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The Photolysis of 3,4-Bis(hydroxydiphenylmethyl)cyclobut-3-ene-1,2-dione and Related Compounds. The Formation of a New Bislactone, 4,4,8,8-Tetraphenyl-3,7-dioxabicyclo[3.3.0]oct-1(5)-ene-2,6-dione

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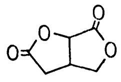
The photolysis of 3,4-bis(hydroxydiphenylmethyl)cyclobut-3-ene-1,2-dione (**1**) in benzene afforded 4,4,8,8-tetraphenyl-3,7-dioxabicyclo[3.3.0]octane-2,6-dione (**3**) in an 80% yield. The photolysis of **1** in MeOH afforded 4,4,8,8-tetraphenyl-3,7-dioxabicyclo[3.3.0]oct-1(5)-ene-2,6-dione (**4**), 4-methoxycarbonyl-3,3-diphenyl-5-diphenylmethylene-2-oxacyclopentan-1-one (**5**), and 4-carboxy-3,3-diphenyl-5-diphenylmethyl-2-oxacyclopent-4-en-1-one (**6**), in 3, 8, and 22% yields respectively. The mechanisms of the formation of the **5** and **6** are discussed. The photolysis of 3-hydroxydiphenylmethyl-4-diphenylmethoxymethylcyclobut-3-ene-1,2-dione (**14**) and 3,4-bis(diphenylmethyl)cyclobut-3-ene-1,2-dione (**18**) was also investigated.

Since the isolation of a novel fungicidal bislactone, *avenaciolide*, which has a 2,7-dioxabicyclo[3.3.0]octane-3,8-dione system (I),[1,2] some bislactones which have 2,7-dioxabicyclo[3.3.0]octane-3,6-dione (II),[3] 4,8-dioxabicyclo[3.3.0]octa-1,5-diene-3,7-dione (III),[4] 2,8-dioxabicyclo[3.3.0]octane-3,7-dione (IV),[5] and 3,7-dioxabicyclo[3.3.0]octane-2,6-dione (V)[6] systems have been reported. This paper will deal with the formation of the title bislactone, which has a hitherto unknown 3,7-dioxabicyclo[3.3.0]oct-1(5)-ene-2,6-dione (VI) system, and a new synthetic route of the bislactone, with the system of V.

The photolysis of 3,4-bis(hydroxydiphenylmethyl)-cyclobut-3-ene-1,2-dione (**1**) in benzene under nitrogen at room temperature afforded 4,4,8,8-tetraphenyl-3,7-dioxabicyclo[3.3.0]octane-2,6-dione (**3**) in an 80% yield. Because the photochemical ring-opening of cyclobutenedione into bisketene has been established,[7] the initial product of the photolysis of **1** should be bisketene (**2**). In order to trap **2**, the photolysis of **1** was carried out in MeOH. The photolysis, however, afforded 4,4,8,8-tetraphenyl-3,7-dioxabicyclo-[3.3.0]oct-1(5)-ene-2,6-dione (**4**), 4-methoxycarbonyl-3,3-diphenyl-5-diphenylmethylene-2-oxacyclopentan-1-one (**5**), and 4-carboxy-3,3-diphenyl-5-diphenylmethyl-2-oxacyclopent-4-en-1-one (**6**) in 3, 8, and 22% yields respectively. Compound **5** was also obtained from **3**. The treatment of **3** with KOH–MeOH afforded 4-carboxy-3,3-diphenyl-5-diphenylmethylene-2-oxacyclopentan-1-one (**8**). The reaction probably proceeds *via* an anion (**7**), which is formed by the deprotonation of **3** (Scheme 1). The treatment of **8** with $SOCl_2$ and then with MeOH afforded **5**.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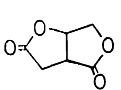
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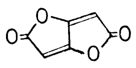
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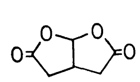
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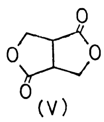
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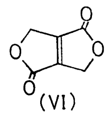
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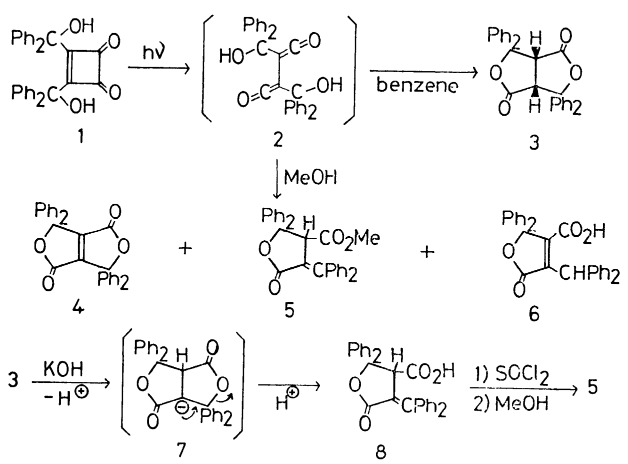
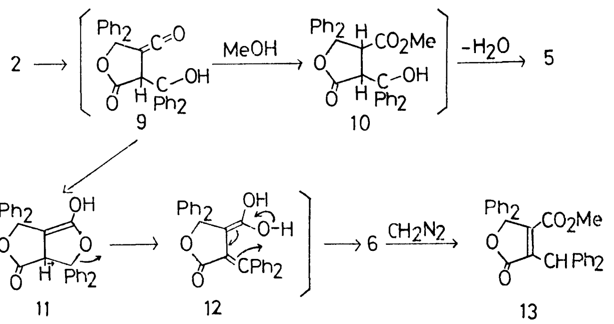
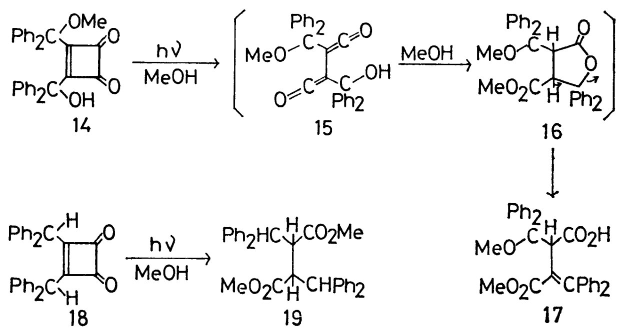


Scheme 1.



Scheme 2.

The formation of **5** and **6** in the photolysis of **1** in MeOH can be interpreted by the reaction sequence shown in Scheme 2. The reaction of **9**, the half-cyclized product of **2**, with MeOH should afford **10**. The dehydration of **10** then finally affords **5**. Because the product ratio of **3**, **4**, and **5** was not varied by a prolonged irradiation of **1** in MeOH, interconversion among the three products during the photolysis can be ruled out. The ring-cleavage of **11**, which is formed by an intramolecular cyclization of **9**, affords **6** *via* the diol (**12**). The reaction of **6** with CH_2N_2 afforded 4-methoxycarbonyl-3,3-diphenyl-5-diphenylmethyl-2-oxacyclopent-4-en-1-one (**13**). Nevertheless, the pathway of the formation of **4** is not clear.



Scheme 3.

The photolysis of 3-hydroxydiphenylmethyl-4-methoxydiphenylmethylcyclobut-3-ene-1,2-dione (**14**) in MeOH afforded 3-methoxycarbonyl-3-diphenylmethylene-2-methoxydiphenylmethylpropionic acid (**17**) in a 65% yield. A possible pathway for the formation of **17** is the ring-cleavage of **16**, which is produced by an intramolecular cyclization of the initially formed bisketene intermediate (**15**) (Scheme 3). The photolysis of 3,4-bis(diphenylmethyl)cyclobut-3-ene-1,2-dione (**18**) in MeOH afforded dimethyl 2,3-bis(diphenylmethyl)succinate (**19**) in a 23% yield. However, both **14** and **18** were inert to the photolysis in benzene.

Experimental

All the melting points are uncorrected. Photolysis was carried out at room temperature under a nitrogen atmosphere, using light from a 100-W high-pressure mercury lamp (Riko Kagaku Sangyo Co.), filtered through Pyrex glass. The IR, UV, and NMR spectra were measured in Nujol mull, EtOH, and $CDCl_3$ respectively, unless otherwise stated. The mass spectra were measured with an ionization energy of 75 eV.

*Photolysis of **1** in Benzene.* A solution of **1**[8] (0.5 g) in benzene (150 ml) was irradiated under stirring for 5.5 hr. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **3** as colorless needles; 0.4 g (80%); mp 227—228 °C. IR: 1780 (C=O) and 1210 and 1180 cm^{-1} (lactone); $\lambda_{max}^{CHCl_3}$: 242 (1400), 253 (1000), 259 (1200), 262 (1000), and 269 sh nm (ε, 700); NMR: 2.6—3.2 (m, Ph, 20 H) and 5.85 τ (s, CH, 2H); MS: *m/e* (rel intensity) 446 (M$^+$, 100), 402 (M$^+$ $-CO_2$, 7), 358 (M$^+$ $-2CO_2$, 15), 264 (M$^+$ $-Ph_2CO$, 70), and 236 (M$^+$$-(Ph_2CO+CO)$, 62).

Found: C, 80.95; H, 4.75%. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97%.

*Photolysis of **1** in MeOH.* A solution of **1** (3 g) in MeOH (500 ml) was irradiated under stirring for 6 hr. The crude crystals which separated out after the concentration of the reaction mixture to *ca.* 5 ml were collected by filtration. Recrystallization from MeOH afforded **4** as colorless plates; 0.075 g (3%); mp 280—281 °C. IR: 1765 (C=O) and 1080 and 1010 cm^{-1} (lactone); $\lambda_{max}^{CHCl_3}$: 275 sh nm (ε, 2700); NMR: 2.6—3.2 τ (m, Ph); MS: *m/e* (rel intensity) 444 (M$^+$, 31)· 400 (M$^+$$-CO_2$, 23), 356 (M$^+$$-2CO_2$, 38), 278 (M$^+$$-Ph_2C$, 100), and 218 (M$^+$ $-CO_2-Ph_2CO$, 70).

Found: C, 81.08; H, 4.31%. Calcd for $C_{30}H_{20}O_4$: C, 81.06; H, 4.54%.

The MeOH solution left after the separation of the crude **4** was evaporated to dryness, and the residue was recrystallized from benzene–MeOH to afford **6** as colorless prisms; 0.653 g (22%); mp 204—205 °C. IR: 2800—2500 (OH), 1720 (C=O), and 1635 cm^{-1} (C=C); λ_{max}: 240 sh nm (ε, 8500); NMR: 2.2—3.0 (m, Ph, 20H) and 3.88 τ (s, CH, 1H).

Found: C, 80.84; H, 4.86%. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97%.

The benzene–MeOH solution left after the separation of **6** was evaporated to dryness, and the residue was chromatographed on Al_2O_3 with benzene to afford **5** as colorless prisms, after recrystallization from acetone–MeOH; 0.24 g, (8%); mp 189—190 °C. IR: 1775 and 1730 (C=O), 1630 (C=C), 1210 (ester), and 1120 cm^{-1} (lactone); λ_{max}: 287 nm (ε, 11600); NMR: 2.5—3.5 (m, Ph, 20H), 5.6 (s, CH, 1H), and 6.85 τ (s, CH_3, 3H).

Found: C, 80.65; H, 5.35%. Calcd for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25%.

*Methyl Ester of **6**.* A solution of **6** (0.1 g) in THF (10 ml) was combined with a CH_2N_2-ether solution (10 ml), and the mixture was kept at 0 °C overnight. The crude crystals left after the evaporation of the solvent were recrystallized from acetone-MeOH to afford **13** as colorless prisms; 0.09 g (87%); 131—133 °C. IR: 1780 and 1740 (C=O), 1650 (C=C), and 1230 cm^{-1} (ester); λ_{max}: 240 sh nm (ε, 8200); NMR: 2.3—2.8 (m, Ph, 20H), 4.06 (s, CH, 1H), and 6.62 τ (s, CH_3, 3H).

Found: C, 80.63; H, 5.36%. Calcd for $C_{31}H_{24}O_4$: C, 80.85; H, 5.25%.

*Hydrolysis of **3**.* A solution of **3** (0.10 g) in 5% KOH–MeOH (10 ml) was heated under reflux for 1 hr. The crude crystals which were separated out by the acidification of the reaction mixture were recrystallized from CCl_4 to afford **8** as colorless prisms; 0.08 g (80%); mp 206—207 °C. IR: 2800—2500 (OH), 1780 and 1740 (C=O), and 1620 cm^{-1} (C=C); λ_{max}: 286 nm (ε, 10900).

Found: C, 80.54; H, 5.07%. Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97%.

A mixture of **8** (0.04 g), benzene (15 ml), and $SOCl_2$ (0.05 ml) was heated under reflux for 9 hr. The crude product left after the evaporation of the solvent was dissolved in MeOH (20 ml), and the solution was heated under reflux for 6 hr. The crude crystals left after the evaporation of the solvent were recrystallized from MeOH to afford **5**; 0.02 g (48%).

*Photolysis of **14** in MeOH.* A solution of **14**[8] (0.4 g) in MeOH (150 ml) was irradiated under stirring for 3.5 hr. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **17** as colorless needles; 0.277 g (65%); mp 179—180 °C. IR: 2800—2600 (OH), 1710 (C=O), and 1230 cm^{-1} (ester); λ_{max}: 252 (8800), 263 sh (8200), and 270 sh nm (ε, 7200); NMR: 2.3—3.3 (m, Ph, 20 H), 5.31 (s, CH, 1H), 6.68 (s, CH_3,3H), and 6.87 τ (s, CH_3, 3H).

Found: C, 77.84; H, 5.95%. Calcd for $C_{32}H_{28}O_5$: C, 78.03; H, 5.73%.

*Photolysis of **18** in MeOH.* A solution of **18**[8] (0.5 g) in MeOH (150 ml) was irradiated under stirring for 4 hr. The crude crystals left after the evaporation of the solvent were recrystallized from acetone–MeOH to afford **19** as colorless needles; 0.16 g (23%); mp 166—167 °C. IR: 1740 (C=O) and 1220 cm^{-1} (ester); λ_{max}: 260 nm (ε, 1000); NMR: 2.5—3.5 (m, Ph, 20 H), 5.55 (d, *J*=12 Hz, CH, 2H), 6.52 (s, CH_3, 6H), and 6.60 τ (d, *J*=12 Hz, CH, 2H).

Found: C, 80.45; H, 6.12%. Calcd for $C_{32}H_{28}O_4$: C, 80.64; 5.92%.

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