The Photochemical Reaction of 1,1,4,4-Tetramethyl-2,3-tetralindione with Hydrogen Donors

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The photochemical reaction of 1,1,4,4-tetramethyl-2,3-tetralindione, **1**, with hydrogen donors, such as xanthene and aldehyde, in the liquid phase has been investigated. When xanthene was selected as the hydrogen donor, the main products were the "1,2-adduct," photo-reduced α-keto alcohol, and 9,9′-bixanthenyl. The photolysis of **1** and an aldehyde gave the mixture of the "1,2-adduct" and the "1,4-adduct." However, in the reaction with isobutyraldehyde another type of "1,2-adduct" was obtained, *i.e.*, a combination product between the semidione radical and the isopropyl radical resulting from the decarbonylation of the isobutyryl radical, together with propene and carbon monoxide. The usual type of "1,2-adduct," the "1,4-adduct," and the photo-reduced product (α-keto alcohol) were the minor products in the reaction. It was also confirmed that the original "1,4-adduct" obtained from **1** and acetaldehyde rearranged photochemically to a different type of "1,2-adduct," but no reverse rearrangement was observed under the present conditions. The mechanisms of the reactions were discussed on the basis of product analysis and the examination of the reaction by means of CIDNP.

The photo-excited α-diketone abstract the hydrogen atom from the suitable hydrogen donor, giving the semidione radical.[1] In our previous study,[2] it was reported that 3,3-dimethyl-1,2-indandione also abstracts the hydrogen atom from aldehydes. However, no appreciable amounts of products were obtained in most cases because of the occurrence of a back reaction from the unstable intermediates produced by the attack of the acyl radicals on the aromatic ring of the conjugated semidione radical. This paper will deal with the photochemistry of 1,1,4,4-tetramethyl-2,3-tetralindione **1** as a non-enolizable α-diketone whose dicarbonyl group can not conjugate with aromatic π-electrons.

A few papers have appeared on the photochemical reaction of 1,1,4,4-tetramethyl-2,3-tetralindione, **1**, with some hydrogen donors.[3,4] However, the mechanism of the reaction has not yet been discussed. In order to understand the characteristics of the photochemical reaction, the mechanism of the reaction has now been investigated by means of the CIDNP technique.

Results and Discussion

In all of the photochemical reactions described below, a benzene solution of **1** and a hydrogen donor in a usual glass tube was irradiated from the outer side by means of a 300W high-pressure mercury arc lamp at room temperature.

The irradiation of **1** and xanthene gave a "1,2-adduct," 3-hydroxy-1,1,4,4-tetramethyl-3-xanthenyl-2-tetralone, **2**; as a photo-reduced product, 3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **3**, and 9,9′-bixanthenyl, **4**, in yields of 42, 50, and 45% respectively. As Fig. 1 shows, the polarized absorption signals which were

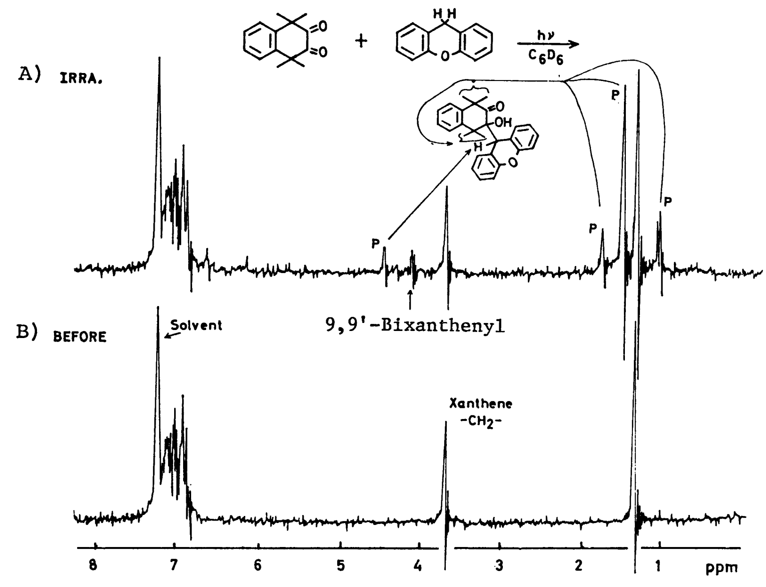
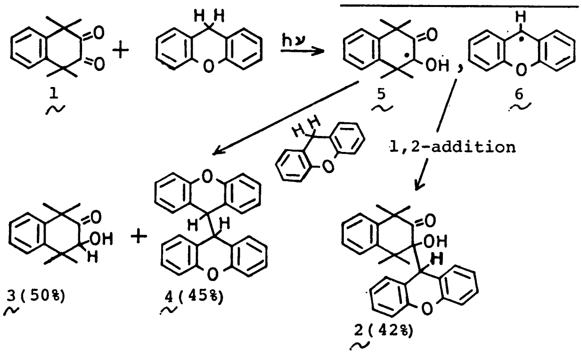


Fig. 1. A): PMR signals observed in the course of the photochemical reaction of 1,1,4,4-tetramethyl-2,3-tetralindione with xanthene during irradiation. P, polarized signals.
B): PMR signals observed before irradiation.

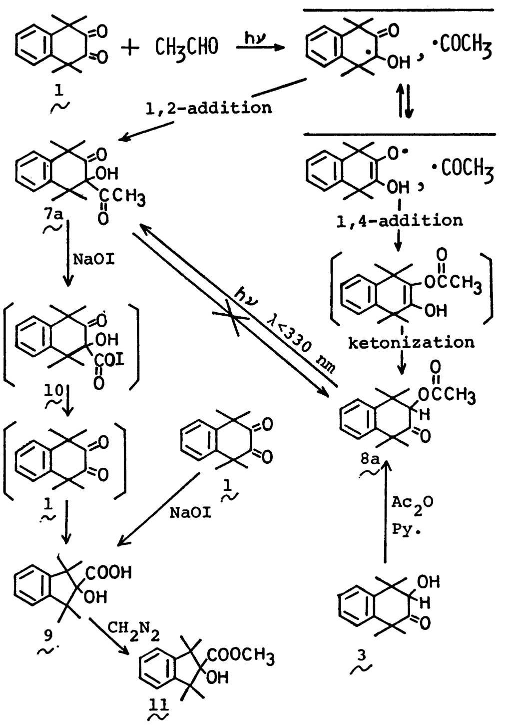
assigned to protons of the “1,2-adduct,” **2**, were observed in the course of the photochemical reaction. It can be explained by Kaptein's simple rule[5] that the “1,2-adduct,” **2**, results from the in-cage combination of the semidione radical, **5** ($g\simeq 2.0046$[6]), and the xanthenyl radical, **6** ($g\simeq 2.0057$[7]), from the triplet pair.[8] However, the semidione radical, **5**, and the xanthenyl radical, **6**, might partly escape from the cage and encounter another xanthene molecule, giving the reduced product, **3**, and 9,9′-bixanthenyl.



Scheme 1. Proton written with Gothic letter showed polarization.

When acetaldehyde was used as the hydrogen donor, a “1,2-adduct,” 3-acetyl-3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **7a**, and a ketonization product after 1,4-addition, 3-acetoxy-1,1,4,4-tetramethyl-2-tetralone, **8a**, were obtained in yields of 32 and 34% respectively. The “1,2-adduct,” **7a**, was identified by means of its spectral properties and by an iodoform test. The last procedure changed **7a** to 2-hydroxy-1,1,3,3-tetramethylindan-2-carboxylic acid, **9** (mp 181—184 °C[9]), quantitatively *via* the formation of 3-hydroxy-2-oxo-1,1,4,4-tetramethyl-2-tetralin-3-carboxylic acid, **10**, which was then easily decarboxylated to give **1**.[10] In fact, a benzilic-acid rearrangement converted **1** to **9** quantitatively under the same conditions. The product, **9**, was esterified with diazomethane, giving methyl 2-hydroxy-1,1,3,3-tetramethylindan-2-carboxylate, **11** (mp 77.5—78.5 °C[11]), quantitatively. The other product, **8a**, was identified by means of its spectral properties and by comparison with an authentic sample prepared by the acetylation of 3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **3**, in the presence of pyridine.

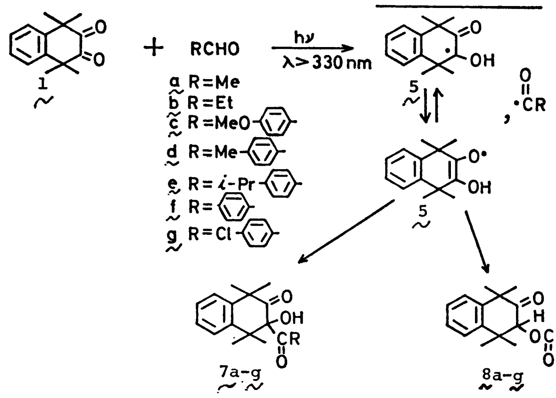
On irradiation for two days, 3-acetoxy-1,1,4,4-tetramethyl-2-tetralone, **8a**, was slowly changed to **7a** in a 17% yield, whereas no reverse conversion could be observed. A filter solution[12] was employed to cut the light of the wavelengths shorter than 330 nm. On irradiation with the light through the filter solution, **8a** remained unchanged. This is similar to the case with **7a**. Under the same conditions, **1** and acetaldehyde reacted photochemically to give **7a** and **8a** in yields of 34 and 41% respectively. In the course of the photochemical reaction of **1** and acetaldehyde, the CIDNP technique gave a only limited information because of the contingent coincidence of the acetyl protons of **7a** and **8a** in their chemical shifts in benzene-d_6. On irradiation with the light through the filter solution, **1** and other aldehydes, propionaldehyde, *p*-anisaldehyde, *p*-tolualdehyde, *p*-isopropylbenzaldehyde, benzaldehyde, and *p*-chlorobenzaldehyde, reacted photochemically, giving the corresponding “1,2-adducts,” 3-acyl-3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **7b**—**g**, and the respective “1,4-adducts,” 3-acyloxy-1,1,4,4-tetramethyl-2-tetralone, **8b**—**g**. The yields of **7a**—**g** and **8a**—**g** are



Scheme 2.

Table 1. Yield of 3-acyl-3-hydroxy-1,1,4,4-tetramethyl-2-tetralone and 3-acyloxy-1,1,4,4-tetramethyl-2-tetralone

	Yield (%) of **7**	Yield (%) of **8**
a	34	41
b	34	39
c	17	77
d	41	20
e	66	32
f	38	13
g	26	15



Scheme 3.

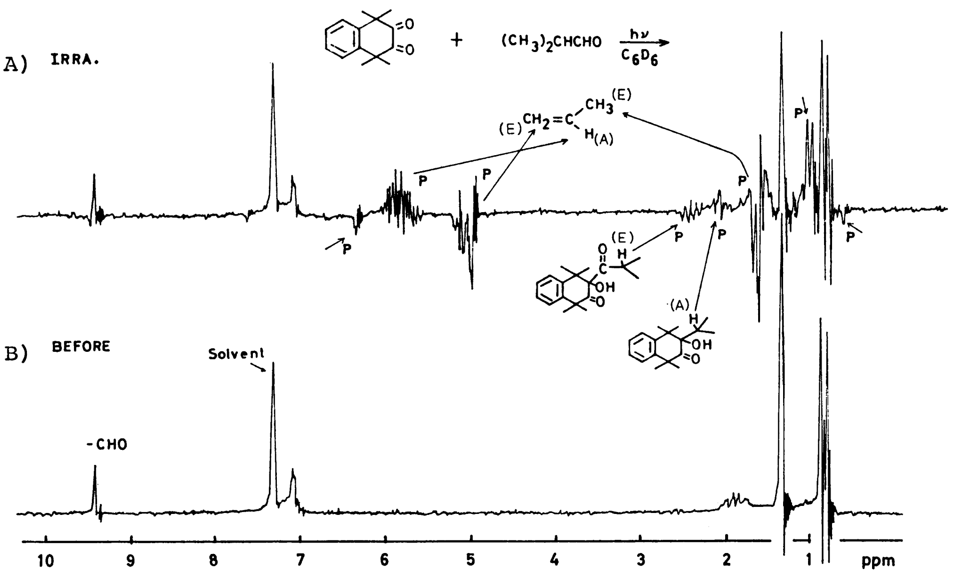
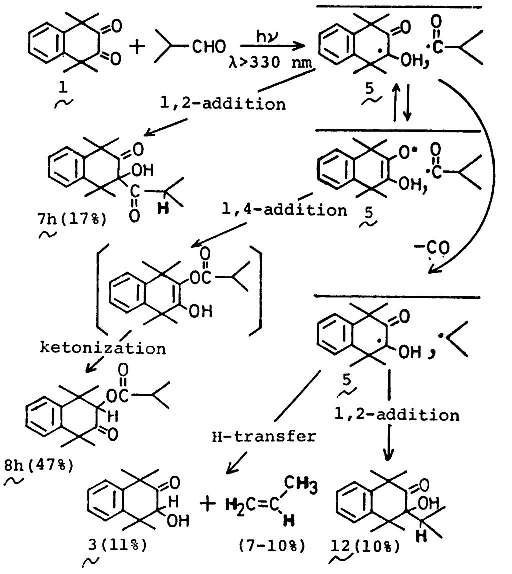


Fig. 2. A): PMR signals observed in the course of the photochemical reaction of 1,1,4,4-tetramethyl-2,3-tetralindione with isobutyraldehyde during irradiation. P, polarized signals.
B): PMR signals observed before irradiation.

summarized in Table 1. In conclusion, the photochemical reactions of **1** with aldehydes can be described as are shown in Scheme 3.

On the other hand, the irradiation of **1** with isobutyraldehyde gave a "1,2-adduct"; 3-hydroxy-3-isobutyryl-1,1,4,4-tetramethyl-2-tetralone, **7h** (17%), a "1,4-adduct"; 3-isobutyryloxy-1,1,4,4-tetramethyl-2-tetralone, **8h** (47%), a 1,2-addition product resulting from the decarbonylation, **12** (10%), a reduced product, **3** (11%), an oxidized product; α,α,α′,α′-tetramethyl-*o*-phenylenediacetic anhydride **13** (5%), and propene (7—10%), accompanied by the evolution of carbon monoxide (45—63%). Carbon monoxide was identified by the use of palladium chloride-test paper. The product, **13**, could be formed by the reaction of the semidione radical, **5**, with oxygen.[11] As Fig. 2 shows, in the course of the photochemical reaction of **1** with isobutyraldehyde, a multiplet emission signal was observed in the region corresponding to the methine proton of the "1,2-adduct,' **7h**. In addition, a multiplet absorption signal was observed corresponding to the methine proton of the other "1,2-adduct," **12**, accompanied by the other strongly polarized signals corresponding to the signals of propene;[13] these signals assigned by comparison with the signals of the synthesized authentic sample. Thus, the "1,2-adduct," **7h**, might result from the in-cage combination of the semidione radical, **5**, and the isobutyryl radical *via* the triplet pair. Similarly, **12** may be formed from the in-cage combination of the semidione radical, **5**, with the isopropyl radical ($g \cong 2.0032$[14]) *via* the triplet pair. Propene and the reduced product, **3**, might result from the dehydrogenation of the isopropyl radical by **5** *via* the triplet pair. The reaction mechanism is shown in Scheme 4. The decarbonylation and 1,2-addition reactions may be competitive, and the relative rates may depend on the stabilities of the related radicals.[15] Although the combination, disproportionation, or escape of the related radicals may occur competitively, depending on the stability of the radicals concerned, the steric repulsion between the related radicals in the radical pair could be another controlling factor. The combination of the semidione radical, **5**, with the isopropyl radical or xanthenyl radical would be more hindered sterically than that of **5** with acyl radicals. This is the reason for the formation of the reduction product, **3**, in the reactions with isobutyraldehyde and with xanthene.



Scheme 4. Protons written with Gothic letter showed polalization.

Experimental

The melting points described are uncorrected. The infrared spectra (KBr disk or a liquid film) were taken with a JASCO

IR-G spectrometer. The PMR spectra were measured with a JEOL PS-100 MHz spectrometer, using TMS as the internal standard. The ultraviolet and visible spectra were recorded by means of a Shimadzu UV-200 spectrometer. The CIDNP spectra were observed using a JEOL PS-100 MHz spectrometer, equipped with a modified NMR probe for irradiation.16)

Materials. 1,1,4,4-Tetramethyl-2,3-tetralindione, **1**, was prepared by the oxidation of 1,1,4,4-tetramethyl-2-tetralone with selenium dioxide17) and was purified by sublimation; mp 59—61 °C (lit,61—62 °C17)). IR(KBr): 1710 cm^{-1} (C=O). PMR (CCl$_4$): δ; 1.24 (s, 12H), 7.12 ppm (s, 4H). UV$_{max}$ (EtOH): 286 nm (ε: 443), 387 (10), 396 (15). The xanthene was commercially obtained and was purified by recrystallization from ethanol. The acetaldehyde was prepared by the depolymerization of paraldehyde. The other aldehydes were commercially obtained and were distilled before use.

General Procedure. **1** (0.5—1.0 mmol) and 2—6 equivalents of a hydrogen donor were dissolved in 20 ml of dry benzene, and then the solution was irradiated from the outer side by means of a 300W high-pressure mercury arc lamp through a water layer 5 cm thick or a filter solution 1 cm thick at room temperature. After the solution had become colorless, irradiation was stopped. After the removal of the solvent, the total product was separated by TLC, using a benzene and hexane mixture as the developing solvent. The filter solution used for light-cutting was an aqueous solution (50 ml) of sodium bromide (24.45 g) and lead nitrate (0.15 g).

Photochemical Reaction of 1 with Xanthene. A benzene solution of **1** (244 mg, 1.1 mmol) and two equivalents of xanthene was irradiated for about 5 h. 9,9′-Bixanthenyl, **4** (363 mg, 45%), 3-hydroxy-1,1,4,4-tetramethyl-3-xanthenyl-2-tetralone, **2** (486 mg, 42%), and 3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **3** (180 mg, 50%), were thus obtained. **2**; white plates; mp 149 °C. IR (KBr): 3450 (OH), 1695 cm^{-1} (C=O). PMR (CCl$_4$): δ; 0.75 (s, 3H), 0.94 (s, 3H), 1.48 (s, 3H), 1.84 (s, 3H), 3.02 (s, 1H; OH), 4.12 (s, 1H), 5.8—7.1 ppm (m, 12H). Found: C, 81.52; H, 6.64%. Calcd for $C_{27}H_{26}O_3$: C, 81.38; H, 6.58%. **3**; white crystals; mp 39.0—41.0 °C (lit, 40—42 °C3)). IR (KBr): 3450 (OH), 1710 cm^{-1} (C=O). PMR (CCl$_4$): δ; 0.87 (s, 3H), 1.40 (s, 3H), 1.44 (s, 3H), 1.49 (s, 3H), 3.52 (d, 1H; OH), 4.20 (d, 1H), 6.9—7.2 ppm (m, 4H). **4**; white crystals; mp 211 °C.

Photochemical Reaction of 1 with Acetaldehyde. A solution of **1** (82 mg, 0.4 mmol) and acetaldehyde (77 mg, 1.8 mmol) was irradiated for about 6 h. 3-Acetyl-3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **7a** (34 mg, 34%), and 3-acetoxy-1,1,4,4-tetramethyl-2-tetralone, **8a** (32 mg, 32%), were thus obtained. **7a**; white plates; mp 80.5—81.0 °C. IR (KBr): 3400 (OH), 1700 cm^{-1} (C=O). PMR (CCl$_4$): δ; 0.91 (s, 3H), 1.33 (s, 3H), 1.40 (s, 3H), 1.43 (s, 3H), 2.00 (s, 3H), 4.63 (s, 1H; OH), 6.9—7.1 ppm (m, 4H). UV$_{max}$ (EtOH): 315 nm (ε; 150). Found: C, 73.77; H, 7.77%. Calcd for $C_{16}H_{20}O_3$: C, 73.86; H, 7.76%. **8a**; white plates; mp 106.5—107.0 °C. IR (KBr): 1735, 1716 cm^{-1} (C=O). PMR (CCl$_4$): δ; 1.03 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 1.48 (s, 3H), 2.13 (s, 3H), 5.24 (s, 1H), 6.9—7.1 ppm (m. 4H). UV$_{max}$ (EtOH): 285 nm (ε: 38), 300 (23). Found: C, 73.69; H, 7.91%. Calcd for $C_{16}H_{20}O_3$: C, 73.86; H, 7.76%.

Iodoform Reaction of 7a. To a solution of iodine (77 mg) and sodium hydroxide (141 mg) in water (10 ml), we added a solution of **7a** (24 mg) in ether (3 ml). After stirring at room temperature for 24 h, the solution was acidified with hydrochloric acid and extracted with ether. The ethereal solution was dried over sodium sulfate and evaporated, giving white crystals of 2-hydroxy-1,1,3,3-tetramethylindan-2-carboxylic acid, **9** (21 mg); mp 181—184 °C (lit, 188—189 °C9)). IR(KBr): 3450 (OH), 1690 cm^{-1} (C=O). PMR (CDCl$_3$): δ; 1.34 (s, 6H), 1.68 (s, 6H), 7.0—7.4 ppm (m, 4H).

Esterification of 9 with Diazomethane. A ethereal solution of diazomethane was added to a solution of **9** (13 mg) in ether at room temperature. After the removal of the solvent, white crystals of methyl 2-hydroxy-1,1,3,3-tetramethylindan-2-carboxylate, **11** (14 mg), were obtained; mp 72.0—74.0 °C (lit, 77.5—78.5 °C11)). IR(KBr): 3450 (OH), 1705 cm^{-1} (C=O). PMR (CCl$_4$): δ; 1.16 (s, 6H), 1.30 (s, 6H), 3.52 (s, 3H), 6.9—7.1 ppm (m, 4H). Mass: *m/e*; 248 (M$^+$), 189 (M$^+$−COOCH$_3$, base), 171 (M$^+$−COOCH$_3$·H$_2$O).

Benzilic Acid Rearrangement of 1. **1** (22 mg) was converted to **9** (24 mg) under the conditions described in "*Iodoform Reaction of 7a.*"

Acetylation of 3. A mixture of **3** (26 mg), acetic anhydride (10 ml), and pyridine (10 ml) was warmed for 3 h at 80 °C. After the subsequent evaporation of the liquid phase, white crystals of **8a** (29 mg) were obtained; mp 107 °C.

Irradiation of 7a and 8a. The irradiation of a benzene solution of **8a** (13 mg) for 2 days gave a mixture of the starting material, **8a** (8 mg, 60%), and **7a** (2 mg, 17%). However, the irradiation of **7a** under the same conditions gave no reaction. On irradiation through the filter solution13) (transmitting the light ≥330 nm) for 4 days, **8a** remained unchanged. **7a** was also recovered unchanged.

Photochemical Reaction of 1 with Acetaldehyde with the Use of the Filter Solution. On irradiation through the filter solution, **1** (108 mg, 0.5 mmol) and acetaldehyde (75 mg, 1.7 mmol) reacted to give **7a** (96 mg, 34%) and **8a** (102 mg, 41%).

Photochemical Reaction of 1 with Propionaldehyde. A benzene solution of **1** (119 mg, 0.6 mmol) and propionaldehyde (166 mg, 2.9 mmol) was irradiated through the filter solution to give 3-hydroxy-3-propionyl-1,1,4,4-tetramethyl-2-tetralone, **7b** (52 mg, 34%), and 3-propionyloxy-1,1,4,4-tetramethyl-2-tetralone, **8b** (59 mg, 39%). **7b**; white plates; mp 116.0—118.0 °C. IR (KBr): 3400 (OH), 1695 cm^{-1} (C=O). PMR (CCl$_4$): δ; 0.84 (t, 3H), 0.92 (s, 3H), 1.31 (s, 3H), 1.36 (s, 3H), 1.44 (s, 3H), 2.24 (q, 2H), 4.64 (s, 1H; OH), 6.9—7.1 ppm (m, 4H). Found: C, 74.41; H, 7.82%. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%. **8b**; white plates; mp 67.0—68.0 °C. IR(KBr): 1745, 1725 cm^{-1} (C=O). PMR (CCl$_4$): δ; 1.07 (s, 3H), 1.24 (t, 3H), 1.40 (s, 3H), 1.48 (s, 3H), 1.53 (s, 3H), 2.49 (q, 2H), 5.36 (s, 1H), 7.0—7.4 ppm (m, 4H). Found: C, 74.13; H, 8.31%. Calcd for $C_{17}H_{22}O_3$: C, 74.42; H, 8.08%.

Photochemical Reaction of 1 with p-*Anisaldehyde.* A benzene solution of **1** (146 mg, 0.7 mmol) and *p*-anisaldehyde (341 mg, 2.5 mmol) was irradiated through the filter solution to give 3-hydroxy-3-*p*-methoxybenzoyl-1,1,4,4-tetramethyl-2-tetralone, **7c** (41 mg, 17%), and 3-*p*-methoxybenzoyloxy-1,1,4,4-tetramethyl-2-tetralone, **8c** (190 mg, 77%). **7c**; white needles; mp 153.5—154.5 °C. IR (KBr): 3350 (OH), 1703 cm^{-1} (C=O). PMR (CCl$_4$): δ; 0.96 (s, 3H), 1.23 (s, 3H), 1.52 (s, 3H), 1.57 (s, 3H), 3.77 (s, 3H), 4.64 (s, 1H; OH), 6.64—7.64 (dd, 4H), 6.9—7.1 ppm (m, 4H). Found: C, 74.69; H, 7.04%. Calcd for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86%. **8c**; white prisms; mp 132.5—133.0 °C. IR (KBr); 1735, 1705 cm^{-1} (C=O). PMR (CCl$_4$): δ; 1.16 (s, 3H), 1.40 (s, 3H), 1.52 (s, 3H), 1.56 (s, 3H), 3.76 (s, 3H), 5.52 (s, 1H), 6.74—7.86 (dd, 4H), 6.9—7.1 ppm (m, 4H). Found: C, 74.73; H, 6.87%. Calcd for $C_{22}H_{24}O_4$: C, 74.97; H, 6.86%.

Photochemical Reaction of 1 with p-*Tolualdehyde.* The irradiation of **1** (124 mg, 0.6 mmol) and *p*-tolualdehyde (321 mg, 2.7 mmol) in benzene by the use of the filter solution gave 3-hydroxy-3-*p*-toluoyl-1,1,4,4-tetramethyl-2-tetralone, **7d** (79 mg, 41%), and 3-*p*-toluoyloxy-1,1,4,4-tetramethyl-2-tetralone, **8d** (39 mg, 20%). **7d**; white needles; mp 171.5—173.0 °C.

IR (KBr): 3450 (OH), 1710, 1670 cm^{-1} (C=O). PMR (CCl_4): δ; 0.92 (s, 3H), 1.16 (s, 3H), 1.48 (s, 3H), 1.51 (s, 3H), 2.30 (s, 3H), 4.62 (s, 1H; OH), 6.8—7.5 ppm (m, 8H). Found: C, 78.25; H, 7.45%. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19%. **8d**; white prisms; mp 137.5—138.0 °C. IR (KBr): 1730, 1705 cm^{-1} (C=O). PMR (CCl_4): δ; 1.18 (s, 3H), 1.41 (s, 3H), 1.53 (s, 3H), 1.56 (s, 3H), 2.40 (s, 3H), 5.53 (s, 1H), 7.0—7.8 ppm (m, 8H). Found: C, 78.59; H, 7.36%. Calcd for $C_{22}H_{24}O_3$: C, 78.54; H, 7.19%.

Photochemical Reaction of 1 with p-*Isopropylbenzaldehyde.* A solution of **1** (134 mg, 0.6 mmol) and *p*-isopropylbenzaldehyde (332 mg, 2.0 mmol) in benzene was irradiated by the use of the filter solution to give 3-hydroxy-3-*p*-isopropylbenzoyl-1,1,4,4-tetramethyl-2-tetralone, **7e** (149 mg, 66%), and 3-*p*-isopropylbenzoyloxy-1,1,4,4-tetramethyl-2-tetralone, **8e** (71 mg, 32%). **7e**; white needles; mp 126.0—127.0 °C. IR (KBr): 3420 (OH), 1720, 1675 cm^{-1} (C=O). PMR (CCl_4): δ; 0.91 (s, 3H), 1.15 (s, 3H), 1.16 (s. 3H), 1.22 (s, 3H), 1.43 (d, 6H), 2.8 (m, 1H), 4.56 (s, 1H; OH), 6.9—7.4 ppm (m, 8H). Found: C, 79.14; H, 7.82%. Calcd for $C_{24}H_{28}O_3$: C, 79.07; H, 7.76%. **8e**; white prisms; mp 117.0—118.0 °C. IR (KBr): 1735, 1710 cm^{-1} (C=O). PMR (CCl_4): δ; 1.20 (s, 3H), 1.25 (s, 3H), 1.32 (s, 3H), 1.44 (s, 3H), 1.48 (d. 6H), 2.92 (m, 1H), 5.60 (s, 1H), 7.0—7.9 ppm (m, 8H). Found: C, 79.03; H, 7.98%. Calcd for $C_{24}H_{28}O_3$: C, 79.07; H, 7.76%.

Photochemical Reaction of 1 with Benzaldehyde. A benzene solution of **1** (131 mg, 0.6 mmol) and benzaldehyde (397 mg, 3.7 mmol) was irradiated by the use of the filter solution. The products were 3-benzoyl-3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **7f** (79 mg, 38%), and 3-benzoyloxy-1,1,4,4-tetramethyl-2-tetralone, **8f** (27 mg, 13%). **7f**; white needles; mp 169.0—171.0 °C. IR (KBr): 3400 (OH), 1710, 1670 cm^{-1} (C=O). PMR (CCl_4): δ; 0.92 (s, 2H), 1.19 (s, 3H), 1.50 (s, 6H), 4.64 (s, 1H; OH), 6.9—7.7 ppm (m, 9H). Found: C, 78.02; H, 6.78%. Calcd for $C_{21}H_{23}O_3$: C, 78.23; H, 6.88%. **8f**; white prisms; mp 134.5—135.5 °C. IR (KBr): 1735, 1710 cm^{-1} (C=O). PMR (CCl_4): δ; 1.22 (s, 2H), 1.45 (s, 2H), 1.58 (s, 3H), 1.61 (s, 3H), 5.70 (s, 1H), 7.2—8.2 ppm (m, 9H). Found: C, 78.01; H, 6.72%. Calcd for $C_{21}H_{22}O_3$: C, 78.23; H, 6.88%.

Photochemical Reaction of 1 with p-*Chlorobenzaldehyde.* A benzene solution of **1** (126 mg, 0.6 mmol) and *p*-chlorobenzaldehyde (396 mg, 3.7 mmol) was irradiated by the use of the filter solution to give 3-*p*-chlorobenzoyl-3-hydroxy-1,1,4,4-tetramethyl-2-tetralone, **7g** (53 mg, 26%), and 3-*p*-chlorobenzoyloxy-1,1,4,4-tetramethyl-2-tetralone, **8g** (32 mg, 15%). **7g**; white needles; mp 153.0—153.5 °C. IR (KBr): 3430 (OH), 1710, 1670 cm^{-1} (C=O). PMR (CCl_4): δ; 0.92 (s, 3H), 1.18 (s, 3H), 1.48 (s, 6H). 4.56 (s, 1H; OH), 6.9—7.5 ppm (m, 8H). Found: C, 70.38; H, 5.94; Cl, 9.85%. Calcd for $C_{21}H_{21}O_3Cl$: C, 70.67; H, 5.94; Cl, 9.93%. **8g**; white prisms; mp 164.0—164.5 °C. IR (KBr): 1735, 1710 cm^{-1} (C=O). PMR (CCl_4): δ; 1.16 (s, 3H), 1.38 (s, 3H), 1.50 (s, 5H), 1.52 (s, 3H), 5.44 (s, 1H), 6.9—7.1 (m, 4H), 7.2—7.8 ppm (AB-q, 4H). Found: C, 70.87; H, 6.24; Cl, 9.74%. Calcd for $C_{21}H_{21}O_3Cl$: C, 70.67; H, 5.94; Cl, 9.93%.

Photochemical Reaction of 1 with Isobutyraldehyde. The photolysis of **1** (187 mg, 0.9 mmol) and isobutyraldehyde (193 mg, 2.7 mmol) in benzene by the use of the filter solution gave a mixture of 3-hydroxy-3-isobutyryl-1,1,4,4-tetramethyl-2-tetralone, **7h** (49 mg, 17%), 3-isobutyryloxy-1,1,4,4-tetramethyl-2-tetralone, **8h** (127 mg, 47%), 3-hydroxy-3-isopropyl-1,1,4,4-tetramethyl-2-tetralone, **12** (20 mg, 10%), and the reduced product, **3** (22 mg, 11%), accompanied by the evolution of a gas (carbon monoxide) (49—63%), which was identified by means of palladium chloride-test paper; the color changed from yellow to brown. The yield of carbon monoxide was measured volumetrically. **7h**; white needles; mp 84.5—85.5 °C. IR (KBr): 3420 (OH), 1690 cm^{-1} (C=O). PMR (CCl_4): δ; 0.88 (d, 3H), 0.96 (s, 3H), 1.00 (d, 3H), 1.38 (s, 6H), 1.50 (s, 3H), 3.20 (m, 1H), 4.82 (s, 1H; 0H), 7.2—7.3 ppm (m, 4H). Found: C, 74.95; H, 8.54%. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39%. **8h**; colorless oil. IR (liq. film): 1740, 1730 cm^{-1} (C=O). PMR (CCl_4): δ; 1.08 (s, 2H), 1.22—1.24 (dd, 6H), 1.40 (s, 3H), 1.49 (s, 3H), 1.54 (s, 3H), 2.66 (m, 1H), 5.40 (s, 1H), 7.1—7.4 ppm (m, 4H). Mass: *m/e*; 288 (M^+). Found: C, 75.25; H, 8.48%. Calcd for $C_{18}H_{24}O_3$: C, 74.97; H, 8.39%. **12**; white crystals; mp 36.0—37.0 °C. IR (KBr); 3470, 3420 (OH), 1695 cm^{-1} (C=O). PMR (CCl_4): δ; 0.56 (d, 3H), 0.89 (d, 3H), 0.98 (s, 3H), 1.48 (s, 3H), 1.53 (s, 3H), 1.56 (s, 3H), 2.00 (m, 1H), 3.84 (s, 1H; OH), 7.1 ppm (m, 4H). Mass: *m/e*; 260 (M^+). Found: C, 78.27; H, 9.38%. Calcd for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29%.

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