concentration was enough to absorb more than 99% of the incident light from the lamp in the nπ* region of the enone. To each solution was added 50 μl of CF_3COOH (0.32M) and the solution in the Pyrex tube was irradiated under argon using a Rikosha merry-go-round type irradiation apparatus equiped with a 450W high pressure mercury lamp. The relative rates—the relative quantum yield—of the product were determined by GLC analysis of the product using 3-phenyl-1,3-dihydroisobenzofuran-1-one as an internal reference. The results are shown in Fig. 1.

Photoreaction of IIIa and IIIb in the Presence of Lewis Acid. a) Preparative Experiments: The solution of IIIa or IIIb (800 mg) in 150 ml of thiophene-free benzene containing a Lewis acid (0.05M) was irradiated for 20 h in the same manner as described for the reaction in benzene. The Lewis acid was removed by passing an alumina column by benzene. Alumina chromatography eluted by hexane-dichloromethane and recrystallization from hexane gave the cyclized product VIIIa (25%/BF_3-Et_2O, 63%/$SnCl_4$) or VIIIb (30%/BF_3-Et_2O). The reactions on other solvents are summarized in Table 2. VIIIa; mp 78 °C. Found: C, 84.00; H, 8.54%. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47%. MS *m/e* 214(M^+). IR(neat): 1705, 760, and 700 cm^{-1}. NMR(CCl_4): δ 7.26 (5H, m) and 3.30—3.60 (1H, m). VIIIb; mp 82 °C. Found: C, 84.11; H, 8.85%. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83%. MS *m/e* 228 (M^+). IR(neat): 1710, 760, and 700 cm^{-1}. NMR(CCl_4): δ 7.00 (5H, m) and 3.00—3.40 (1H, m).

b) Solvent Effect: The 0.1 M solution of IIIa in 8 ml of cyclohexane, benzene, toluen, or *o*-xylene containing 0.05 M BF_3-Et_2O was irradiated for 20 h in the same manner as the irradiation of IIIa in the presence of CF_3COOH. The products VIIa and VIIIa were analyzed by GLC (3% OV-17 on Chromosorb W, 190 °C) using an internal reference and the results are summarized in Table 2.

Permanganate Oxidation of the Product VIIIa and VIIIb. The mixture of the one of the products (10 mg) and $KMnO_4$ (36 mg) in 1 ml of water was stirred for 15 h at room temperature. The reaction mixture was extracted with benzene after addition of concd-HCl and the extract treated with an ethereal solution of diazomethane. The methyl ester was identified as methyl benzoate by GLC analysis (3% OV-17 on Chromosorb W). No trace of methyl phthalate was detected.

Quenching Experiments. a): Six Pyrex tubes containing enone IIIa (25 mg), CF_3COOH (15 μl), and dried toluene (3 ml) had 0, 3, 6, 10, 12, and 15μl of 1,3-pentadiene added. The solutions were irradiated using a merry-go-round apparatus for 2 h. After passing the solution through alumina, each sample was analyzed by GLC using an internal reference. Stern-Volmer plots of the product formation gave a linear plot with $k_q\tau$ value of 88 M^{-1}.

b): The mixture of IIIa (21.8 mg), BF_3-Et_2O (20 μl), and benzene (3 ml) containing varing amounts of 1,3-pentadiene was irradiated for 35 h in the same manner as the experiment (*a*) in this section. The product was identified by GLC using ethyl oleate as an internal reference. The Stern-Volmer plots of the product formation were found to be linear having a $k_q\tau$ value of 158 M^{-1}.

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