

of **7** collected by preparative glpc under the conditions described above showed mp 95–98°; a mixture melting point with an authentic sample of **7**,^{1b} mp 95–98°, showed no depression, mp 95–98°; peak 3 (76%), retention time 14 min 50 sec, bicyclo-[5.1.1]non-2-en-9-one (**8**) (a sample of **8** collected by preparative glpc under the above conditions showed mp 74–75.5°; a mixture

melting point with a sample of starting **8**, mp 74–75.5°, showed no depression, mp 74–75.5°).

Acknowledgments. We are especially grateful to Dr. C. D. Broaddus for his collaboration in the metalation of cyclooctene.

Photoinduced Reactions. VI. The Photochemical Formation of the Ketone Tautomer of a Phenol from 2,4,6-Tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone^{1,2}

Teruo Matsuura and Katsuyuki Ogura

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. Received February 13, 1967

Abstract: A reinvestigation of the photochemical transformation of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (**I**) to an isomeric photoketone and a photophenol, to which structures **II** and **IIIa** had been previously assigned, respectively, was carried out. The structure of the photoketone was revised to **IV** which is the ketone tautomer of a phenol **VIb** derived from **IV**. Structure **IIIa** for the photophenol was confirmed. A lumiketone **II**, which was shown to be an intermediate leading onward to the photoketone and the photophenol, was also isolated. Evidence is reported for the $n\text{--}\pi^*$ excitation in the primary process of the reaction.

In a previous publication³ we reported that irradiation of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (**I**) in methanol or ether with a low-pressure mercury lamp give a photoketone, $\text{C}_{19}\text{H}_{32}\text{O}_2$, isomeric to **I**, and a photophenol, $\text{C}_{15}\text{H}_{24}\text{O}_2$, in low yields, along with a trace of 2,4,6-tri-*t*-butylphenol, and structures **II** and **IIIa** were assigned, respectively. In the present paper we wish to report the results obtained from the reinvestigation of this reaction; *i.e.*, the photoketone has the revised structure **IV** which is the ketone tautomer of a phenol **VIb**.

Irradiation of **I** in various organic solvents with a high-pressure mercury lamp (Pyrex filter) yielded a mixture of the photoketone⁴ and the photophenol in high yields. These results are summarized in Table I. It should be noted that the ratio of the photophenol to the photoketone decreases with the increase of the polarity of the solvents. The role of the solvent in this reaction will be discussed later.

The structure of the photophenol which had been previously assigned as **IIIa** was strongly supported by nmr analysis of its methyl ether **IIIb**. In the nmr spectrum of **IIIb**, two *t*-butyl (τ 8.63), two methoxyl (τ 6.15), and two aromatic protons (τ 3.05) are magnetically equivalent. With other possible structures of 3,4- and 5,6-di-*t*-butylguaiacols³ (**IXa** and **IXb**), it would be difficult to explain such a magnetic equivalence.

Pyrolysis or acid-catalyzed reaction of the photoketone resulted in the elimination of a *t*-butyl group to

Table I. The Yields of Photophenol **IIIa** and Photoketone **IV** on Irradiation of **I** in Various Solvents

Expt no.	Solvent	Yields, % ^c		
		IIIa	IV	IIIa:IV
1	Petroleum ether ^a	41	51	0.83
2	Ether ^a	35	46	0.75
3	Benzene ^a	38	53	0.72
4	Pyridine ^a	35	56	0.64
5	Ethyl acetate ^a	33	53	0.62
6	N,N-Dimethylformamide ^a	18	81	0.22
7	Benzene-methanol (1:1) ^a	9	80	0.11
8	Methanol ^a	2	62	0.03
9	Ether ^b	28	29 ^d	...
10	Methanol ^b	3	29 ^d	...

^a With a high-pressure mercury lamp using a Pyrex filter. ^b With a low-pressure mercury lamp using a Vycor filter. ^c The yields were based on the consumed **I** and were estimated by vpc analysis (see Experimental Section). ^d 2,4,6-Tri-*t*-butylphenol was formed in 3–4% yield.

yield a crystalline phenol **Va** which, on methylation, gave 4,6-di-*t*-butylresorcinol dimethyl ether (**Vb**) (Scheme I).⁵ Treatment of the photoketone with sodium hydride in dimethyl sulfoxide or with sodium methoxide in methanol gave an anion **VIa**. Hydrolysis of **VIa** yielded a phenol **VIb**, which could not be isolated in a pure form, but was easily oxidized by air to a ketone hydroperoxide **VIII**. The nmr spectrum of phenol **VIb** shows six singlets at τ 3.02 (1 H, aromatic proton), 5.06 (1 H, phenolic hydroxyl), 6.43 (3 H, methoxyl), 8.45 (9 H, *t*-butyl), 8.58 (9 H, *t*-butyl), and 8.65 (9 H, *t*-butyl). Mild treatment of phenol **VIb** with hydrobromic acid-acetic acid (1:24) afforded **Va**. Methylation of anion **VIa** gave a tri-*t*-butyldimethoxybenzene, the structure of which can be assigned as either 2,4,6-**VIc** or 4,5,6-tri-*t*-butylresorcinol

(5) M. S. Carpenter, W. M. Easter, and T. F. Wood, *J. Org. Chem.*, **16**, 586 (1951).

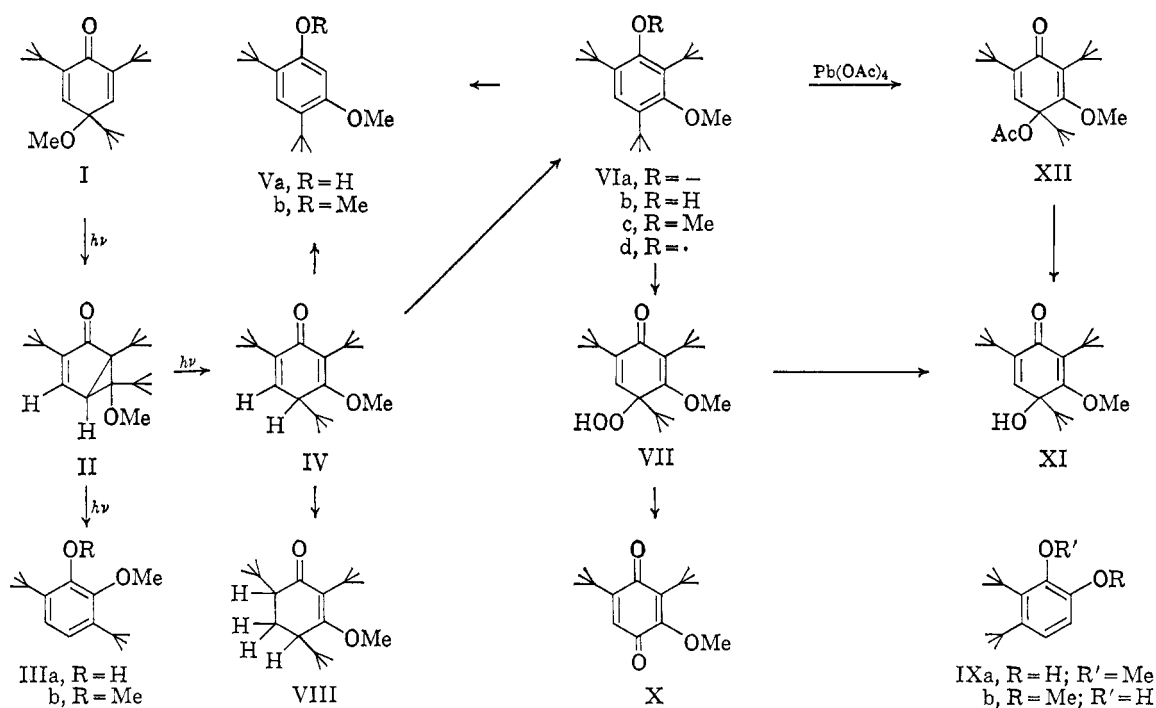
(1) Part V: T. Matsuura and K. Ogura, *Bull. Chem. Soc. Japan*, **40**, 945 (1967).

(2) This work was supported in part by U. S. Public Health Service Research Grant AM 07955, from the National Institute of Arthritis and Metabolic Diseases.

(3) T. Matsuura, *Bull. Chem. Soc. Japan*, **37**, 564 (1964).

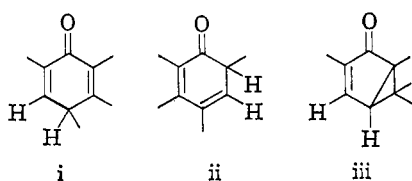
(4) Irradiation of the photoketone with a high-pressure mercury lamp for a longer time gave a new compound, the structure of which is being studied and will be reported in a forthcoming paper.

Scheme I



dimethyl ether from its nmr spectrum: τ 8.63 (18 H, singlet, two equivalent *t*-butyl groups), 8.52 (9 H, singlet, a *t*-butyl group), 6.35 (6 H, singlet, two equivalent methoxy groups), and 2.98 (1 H, singlet, an aromatic proton). The highly strained 4,5,6-substituted structure was excluded, since the ultraviolet spectrum ($\lambda_{\text{max}}^{\text{EtOH}}$ 280 m μ) showed only the absorption of usual aromatic compounds.⁶ Thus, the structures of phenol VIb and its methyl ether VIc were established.

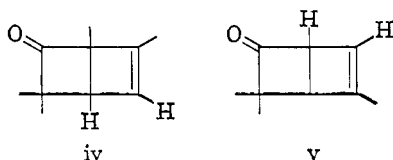
These results indicate that the photoketone has a six-membered carbocyclic ring. Furthermore, a pair of doublets (τ 3.67 and 7.03; J = 6 cps) in its nmr spectrum indicates the presence of a moiety $>\text{C}=\text{CHCH}<$. Therefore the ring system of the photoketone should be represented by formulas i, ii, or iii.⁷



Hydrogenation of the photoketone with 10% palladium on charcoal afforded a dihydro derivative VIII, whose absorption maxima ($\lambda_{\text{max}}^{\text{EtOH}}$ 255 m μ , $\nu_{\text{max}}^{\text{KBr}}$ 1680 and 1600 cm^{-1}) correspond to a 2,3-disubstituted 2-cyclohexenone. This and the infrared bands of the photo-

(6) For reports on the ultraviolet spectra of 1,2,3-tri-*t*-butylbenzene derivatives, which show an abnormal benzenoid absorption near 310 m μ see: (a) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3808 (1964); (b) H. G. Viehe, R. Merenyi, J. F. M. Oth, and P. Nalange, *Angew. Chem.*, 76, 888 (1964).

(7) Infrared bands ($\nu_{\text{max}}^{\text{KBr}}$ 1650, 1635, and 1600 cm^{-1}) of the photoketone eliminate other possible structures (iv and v) which must have the carbonyl bands in the 1780- cm^{-1} region.



ketone ($\nu_{\text{max}}^{\text{KBr}}$ 1650, 1635, and 1600 cm^{-1}) are not consistent with structure iii. Lumi products (as structure iii) reported previously show the carbonyl bands at a wavenumber higher than 1690 cm^{-1} .⁸ Structure iii cannot account for the formation of VIa and VIII from the photoketone. The ultraviolet spectrum [$\lambda_{\text{max}}^{\text{EtOH}}$ 248 (log ϵ 3.89) and 282 m μ (log ϵ 3.49)] excludes structure ii, which should have a maximum above 300 m μ .⁹ Structure IV which has moiety i was thus established. This product is the first example of the photochemical preparation of the ketone tautomer of a phenol.¹⁰

Phenol VIb was oxidized with alkaline ferricyanide to give a blue phenoxy radical VIc and was easily autoxidized to give ketone hydroperoxide VII, as mentioned before. Treatment of phenol VIb with lead tetraacetate gave an acetoxy ketone XII which, on alkaline hydrolysis, afforded a hydroxy ketone XI. The ketone hydroperoxide VII and hydroxy ketone XI were shown to be identical with the hydroperoxide, mp 146° dec, and its reduction product, mp 147–148.5°, respectively, which had been previously reported.³ The structures of these two compounds, for which bicyclo-[3.1.0]hex-3-en-2-one structures were previously assigned, were now revised as formulas VII and XI which are consistent with their spectral data. Pyrolysis of VII resulted in the loss of a *t*-butyl group to yield a di-*t*-butylmethoxy-*p*-benzoquinone, for which structure X was assigned.

Irradiation of I with the light at 397 ± 7 m μ followed by thin layer chromatography of the reaction mixture

(8) For more details on the spectral data of lumi products, see references cited in a review: K. Schaffner, *Advan. Photochem.*, 4, 81 (1966).

(9) This may also eliminate structure iii which should show a smaller extinction coefficient for the maximum in the region of 230–250 m μ . For references see footnote 8.

(10) For the preparations of ketone tautomers of phenols, see: (a) V. V. Ershov and A. A. Volo'Kin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 680 (1962); *Chem. Abstr.*, 57, 12337c (1962); (b) B. Miller, *J. Am. Chem. Soc.*, 87, 5515 (1965); (c) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, 22, 1439 (1957).

d. Isolation of Lumiketone II. A solution containing 1.70 g of I in 400 ml of petroleum ether (bp 30–60°) was irradiated externally with a 300-w tungsten lamp under bubbling nitrogen and cooled with water for 50 hr. The solvent was evaporated under reduced pressure, and the residue was chromatographed on 20 g of silica gel. Elution with 130 ml of petroleum ether–benzene (7:3) gave 762 mg of crystals which were shown to consist of the starting material, photoketone IV, and photophenol IIIa by tlc analysis. Further elution with 35 ml of petroleum ether–benzene (7:3) gave 54 mg of a yellow oil which was not further investigated. Continuing elution with 150 ml of petroleum ether–benzene (7:3) gave 303 mg (18%) of lumiketone II. Recrystallization from methanol followed by sublimation [78° (5 mm)] afforded colorless needles, mp 80.5–81°; $\nu_{\text{max}}^{\text{KBr}}$ 1692 cm^{-1} with a shoulder at 1705 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 248 $\text{m}\mu$ (log ϵ 3.51) and 265 $\text{m}\mu$ (log ϵ 3.49); nmr spectrum (CDCl_3), τ 3.13 (1 H, doublet, $J = 3.5$ cps), 6.73 (3 H singlet, methoxyl), 7.66 (1 H, doublet, $J = 3.5$ cps), 8.86 (9 H, singlet, *t*-butyl), and 8.88 (18 H, singlet, two *t*-butyl groups).

Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{O}_2$: C, 78.03; H, 11.03. Found: C, 77.69; H, 11.09.

Elution with 200 ml of chloroform gave 497 mg of a mixture of three products. These products were also obtained by mild acid hydrolysis of the lumiketone.¹⁷

Photolysis of Lumiketone II. A solution of 10 mg of lumiketone in 20 ml of benzene–methanol (1:1) was externally irradiated under conditions similar to those described in the photolysis of I. Evaporation of the solvent left yellow crystals, mp 67–82°, which were shown to consist of photoketone IV contaminated with a small amount of photophenol IIIa and a trace of other products, by tlc analysis (silica gel, petroleum ether containing a small amount of benzene) and by its infrared spectrum.

Irradiation of the lumiketone in benzene under similar conditions gave a yellow oil. This oil was shown by tlc analysis to be a mixture of photoketone IV, photophenol IIIa, and a trace of other compounds. The infrared spectrum of the mixture was almost identical with that of a mixture of photoketone IV and photophenol IIIa (53:38 molar ratio).

Methylation of Photophenol IIIa. Photophenol IIIa was methylated according to the method described by Miller and Margulies.¹⁸ A solution containing 472 mg of the photophenol in 15 ml of dry dimethyl sulfoxide was stirred with 100 mg of sodium hydride at room temperature under bubbling nitrogen for 0.5 hr. Then, 5 ml of methyl iodide was added, and the mixture was stirred for 30 min. After the addition of 10 ml of water, the mixture was extracted with petroleum ether (three 30-ml portions). The organic layer was evaporated under reduced pressure to give 485 mg (97%) of pale yellow crystals, mp 68–72°, which, by recrystallization from methanol, afforded the methyl ether IIIb as colorless crystals, mp 74–74.5°; $\lambda_{\text{max}}^{\text{EtOH}}$ 271 $\text{m}\mu$ (log ϵ 3.59); nmr spectrum (CDCl_3), τ 3.05 (2 H, singlet, two aromatic protons), 6.15 (6 H, singlet, two methoxyl groups), and 8.63 (18 H, singlet, two *t*-butyl groups).

Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2$: C, 76.75; H, 10.47. Found: C, 76.35; H, 10.49.

Acid Treatment of Photoketone IV. Photoketone IV (150 mg) was dissolved in 25 ml of a mixture of hydrobromic acid and acetic acid (1:24), and the solution was allowed to stand at room temperature for 1 hr. Dilution with 80 ml of water followed by standing in a refrigerator for 2 days deposited 110 mg (84%) of phenol Va as colorless needles, mp 108.5–109°; $\lambda_{\text{max}}^{\text{EtOH}}$ 282 $\text{m}\mu$ (log ϵ 3.61) with a shoulder at 287 $\text{m}\mu$ (log ϵ 3.56); nmr spectrum (CDCl_3), τ 2.82 (1 H, singlet, an aromatic proton), 3.75 (1 H, singlet, an aromatic proton), 5.22 (1 H, singlet, hydroxyl), 6.24 (3 H, singlet, methoxyl), 8.60 (9 H, singlet), and 8.65 (9 H, singlet). Methylation of phenol Va by a procedure similar to that for photophenol IIIa gave its methyl ether (Vb, 97%), mp 74.5–75° (lit.⁶ mp 75°); $\lambda_{\text{max}}^{\text{EtOH}}$ 277.5 $\text{m}\mu$ (log ϵ 3.78) with a shoulder at 285.5 $\text{m}\mu$ (log ϵ 3.75); nmr spectrum (CDCl_3), τ 2.80 (1 H, singlet, an aromatic proton), 3.51 (1 H, singlet, an aromatic proton), 6.16 (6 H, singlet, two methoxyl groups), and 8.64 (18 H, singlet, two *t*-butyl groups).

This compound was identified as 4,6-di-*t*-butylresorcinol dimethyl ether by a direct comparison of its infrared spectrum with that of an authentic specimen⁶ and mixture melting point determination.

Pyrolysis of Photoketone IV. Distillation of 100 mg of photoketone at 240° gave 73 mg of a yellow oil, which crystallized on standing. Recrystallization from petroleum ether gave 9 mg of colorless crystals, mp 106–107.5°. The product was identical

with phenol Va obtained by acid treatment of IV (by infrared spectrum and mixture melting point).

Hydrogenation of Photoketone IV. A solution of 256 mg of the photoketone in 30 ml of ethyl acetate was shaken with 450 mg of 10% palladium-on-charcoal catalyst at room temperature under an atmosphere of hydrogen until hydrogen uptake ceased (4.5 hr). The catalyst was filtered off, and the filtrate was evaporated to leave 254 mg of a pale yellow solid, mp 60–70°. Recrystallization from methanol gave 158 mg of the dihydropotoketone VIII, mp 80–81°; $\nu_{\text{max}}^{\text{KBr}}$ 1680 and 1600 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 255 $\text{m}\mu$ (log ϵ 3.85); nmr spectrum (CDCl_3), τ 6.50 (3 H, singlet, a methoxyl), 7.3–8.75 (4 H, multiplet), 8.78 (9 H, singlet), 8.98 (9 H, singlet), and 9.09 (9 H, singlet).

Anal. Calcd for $\text{C}_{19}\text{H}_{34}\text{O}_2$: C, 77.49; H, 11.64. Found: C, 77.09; H, 11.70.

Formation of Phenol VIb from Photoketone IV. a. A solution of 292 mg of the photoketone in 15 ml of dry dimethyl sulfoxide was stirred with 100 mg of sodium hydride at room temperature under bubbling nitrogen for 1 hr. After the addition of 30 ml of water, the solution was extracted with petroleum ether (three 50-ml portions). Evaporation of the organic layer under reduced pressure gave 294 mg of pale yellow crystals, mp 118–121°. Recrystallization from methanol gave phenol VIb, mp 125–127°; $\nu_{\text{max}}^{\text{KBr}}$ 3600 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 285 $\text{m}\mu$ (log ϵ 3.39); nmr spectrum (CDCl_3), τ 3.02 (1 H, singlet), 5.06 (1 H, singlet), 6.43 (3 H, singlet), 8.45 (9 H, singlet), 8.58 (9 H, singlet), and 8.65 (9 H, singlet). However, the nmr spectrum of phenol VIb showed that it was contaminated with the ketone hydroperoxide VIII (see below).

b. A solution containing 1.00 g of the photoketone and 1.04 g of sodium methoxide in 25 ml of methanol was allowed to stand at room temperature under nitrogen for 3 hr. Addition of 30 ml of water gave 963 mg of yellow crystals, mp 120–124°, which were identical with phenol VIb obtained above (by infrared spectrum).

Methylation of Phenolate VIa. A solution of phenolate VIa in dimethyl sulfoxide was prepared from 400 mg of photoketone IV as described above. Methyl iodide (3 ml) was added, and the solution was stirred for 1 hr. Addition of 30 ml of water deposited 352 mg (84%) of pale yellow crystals, mp 112–113°. Recrystallization from methanol afforded 2,4,6-tri-*t*-butylresorcinol dimethyl ether (VIc) as colorless plates, mp 115.5–116°; $\lambda_{\text{max}}^{\text{EtOH}}$ 280 $\text{m}\mu$ (log ϵ 3.50); nmr spectrum (CDCl_3), τ 2.98 (1 H, singlet), 6.35 (6 H, singlet), 8.52 (9 H, singlet), and 8.63 (18 H, singlet).

Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2$: C, 78.24; H, 11.20. Found: C, 78.38; H, 11.18.

Acid Treatment of Phenol VIb. Ten drops of concentrated hydrobromic acid was added to a solution containing 105 mg of phenol VIb in 15 ml of acetic acid, and the solution was allowed to stand at room temperature for 1 day. Addition of 30 ml of water deposited 67 mg of crystals. Recrystallization from petroleum ether afforded 40 mg of colorless needles, mp 108.5–109°. These crystals were identical with phenol Va (by infrared spectrum and mixture melting point).

Formation of Ketone Hydroperoxide VII. A solution of 210 mg of phenol VIb in 20 ml of methanol was refluxed for 9 hr and then was evaporated under reduced pressure to leave a solid. Recrystallization from petroleum ether afforded 75 mg of hydroperoxide VII as pale yellow crystals, mp 143–144° dec. This compound was identical with the hydroperoxide, mp 146° dec, which had been obtained previously³ (by infrared spectrum).

Pyrolysis of Hydroperoxide VII. Distillation of 100 mg of hydroperoxide VII at 250° gave 70 mg of a brown oil. This oil (55 mg) was chromatographed on 10 g of silica gel. Elution with 30 ml of petroleum ether–benzene (1:1) gave 9 mg of an oil which was not further investigated. Further elution with 35 ml of petroleum ether–benzene (1:1) gave 25 mg of yellow crystals, mp 42–44°. Recrystallization from methanol afforded quinone X as yellow plates, mp 47–47.5°; $\nu_{\text{max}}^{\text{KBr}}$ 1658 and 1580 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 262 $\text{m}\mu$ (log ϵ 4.02) and 360 $\text{m}\mu$ (log ϵ 2.52); nmr spectrum (CDCl_3), τ 3.97 (1 H, singlet), 6.27 (3 H, singlet), 8.71 (9 H, singlet), and 8.76 (9 H, singlet).

Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$: C, 71.97; H, 8.86. Found: C, 71.79; H, 8.96.

Formation of Hydroxy Ketone XI via Acetoxy Ketone X. A solution of 885 mg of phenol VIb in 100 ml of benzene was stirred with 2.00 g of lead tetraacetate at room temperature under bubbling nitrogen for 50 min. After the addition of 100 ml of water, the benzene layer was separated and washed with a saturated aqueous bicarbonate solution and then with water. The solution was evaporated under reduced pressure, and the residue was chromatographed on 30 g of silica gel. Elution with 100 ml of petroleum ether–ben-

(17) The structure of the products will be discussed in a forthcoming paper.

(18) B. Miller and H. Margulies, *J. Org. Chem.*, **30**, 3895 (1965).

zene(1:1) gave a yellow oil which was not further investigated. Further elution with 50 ml of petroleum ether-benzene (1:1) and then with 15 ml of chloroform gave 433 mg of acetoxy ketone XII as pale yellow crystals, mp 57–60°C; $\nu_{\text{max}}^{\text{KBr}}$ 1743, 1670, 1652, and 1590 cm^{-1} ; $\lambda_{\text{max}}^{\text{EtOH}}$ 247 (log ϵ 3.95) and 280 $\text{m}\mu$ (shoulder, log ϵ 3.43).

Anal. Calcd for $\text{C}_{21}\text{H}_{34}\text{O}_4$: C, 71.96; H, 9.78. Found: C, 72.07; H, 9.70.

This compound (30 mg) was dissolved in 0.2 *N* alcoholic potassium hydroxide and allowed to stand at room temperature overnight. Then, addition of 20 ml of water gave 16 mg of hydroxy ketone XI as colorless plates, mp 142.5–145°. These crystals were identical with the hydroxy ketone, mp 147–148.5°, which had been previously obtained from hydroperoxide VII by potassium iodide reduction.³

Photoinduced Reactions. VII. The Photochemical Formation and the Ground-State Reactions of Bicyclo[2.1.0]pentan-2-one¹

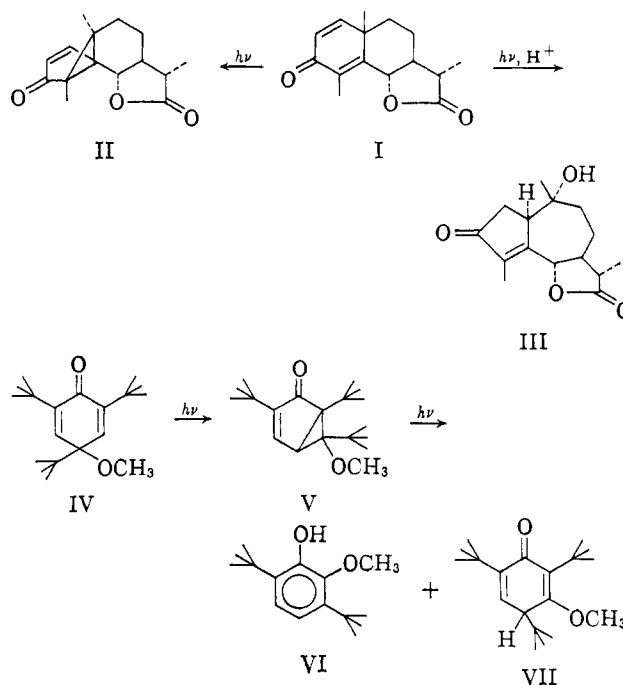
Teruo Matsuura and Katsuyuki Ogura

Contribution from the Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto, Japan. Received February 13, 1967

Abstract: Photolysis of 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (IV) in acetic acid-ethanol-water (2:2:1) afforded two isomeric cyclopentenones, VIII and IX, two isomeric bicyclo[2.1.0]pentan-2-ones, X and XI, and a lactone, XII. Irradiation of VIII and IX in the same media yielded X and XI, respectively, as the major product. On standing at room temperature, X slowly isomerized to give a *ca.* 1:1 mixture of XI and XII. Other ground-state reactions of these two bicyclopentanones leading to several types of products were also investigated. Mechanisms for the formation of these photoproducts are discussed.

The course of many photochemical reactions in solution depends upon the nature of the solvent. One of the earliest examples is the photochemical behavior of santonin (I). On irradiation in neutral media such as dioxane, I undergoes isomerization to lumisantonin (II).² However, in aqueous acidic media such as 45% acetic acid, the formation of lumisantonin is suppressed, and isophotosantonin lactone (III) is the predominant product.² This same hydroxy ketone III can also be nonphotochemically obtained by acid-catalyzed cleavage of lumisantonin (II) with 45% acetic acid.³ Although the photochemical reactions of cross-conjugated cyclohexadienone with a decalin skeleton related to santonin have received considerable mechanistic studies and discussions,^{2,3} relatively little attention has been devoted to the photochemical reactions of monocyclic 2,5-cyclohexadienones in acidic media.⁴ We have shown in a previous paper that, in various neutral solvents, 2,4,6-tri-*t*-butyl-4-methoxy-2,5-cyclohexadienone (IV) is photochemically converted to a photophenol VI and a photoketone VII *via* a lumiketone V.¹ In the present paper we report the photochemical reaction of IV in an acidic solution.

Irradiation of IV in acetic acid-ethanol-water (2:2:1) with a high-pressure mercury arc lamp (Pyrex filter) for a short period of time yielded, in addition to unreacted IV (16%), a mixture of products, from which five isomeric compounds, $\text{C}_{18}\text{H}_{30}\text{O}_2$, namely two stereoisomeric cyclopentenones, VIII (17%) and IX (11%), two stereoisomeric bicyclo[2.1.0]pentan-2-ones, X (18%) and XI (4%), and a lactone, XII (4%), were isolated



in crystalline forms. Prolonged irradiation of IV afforded X (30%) and XI (24%) in higher yield along with photoketone VII¹ (5%).

Structures VIII and IX for these two cyclopentenones were derived from their spectral and chemical properties and also by considering the fact that 2,6-di-*t*-butyl-4-hydroxy-4-phenyl-2,5-cyclohexadienone is photochemically converted to 2,5-di-*t*-butyl-4-benzoyl-2-cyclopentenone in aqueous media.⁵ An ultraviolet maximum at 241 $\text{m}\mu$ (ϵ 5660) of VIII suggests that VIII

(1) Part VI; T. Matsuura and K. Ogura, *J. Am. Chem. Soc.*, **89**, 3846 (1967).

(2) For reviews see: (a) H. E. Zimmerman, *Advan. Photochem.*, **1**, 183 (1963); (b) O. L. Chapman, *ibid.*, **1**, 323 (1963); (c) K. Schaffner, *ibid.*, **4**, 81 (1966); (d) N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1965, p 162.

(3) P. J. Kropp, *J. Am. Chem. Soc.*, **87**, 3914 (1965).

(4) H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966).

(5) E. R. Altwick and C. D. Cook, *J. Org. Chem.*, **29**, 3087 (1964). In this paper, they reported that only one stereoisomer of 2,5-di-*t*-butyl-4-benzoyl-2-cyclopentenones was isolated.