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Photoinduced Reactions. XLIII. Photochemical Reactions of 4-Hydroxy-2,5-cyclohexadienones[1]

Katsuyuki OGURA and Teruo MATSUURA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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Irradiation of 2,4-di-*t*-butyl-4,5-dihydroxy-2,5-cyclohexadienone (V) in methanol afforded a β-diketone (VIII) in a 68% yield. Diketone VIII was also formed on photolysis of a suspension of V in petroleum ether (62%) and an aqueous alkaline solution of V (56%). Photolysis of 2,4-di-*t*-butyl-4-hydroxy-5-methoxy-2,5-cyclohexadienone (VI) in various solvents yields IXa as a main product. On irradiation of VI in methanol, XI which might be formed by the addition of methanol to IXb was also isolated. Irradiation of 2,4,6-tri-*t*-butyl-3-methoxy-4-hydroxy-2,5-cyclohexadienone (VII) in a variety of solvents gave a cyclopentadienone (XIII) in high yields. It is reasonable to assume that the cyclopentadienone XIII is formed by elimination of methanol from a 2-cyclopentenone derivative (XII). The formation of XIII from VII was sensitized by benzophenone and acetophenone, and quenched by piperylene. The mechanisms of these reactions are discussed.

In the photochemical reaction of a 2,5-cyclohexadienone in neutral media, isomerization to a bicyclo[3.1.0]hex-3-en-2-one, the so-called lumi-type ketone, is the most common process (Eq. 1).[2] On the other hand, photolysis of certain 4-hydroxy-2,5-cyclohexadienones was reported to afford 4-acyl-2-cyclopentenones and two reaction pathways were proposed (paths 1 and 2 in Scheme 1). Ganter *et al.* found that the photochemical rearrangement of 3-oxo-10β-hydroxy-17β-acetoxy-$\Delta^{1,4}$-estradiene affords a 4-acyl-2-cyclopentenone derivative along with 17-*O*-acetylestradiol, and they proposed a zwitterion intermediate leading to the acylcyclopentenone *via* path 1 (Eq. (2)).[3] Altwicker and Cook[4] showed that irradiation of 2,6-di-*t*-butyl-4-hydroxy-4-phenyl-2,5-cyclohexadienone gives 2,5-di-*t*-butyl-4-benzoyl-2-cyclopentenone, and they considered the possibility of path 2 for its formation (Eq. (3)). Furthermore, Burkinshaw *et al.*[5] reported the photolysis of several 4-

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[1] Part XLII: K. Ogura and T. Matsuura, This Bulletin, **43**, 3181 (1970).

[2] For example, K. Schaffner, *Advan. in Photochem.*, **4**, 81 (1966).

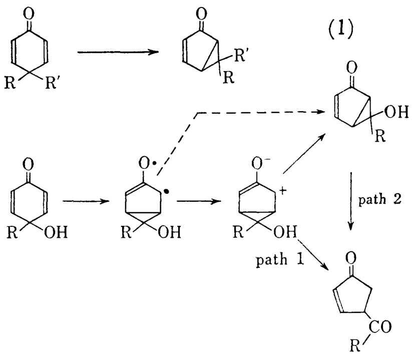
[3] C. Ganter, R. Warszawski, H. Wehrli, K. Schaffner and O. Jeger, *Helv. Chim. Acta*, **46**, 320 (1963).

[4] E. R. Altwicker and C. F. Cook, *J. Org. Chem.*, **29**, 3087 (1964).

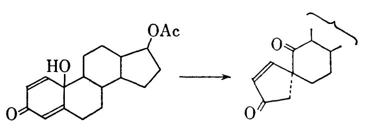
[5] G. F. Burkinshaw, B. R. Favis and P. C. Woodgate, *Chem. Commun.*, **1967**, 607.

hydroxy-2,5-cyclohexadienones to give 4-acyl-2-cyclopentenone derivatives, some of which undergoes further photochemical rearrangement to form Δ^1-butenolides (*e.g.*, Eq. (4)). Recently, we showed[6],[*1] that the photolysis of 2,4,6-tri-*t*-butyl-4-hydroxy-2,5-cyclohexadienone (I) in non-polar media affords the products A and B which are unequivocally formed *via* a bicyclo[3.1.0]hex-3-en-2-one (II), a 4-acyl-2-cyclopentenone derivative IIIa and the further transformed product IVa. The photolysis of I in polar solvents gave the product (IVb) as the main product.

In the present study photochemical reactions of 2,4-di-*t*-butyl-4,5-dihydroxy-2,5-cyclohexadienone (V),[8] 2,4-di-*t*-butyl-4-hydroxy-5-methoxy-2,5-cyclohexadienone (VI),[8] and 2,4,6-tri-*t*-butyl-3-methoxy-4-hydroxy-2,5-cyclohexadienone (VII)[9] were examined in order to investigate the substituent effect upon the course of the photochemical reaction of 4-hydroxy-2,5-cyclohexadienones and to discuss the validity of two possible mechanisms (paths 1 and 2 in Scheme 1) for the formation of 4-acyl-2-cyclopentenones.



Scheme 1



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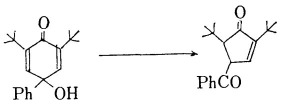

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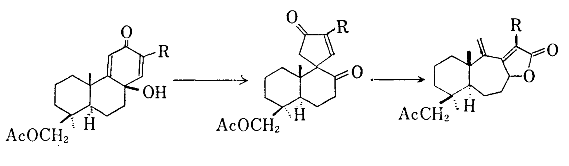

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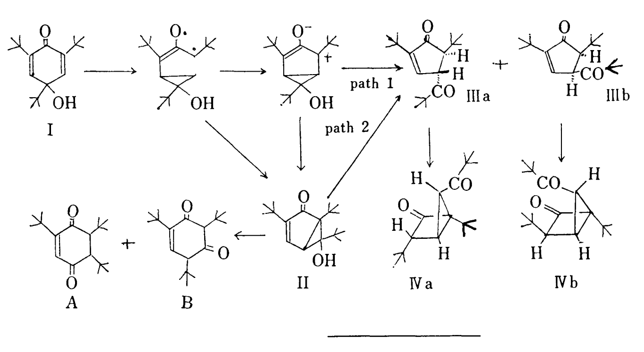

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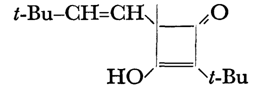
6) T. Matsuura and K. Ogura, *Tetrahedron*, **24**, 6167 (1968).

[*1] Recently Plank *et al.* reported that a vinylcyclobutenone (i) had been isolated from the photolysis of I in benzene.[7]



(i)

7) D. A. Plank, J. C. Floyd and W. H. Starnes, Jr., *Chem. Commun.*, **1969**, 1003.

8) H. Musso and D. Maassen, *Ann. Chem.*, **689**, 93 (1965).

9) T. Matsuura and K. Ogura, *J. Amer. Chem. Soc.*, **89**, 3846 (1967).

Results and Discussion

Photolysis of V. Irradiation of V in methanol with a high-pressure mercury arc lamp (Pyrex filter) afforded a β-diketone (VIII) in a 68% yield. The product was also obtained by the photolysis of a suspension of V in petroleum ether (62%) and of an aqueous alkaline solution of V (56%). The IR spectrum of VIII showed broad bands at 3500—2200, 2100—1750, and 1675—1400 cm^{-1}, indicating the presence of strong hydrogen bonding between a hydroxyl group and a carbonyl group. The UV absorption of VIII (λ_{max}^{EtOH} 248.5 mμ) suggests that VIII has an enone system. In the NMR spectrum of VIII, four singlets appear at τ 1.45 (1H), 4.91 (1H), 8.74 (9H), and 9.00 (9H), and two doublet signals at τ 5.80 and 7.20 (J=2 Hz). These data are consistent with formula VIII, which is the structure expected from the mechanism analogous to the photochemical reaction of 4-hydroxy-2,5-cyclohexadienones (Scheme 1). Since β-diketone VIII is unchangeable on treatment with a base*[2] and the coupling constant (J=2 Hz) between C-4 and C-5 protons of VIII is similar to that of IIIa,[10)] it is suggested that the steric relation between the *t*-butyl and pivaloyl groups of VIII is *trans*. The structure VIII for β-diketone was further supported from the spectral data of its methyl ethers. Treatment of a solution of VIII in absolute methanol with dry hydrogen chloride gave two 3-methoxy-2-cyclopentenone derivatives, IXa (mp 57—61°C) and Xa (mp 35—36°C). Both of them showed similar spectral data which were consistent with the structures IXa and Xa. 3-Methoxy-2-cyclopentenone with a higher melting point (57—61°C) exhibits its IR absorptions at 1705 (2-cyclopentenone), 1693 (pivaloyl) and 1627 cm^{-1} (strong, $\rangle$C=C–O–), and its UV band at 240 mμ (ε 9200). The NMR spectrum of the cyclopentenone (mp 57—61°C) showed three singlets at τ 6.24 (3H, =C–OCH$_3$), 8.75 (9H, =C–*t*-Bu)[10)] and 9.00 (9H, ⪢C-*t*-Bu),[10)] two doublets at τ 4.71 (1H, J=1 Hz) and 7.56 (1H, J=2 Hz), and a quartet at τ 5.83 (1H, J=1 and 2 Hz). On the other hand, in the NMR spectrum of the 3-methoxy-2-cyclopentenone with a lower melting point (35—36°C), six signals appeared at τ 4.79 (1H, singlet), 5.84 (1H, doublet, J=2 Hz), 6.14 (3H, singlet, =C–OCH$_3$), 6.99 (1H, doublet, J=2 Hz), 8.73 (9H, singlet, =C-*t*-Bu)[10)] and 9.03 (9H, singlet, C-*t*-Bu).[10)] The singlet (τ 4.79) and the doublet (τ 6.99) couple slightly with each other. The compound showed its IR bands at 1712 (2-cyclopentenone), 1685 (pivaloyl) and 1596 cm^{-1} (strong, $\rangle$C=C–O–) and its UV absorption at 240 mμ (ε 16100). Formula IXa was assigned to the structure of the 2-cyclopentenone with a higher melting point, because the 2-cyclopentenone (IXa) was also obtained by photolysis of VI which is expected to give IXa (Scheme 1). Thus the lower melting 2-cyclopentenone is represented as formula Xa. It should be noted that a methoxyl signal of IXa appeared at a higher magnetic field (τ 6.26) than that (τ 6.14) of Xa. This may be due to the location of the methoxyl group of IXa in the deshielding area of its pivaloyl group.

Photolysis of VI. Irradiation of VI in methanol with a high-pressure mercury lamp through a Pyrex filter gave the 2-cyclopentenone IXa and a dimethoxycyclopentanone (XI) in 39 and 32% yields, respectively. Dimethoxycyclopentanone XI was shown from its IR bands at 1748 and 1694 cm^{-1} to have two carbonyl groups. The NMR spectrum of XI exhibits four singlets at τ 6.67 (3H, ⪢C–OCH$_3$), 6.83 (3H, ⪢C–OCH$_3$), 8.76 (9H, =C-*t*-Bu)[10)] and 9.00 (9H, ⪢C-*t*-Bu),[10)] a doublet of doublet at τ 5.80 (1H, J=1 and 7 Hz), a multiplet at τ 7.50 (3H), and no signal at fields lower than τ 5.5. This compound was converted into IXa by mild treatment with a base. These data suggest that dimethoxycyclopentanone is formulated as XI. It is considered[6)] that the hydrogen at C-5 position of IXa is derived from a solvent or the hydroxyl hydrogen at C-4 position of VI (*via* an intermolecular or intramolecular hydrogen transfer), and that therefore deuterated compounds IXc and XIa corresponding to IXa and XI should be formed on photolysis of VI in methanol-*O*-d$_1$.[6)] In fact, irradiation of VI in methanol-*O*-d$_1$ afforded the products IXc and XIa. Deuteriocyclopentenone IXc showed its NMR signals corresponding to those of IXa except for the disappearance of the signal of IXa at τ 7.56. This indicates that, in the NMR spectrum of IXa, the proton at C-5 position is coupled with the C-4 proton (J=2 Hz) and the proton at C-2 with the C-4 proton (J=1 Hz). In the NMR spectrum of XIa, the signal at τ 5.80 appeared as a diffused singlet and the intensity of the multiplet signal at τ 7.50 was reduced as compared with that of XI. This supports the observation that the signal of XI at τ 5.80 is attributed to the C-4 proton and the coupling constant between the C-4 and C-5 protons is 7 Hz.

Photolysis of VII. Irradiation of VII in various

Table 1. The sensitized reaction of VII[a)]

exp. No.	VII[b)]	Additive	XIII Yield (%)	Rel. rate
1	62 mg	—	24	1.0
2	62 mg	benzophenone (1.95 g)	15	0.61
3	62 mg	acetophenone (1.30 g)	10	0.41

a) Done with a merry-go-round apparatus using a high-pressure mercury arc lamp.

b) Diluted to 20 ml with benzene.

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*[2] It is known that IIIb (*cis*) is easily converted to IIIa (*trans*) by a mild treatment with a base.[10)]

10) T. Matsuura and K. Ogura, *ibid.*, **89**, 3850 (1967).

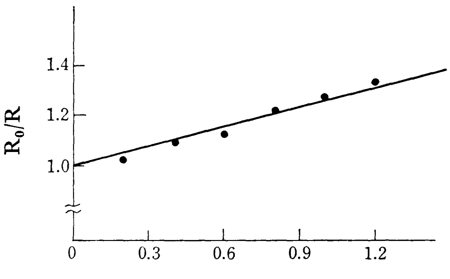

Fig. 1. Photolysis of VII in benzene.
R=the formation rate of XIII
R_0=R in the absence of piperylene

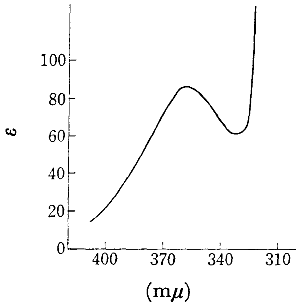

Fig. 2. *n*-π* absorption of VII in cyclohexane.

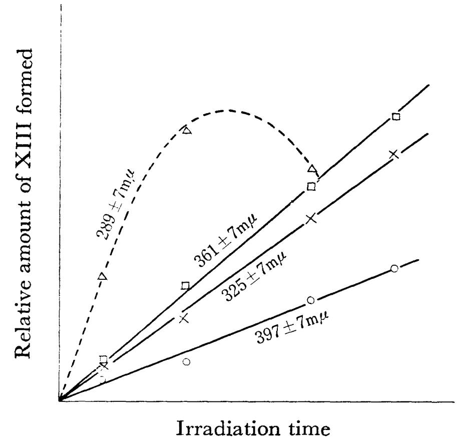

Fig. 3. Photolysis of VII in cyclohexane with selected lights.

solvents with a high-pressure mercury arc lamp (Pyrex filter) gave an orange crystalline product XIII in yields of 76% in petroleum ether, 78% in benzene, 36% in methanol, 33% in acetic acid-ethanol - water (2 : 2 : 1) and 62% in *N*,*N*-dimethylformamide. The NMR spectrum of XIII showed four singlets at τ 8.77 (9H), 8.85 (9H), 8.90 and 3.71 (1H). The product XIII exhibited UV bands at 404 and 262 mμ and IR absorption at 1713 cm^{-1}, characteristic of a cyclopentadienone.[11] Reduction of XIII with zinc in acetic acid afforded cyclopentenones IIIa and IIIb.[10] This led us to assign structure XIII for the orange product.

Since the formation of XIII was sensitized by benzophenone and acetophenone (Table 1) and quenched by piperylene as shown in Fig. 1 (Stern-Volmer plot), it is concluded that XIII is formed *via* the triplet state of VII. The *n*-π* absorption of VII in cyclohexane showed its maximum at 360 mμ as shown in Fig. 2. Photolysis of VII with the selected lights (see Experimental) was performed, the results of which are summarized in Fig. 3. It follows from the experiments with the selected lights that both the *n*-π* and π-π* excitations are responsible for the formation of XIII.

Photolysis of 4,6-Di-*t*-butyl-3-hydroxy-4-acetoxy-2,5-cyclohexadienone (XV). The starting material was prepared by partial acetylation of V with acetic anhydride and pyridine. Irradiation of XV in methanol with a high-pressure mercury arc lamp through a Pyrex filter yielded a methyl ester in 30% yield, for which we assigned structure XVI. The ester showed its IR bands at 1750 (vinyl acetate), 1713 (ester) and 1680 cm^{-1}. In the NMR spectrum, five singlets appeared at τ 6.29 (3H, $COOCH_3$), 6.48 (2H, $-CH_2-$), 7.80 (3H, $=C-OCO-CH_3$), 8.93 (9H, =C-*t*-Bu)[10] and 9.05 (9H, >C-*t*-Bu),[10] and two doublets at τ 4.81 (1H, *J*=11 Hz) and 7.03 (1H, *J*=11 Hz) indicating the presence of a >CH–CH= group. These data are in accord with structure XVI. The formation of XVI can be explained by the addition of methanol to a ketene intermediate XVII which was produced by the photochemical ring fission from a tautomeric form of 2,4-cyclohexadienone (XVb).*[3] Photolysis of XV in *N*,*N*-dimethylformamide or benzene gave a complex mixture of products.

Mechanistic Consideration. The photochemical formation of XI from VI in methanol can be explained by methanol addition to 2-cyclopentenone IX. Considering the facts that XI was not formed by the photolysis of IXa in methanol and that a larger coupling constant (7 Hz) was observed*[4] between the C-5 and C-4 protons in XI, it is reasonable to assume that XI is formed by the addition of methanol to *cis*-2-cyclopentenone IXb. However, we cannot distinguish the two following possibilities; *viz.*, methanol addition to IXb is easier than to IXa because of (1) the presence of a less-hindered site in IXb and (2) the decrease of the steric repulsion between the *t*-butyl and the pivaloyl groups by the

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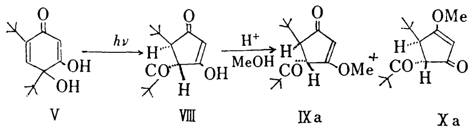
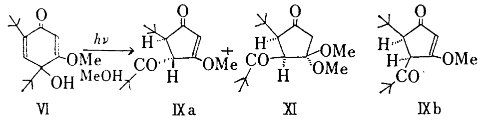
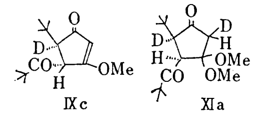
[11] E. N. Garbisch, Jr., and R. F. Sprecher, *J. Amer. Chem. Soc.*, **88**, 3433 (1966); **88**, 3434 (1966) and the references cited therein.

*[3] Although it was reported[8] that only one tautomeric form V is predominant in solution, the UV spectrum of XV in ethanol showed two absorption bands at 285 and 249 mμ indicating the presence of, at least, two tautomeric forms, one of which might be XVb.

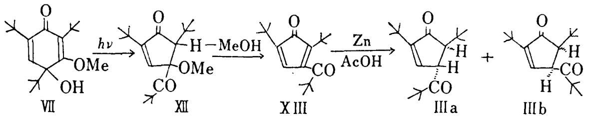
*[4] *Cf.* The coupling constant between the C-4 and C-5 protons in IIIa is 2 Hz and that in IIIb 5 Hz.[10]

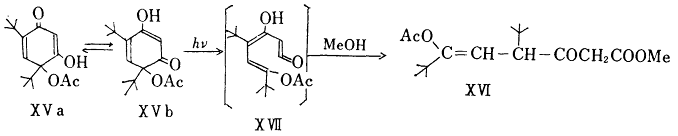


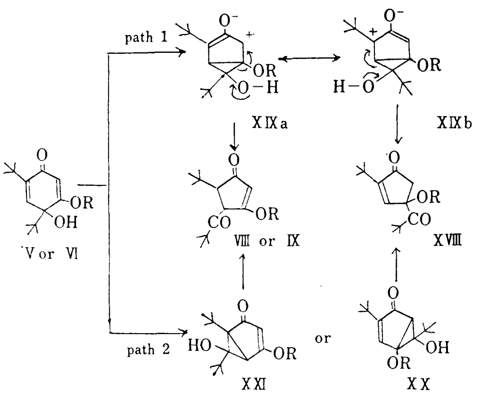




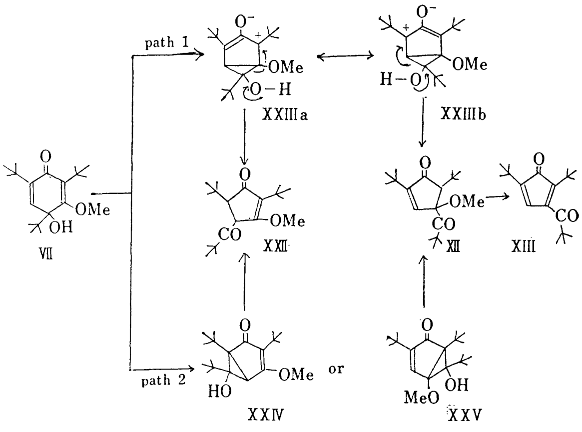
$\mathrm{VI} \xrightarrow[\mathrm{DMF}]{h\nu} \mathrm{IXa} + \mathrm{VIII}$







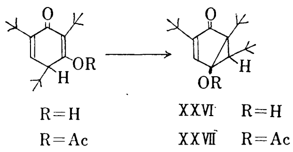
Scheme 2



Scheme 3

transformation of IXb in to XI. Formation of VIII on photolysis of VI in *N*,*N*-dimethylformamide can be also attributed to the addition of water to IXb followed by the elimination of methanol. It is probable that the formation of cyclopentadienone XIII arises from elimination of a methanol molecule from an intermediate XII, which is the product expected from the known transformation of 4-hydroxy-2,5-cyclohexadienones (Scheme 1).

For the formation of VIII from V, IX from VI and XIII from VII, two reaction routes, "path 1" and "path 2", as shown in Schemes 2 and 3 can be written. In the photochemical reactions of V and VI, we cannot explain the predominant formation of VIII and IX, respectively, by the "path 1" mechanism, because it appears reasonable that the resonance structure XIXb is more stabilized by the inductive effect of a *t*-butyl group than XIXa.



We cannot expect a large enough difference between the stabilities of XXIIIa and XXIIIb to control the reaction courses, XXIIIa→XXII and XXIIIb →XII, and the photochemical formation of XXIV from VII has an analogy in the photochemical reactions of 2,4,6-tri-*t*-butyl-3-hydroxy-2,5-cyclohexadienone6) and 2,4,6-tri-*t*-butyl-3-acetoxy-2,5-cyclohexadienone6) which were photochemically isomerized to form the corresponding lumiketones (XXVI and XXVII). Therefore, the "path 2" mechanism seems preferable in the photochemical reaction of VII.

Experimental

Photolysis of 2,4-Di-*t*-butyl-4,5-dihydroxy-2,5-cyclohexadienone (V). *(a) In Methanol.* A solution containing 4.00 g of V8) in 500 m*l* of methanol was irradiated for 3.5 hr with a 450-W high-pressure mercury arc lamp (Ushio UM 450) surrounded by a Pyrex jacket under bubbling nitrogen. After removal of the solvent under reduced pressure, the residue was crystallized from petroleum ether to give 2.52 g of pale yellow crystals, which, by recrystallization from benzene-petroleum ether afforded *β*-diketone VIII as colorless crystals, mp 188—189°C: $\lambda_{\text{max}}^{\text{cyclohexane}}$ 245 mμ (log ε 4.24); $\lambda_{\text{max}}^{\text{EtOH}}$ 248.5 mμ (log ε 4.10); $\lambda_{\text{max}}^{\text{EtOH-OH}^-}$ 265 mμ (log ε 4.25); $\nu_{\text{max}}^{\text{KBr}}$ 3500—2200, 2100—1750, 1705 and 1675—1400 cm^{-1}; the NMR spectrum: τ^{CDCl_3} 1.45 (1H, singlet), 4.91 (1H, singlet), 5.80 (1H, doublet, *J*=2 Hz), 7.20 (1H, doublet, *J*=2 Hz), 8.74 (9H, singlet) and 9.00 (9H, singlet).

Found: C, 70.31; H, 9.61%. Calcd for $C_{14}H_{22}O_8$: C, 70.55; H, 9.31%. The mother liquor was evaporated and the residue was chromatographed on 60 g of silica gel. Elution with 300 m*l* of benzene and then with 800 m*l* of chloroform gave 991 mg of a pale yellow oil which was not further investigated. Elution with 100 m*l* of ether afforded 990 mg of semicrystals which, by recrystallization from benzene - petroleum ether yielded 205 mg of colorless crystals. These crystals were identified as *β*-diketone VIII (by IR). Total yield of VIII amounted to 68%.

(b) In Petroleum Ether. A suspension containing 1.00 g of V in 200 m*l* of petroleum ether was photolyzed for 10.5 hr with a 100-W high-pressure mercury arc lamp (Pyrex filter) under bubbling nitrogen. The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on 40 g of silica gel. Elution with 450 m*l* of petroleum ether - benzene (1 : 1), 200 m*l* of benzene, 200 m*l* of chloroform and 90 m*l* of chloroform - acetone (19 : 1) gave 311 mg of a yellow oil containing a small amount of crystals which was not further investigated. Further elution with 100 m*l* of acetone - chloroform (1 : 9) afforded 616 mg of yellow crystals, which, on washing with petroleum ether and recrystallization from benzene, yielded colorless crystals, mp 185—187°C. These crystals were identified as *β*-diketone VIII (by IR and mixture mp).

(c) In an Alkaline Solution. A solution containing 1.00 g of V and 2.00 g of potassium hydroxide in 200 m*l* of water was irradiated for 10.5 hr under the same conditions as mentioned above. The reaction mixture was acidified with concentrated hydrochloric acid and extracted with three 150-m*l* portions of ether. After washing with water and drying on anhydrous sodium sulfate, the ethereal layer was evaporated under reduced pressure. Recrystallization of the residue from petroleum ether gave 560 mg of pale yellow crystals, mp 187—188°C, which were identified as *β*-diketone (by IR and mixture mp).

Etherification of VIII. A solution containing 2.29 g of VIII in 30 m*l* of absolute methanol was saturated with hydrogen chloride and allowed to stand for 3 hr at room temperature. After removal of the solvent under reduced pressure, the residue was chromatographed on 80 g of silica gel. Elution with 500 m*l* of chloroform gave 17 mg of a pale yellow oil which was not further investigated. Further elution with 500 m*l* of chloroform afforded 517 mg of a pale brown oil which soon crystallized. It was purified by a short-path distillation (100°C/3 mmHg) to yield cyclopentenone Xa as colorless crystals, mp 35—36°C: $\lambda_{\text{max}}^{\text{EtOH}}$ 240 mμ (log ε 4.21); $\nu_{\text{max}}^{\text{KBr}}$ 1712, 1685 and 1596 cm^{-1}; the NMR spectrum: τ^{CDCl_3} 4.79 (1H, singlet), 5.84 (1H, doublet, *J*=2 Hz), 6.14 (3H, singlet), 6.99 (1H, *J*=2 Hz), 8.73 (9H, singlet) and 9.03 (9H, singlet).

Found: C, 71.11; H, 9.33%. Calcd for $C_{15}H_{24}O_3$: C, 71.39; H, 9.59%. Elution with 100 m*l* of chloroform gave 257 mg of a pale brown oil which was shown by TLC analysis to be a mixture of IXa and Xa. Continuous elution with 200 m*l* of chloroform afforded 638 mg of pale brown crystals, mp 56—59°C, which were identified as cyclopentenone IXa, the photolysis product of VI described below (by IR, VPC and mixture mp). Elution with 500 m*l* of chloroform yielded 118 mg of a pale brown oil which was not further investigated. Further elution with 300 m*l* of chloroform-acetone (9 : 1) gave 622 mg of colorless crystals which were identified as VII (by IR).

Photolysis of VI. *a) In Methanol.* A solution containing 500 mg of VI8) in 180 m*l* of methanol was irradiated for 6 hr with a 100-W high pressure mercury arc lamp (Pyrex filter) under bubbling nitrogen. After evaporation of the solvent under reduced pressure, the residue was chromatographed on 15 g of silica gel. Elution with 200 m*l* of benzene gave 57 mg of a pale yellow oil which was not further investigated. Further elution with 150 m*l* of benzene and 280 m*l* of chloroform yielded 143 mg of colorless crystals, which, on recrystallization from petroleum ether, afforded dimethoxycyclopentanone XI as colorless crystals, mp 97—98°C: $\nu_{\text{max}}^{\text{KBr}}$ 1748 and 1694 cm^{-1}; the NMR spectrum: τ^{CDCl_3} 5.80 (1H, doublet of doublet, *J*=1 and 7 Hz), 6.67 (3H, singlet), 6.83 (3H, singlet), 7.50 (3H, multiplet), 8.76 (9H, singlet) and 9.00 (9H, singlet).

Found: C, 67.35; H, 9.89%. Calcd for $C_{16}H_{28}O_4$: C, 67.57; H, 9.93%. Elution with 50 m*l* of chloroform gave 115 mg of a yellow oil which was shown by VPC analysis to contain mainly IXa. Continuous elution with 50 m*l* of chloroform afforded 114 mg of a yellow oil, which was purified by a preparative VPC and a short-path distillation (130°C/3 mmHg) to yield cyclopentenone IXa as colorless crystals, mp 57—61°C: $\lambda_{\text{max}}^{\text{EtOH}}$ 240 mμ (log ε 3.96); $\nu_{\text{max}}^{\text{KBr}}$ 1705, 1693 and 1627 cm^{-1}; the NMR spectrum: τ^{CDCl_3} 4.71 (1H, doublet, *J*=1 Hz), 5.83 (1H, quartet, *J*=1 and 2 Hz), 6.24 (3H, singlet), 7.56 (1H, doublet, *J*=2 Hz), 8.75 (9H, singlet) and 9.00 (9H, singlet).

Found: C, 71.69; H, 9.76%. Calcd for $C_{15}H_{24}O_3$:

C, 71.39; H, 9.59%.

b) In N,N-Dimethylformamide. A solution containing 500 mg of VI in 80 m*l* of *N*,*N*-dimethylformamide was irradiated for 6 hr under the same conditions as described in a). Ether (150 m*l*) was added into the reaction mixture, and then the solution was washed with water and dried on anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed on 10 g of silica gel. Elution with 225 m*l* of chloroform gave 164 mg of a pale yellow oil which was not further investigated. Further elution with 30 m*l* of chloroform afforded 174 mg of a pale brown oil which was re-chromatographed on 10 g of silica gel and yielded 99 mg of IXa (identified by IR and VPC). Elution with 100 m*l* of chloroform gave 43 mg of pale yellow crystals which were identified as V (by IR).

c) Quantitative Analysis by VPC. A Pyrex tube (10 mm diameter) containing 100 mg of VI and 5 m*l* of a solvent was externally irradiated with a 450-W high-pressure mercury arc lamp, after the atomosphere was replaced with nitrogen. The reaction mixture was analyzed by VPC (silicon DC 550, 1.5 m; column temperature, 210°C. carrier gas; helium, 1.5 kg/cm^2). The yields of IXa were 28% in *n*-hexane, 32% in benzene, 44% in *N*,*N*-dimethylformamide and 39% in methanol. The yield of XI in methanol was 32%.

Treatment of XI with a Base. Forty mg of XI was added to 3 m*l* of 1 N methanolic potassium hydroxide and the mixture was allowed to stand for 1 hr at room temperature. After addition of 100 m*l* of water, the reaction mixture was extracted with two 15-m*l* portions of ether. The ethereal layer was washed with water and dried on anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by a short-path distillation (95°C/3 mmHg) to yield 32 mg of colorless crystals, mp 55—61°C, which were identified as IXa (by IR, VPC and mixture mp).

Photolysis of VII. *a) In Methanol.* A solution containing 500 mg of VII[9] in 150 m*l* of methanol was irradiated for 1.5 hr with a 100-W high-pressure mercury arc lamp surrounded by a Pyrex jacket under bubbling nitrogen. After evaporation of the solvent under reduced pressure, the residue was chromatographed on 15 g of silica gel. Elution with 20 m*l* of petroleum ether - benzene (7 : 3) gave 8 mg of a yellow oil which was not further investigated. Further elution with 40 m*l* of the same solvent afforded 160 mg (36%) of orange crystals, which, on recrystallization from methanol, yielded cyclopentadienone XIII as orange crystals, mp 75—76°C: $\lambda_{\max}^{\text{KBr}}$ 404 (log ε 2.66) and 262 mμ(3.30); $\nu_{\max}^{\text{KBr}}$ 1713, 1683 and 1593 cm^{-1}; the NMR spectrum: τ^{CCl_4} 3.71 (1H, singlet), 8.77 (9H, singlet), 8.85 (9H, singlet) and 8.90 (9H, singlet); the mass spectrum: *m/e* 276 (parent peak).

Found: C, 77.22; H, 10.12%. Calcd for $C_{18}H_{28}O_2\cdot 1/4CH_3OH$: C, 77.06; H, 10.28%.

b) In Petroleum Ether. A solution containing 500 mg of VII in 150 m*l* of petroleum ether was irradiated for 1 hr and 50 min under the same conditions as described above. After removal of the solvent under reduced pressure, the residue was chromatographed on 15 g of silica gel. Elution with 10 m*l* of petroleum ether - benzene (7 : 3) gave 6 mg of a yellow oil which was not further investigated. Further elution with the same solvent afforded 340 mg (76%) of orange crystals, which were purified by recrystallization from methanol to yield 207 mg of orange crystals, mp 74—76°C. These crystals were identified as cyclopentadienone XIII (by IR).

c) In Benzene. A solution containing 1.10 g of VII in 180 m*l* of benzene was irradiated for 3 hr under the same conditions as mentioned in a). The reaction mixture was evaporated under reduced pressure and the residue was chromatographed on 30 g of silica gel. Elution with 20 m*l* of petroleum ether - benzene (7 : 3) gave 7 mg of a yellow oil which was not further investigated. Further elution with 110 m*l* of the same solvent afforded 765 mg (78%) of orange crystals which were identified as XIII (by IR).

d) In N,N-Dimethylformamide. A solution containing 500 mg of VII in 80 m*l* of *N*,*N*-dimethylformamide was irradiated for 1 hr under the same conditions as described above. Ether (150 m*l*) was added to the reaction mixture and the ethereal solution was washed with water. After drying on anhydrous sodium sulfate and evaporating the solvent under reduced pressure, the residue was chromatographed on 20 g of silica gel. Elution with petroleum ether - benzene (1 : 1) gave 279 mg (62%) of orange crystals which were identified as XIII (by IR).

e) In Acetic Acid - Ethanol - Water. A solution containing 500 mg of VII in 80 m*l* of acetic acid - ethanol - water (2 : 2 : 1) was photolyzed for 1 hr under the same conditions as mentioned above. After ether (300 m*l*) was added, the reaction mixture was washed with water and then with aqueous bicarbonate solution. After being dried on anhydrous sodium sulfate and the solvent evaporated under reduced pressure, the residue was chromatographed on 30 g of silica gel. Elution with 100 m*l* of petroleum ether - benzene (7 : 3) gave 19 mg of a yellow oil which was not further investigated. Further elution with 80 m*l* of the same solvent afforded 146 mg (33%) of orange crystals which were identified as XIII (by IR).

f) Quenching Experiment. Seven samples were prepared as shown in Table 2 and the atmospheres were replaced with nitrogen. The samples were irradiated for 20 min with a 450-W high-pressure mercury arc lamp surrounded by a Pyrex water-cooled jaket using a merry-go-round apparatus.[12]

TABLE 2.

Exp. No.	VII (mg)	Solution A[a] (m*l*)	Benzene (m*l*)
1	62	—	20
2	62	1	19
3	62	2	18
4	62	3	17
5	62	4	16
6	62	5	15
7	62	6	14

a) Solution A was prepared by diluting 6.87 g of freshly distilled piperylene to 25 m*l* with benzene.

The yield of XIII in each sample was determined

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[12] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

by VPC analysis (silicon DC 550, 1.5 m; 210°C; Carrier gas; helium, 1.0 kg/cm^2). The results are summarized in Fig. 1.

g) With Selected Light. Selected light was obtained by a concave radiating monochromator (Japan Spectroscopic Co., Model CRM-50).[9,13] The experiment was carried out with a solution of 0.167 mg of VII in 3 m*l* of cyclohexane. The progress of the reaction was followed by the increase of a maximum at 406 mμ attributed to the absorption of XIII. The results are summarized in Fig. 2.

Reduction of XIII with Zinc in Acetic Acid. Zinc dust (6.0 g) was added to a solution of XIII (222 mg) in 20 m*l* of acetic acid. The reaction mixture was warmed at 50°C until the orange color disappeared. After removal of the deposited solid by filtration, 60 m*l* of water was added to the filtrate and the mixture was extracted with two 100-m*l* portions of ether. After the ethereal layer was washed with water and with aq. bicarbonate solution and dried on anhydrous sodium sulfate, the solvent was evaporated under reduced pressure. The residue was chromatographed on 7 g of silica gel. Elution with 30 m*l* of petroleum ether - benzene (1 : 1) gave 14 mg of a yellow oil which was not further investigated. Further elution with 45 m*l* of the same solvent afforded 73 mg of pale yellow crystals which, on recrystallization from methanol, yielded 13 mg of colorless crystals, mp 76—77.5°C, identified as IIIb[10] (by IR). Elution with 175 m*l* of petroleum ether - benzene (1 : 1) gave 48 mg of pale yellow crystals, which was purified by recrystallization from methanol to yield 13 mg of colorless crystals, mp 75—78°C, identified as IIIa[10] (by IR and mixture mp).

Preparation of XV. A solution containing 4.00 g of V in 30 m*l* of acetic anhydride and 15 m*l* pyridine was allowed to stand overnight at room temperature. After 150 m*l* of ice was added, the deposited crystals were separated by filtration and purified by recrystallization from ether - petroleum ether to afford colorless crystals, mp 52—53°C (with very slow heating). The mp was raised by rapid heating to 82.5—84°C. This behavior of the mp may be due to thermal tautomerization of XV. ν_{max}^{KBr} 3500—2600, 1745, 1730, 1685, 1655, 1625, 1595 and 1555 cm^{-1}; $\nu_{max}^{CHCl_3}$ 1735, 1685 and 1740 (sh) cm^{-1}; λ_{max}^{EtOH} 285 (log ε 3.02) and 249 mμ (3.59); $\lambda_{max}^{cyclohexane}$ 251 mμ (3.51); the NMR spectrum: τ^{CDCl_3} 3.60 (1H, singlet), 6.50 (1H, doublet, J=21 Hz), 6.63 (1H, doublet, J=21 Hz), 7.91 (3H, singlet), 8.75 (9H, singlet) and 8.99 (9H, singlet).

Found: C, 64.03; H, 8.96%. Calcd for $C_{16}H_{24}O_4\cdot H_2O$: C, 64.40; H, 8.78%.

Photolysis of XV. A solution containing 530 mg of XV in 170 m*l* of methanol was irradiated for 10 hr with a 100-W high-pressure mercury arc lamp (Pyrex filter) under bubbling nitrogen. After removal of the solvent under reduced pressure, the residue was chromatographed on 20 g of silica gel. Elution with 180 m*l* of chloroform gave 155 mg of a pale yellow oil which was not further investigated. Further elution with 250 m*l* of chloroform afforded 176 mg (30%) of pale yellow crystals, which, on recrystallization from petroleum ether, gave ester XVI as colorless crystals, mp 52.5—53°C: ν_{max}^{KBr} 1750, 1712 and 1680 cm^{-1}; λ_{max}^{EtOH} 255 mμ (log ε 3.50); the NMR spectrum: τ^{CDCl_3} 4.81 (1H, J=11 Hz), 6.29 (3H, singlet), 6.48 (2H, singlet), 7.03 (1H, doublet, J=11 Hz), 7.80 (3H, singlet), 8.93 (9H, singlet) and 9.05 (9H, singlet).

Found: C, 65.25; H, 9.29%. Calcd for $C_{17}H_{28}O_5$: C, 65.36; H, 9.03%.

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13) Y. Yamada, H. Uda and K. Nakanishi, *Chem. Commun.*, **1966**, 403.