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Photochemical Conversion of Methoxyketene Intermediate into Methyl Ester in the Photolysis of 2-Methoxy-3-diphenylmethyl-4-diphenylmethylene-2-cyclobuten-1-one

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Synopsis. The photolysis of methylenecyclobutenone in the presence of benzophenone or oxygen affords the one carbon diminished product, methyl 4,4-diphenyl-2-diphenylmethyl-2,3-butadienoate. The reaction pathway is discussed.

Nozaki and his collaborators reported that the photochemical conversion of diphenylketene into benzophenone under nitrogen atmosphere in a higher yield than 50% is puzzling.[1] We found that the photolysis of methylenecyclobutenone (**1**) in the presence of benzophenone or oxygen affords the one carbon diminished product, methyl 4,4-diphenyl-2-diphenylmethyl-2,3-butadienoate (**5**), and that the reaction can well be rationalized by means of the cycloaddition reaction of the methoxyketene intermediate (**2**) initially produced by the α-cleavage of **1**, with benzophenone or oxygen.

The irradiation of a solution of **1** and benzophenone in benzene under nitrogen atmosphere for 5 h afforded **5** in 31% yield. The structure of **5** was elucidated on the basis of its reaction with bromine which affords 3-bromo-4,4-diphenyl-2-diphenylmethyl-2-buten-4-olide (**6**). Base-catalyzed hydrolysis of **5** afforded the corresponding acid (**7**). The formation of **5** can be interpreted by assuming the cycloaddition product (**3**) of **2** and benzophenone as an intermediate. The intermediacy of **2** is undoubted, since the photochemical α-cleavage of methylenecyclobutenone to alleneketene has been established.[2] The ring cleavage of **3** can give **5** and diphenylketene, the latter being converted into benzophenone in the same manner as reported.[1]

The photolysis of **1** in benzene under oxygen atmosphere also afforded **5** in 10% yield. This can be interpreted by assuming **4** as an intermediate, decarboxylation of which affords **5**. Since neither benzophenone nor oxygen is necessary for the photochemical α-cleavage of methylenecyclobutenone,[2] benzophenone and oxygen would only be used for the formation of **3** and **4**, respectively. In their absence, the photolysis of **1** in benzene did not give **5**, **1** being recovered unchanged. This shows that the photochemical α-cleavage of **1** to **2** is reversible.

Experimental

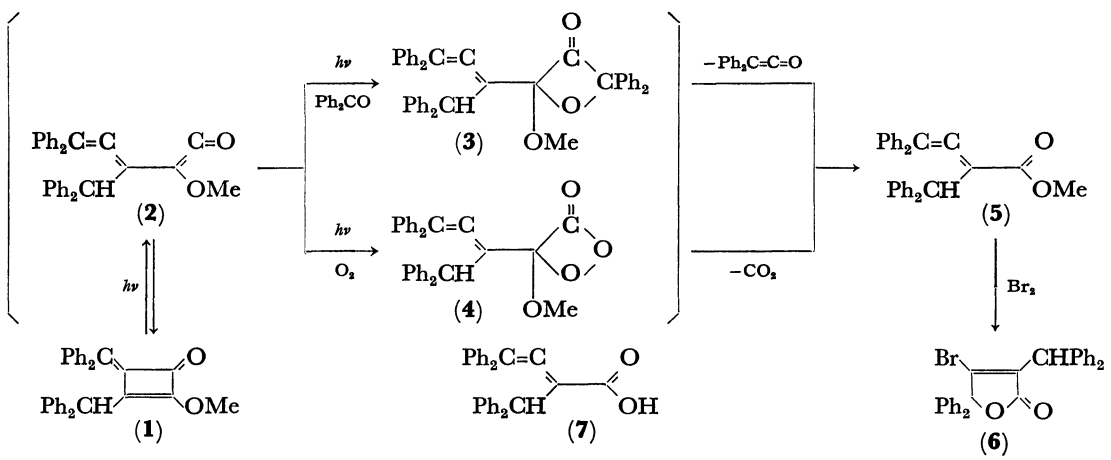
All the melting points are uncorrected. Photolysis was carried out at room temperature, with light from a 400-W high-pressure mercury lamp (Riko Kagaku Sangyo Co.), filtered through Pyrex glass. The IR, UV, and NMR spectra were measured in Nujol mull, $CHCl_3$, and $CDCl_3$, respectively. The mass spetrum was measured with an ionization energy of 75 eV.

*Photolysis of **1** in the Presence of Benzophenone.* A solution of **1** (0.1 g) and benzophenone (0.07 g) in benzene (250 ml) was irradiated under nitrogen atmosphere for 8 h. The crude crystals remaining after evaporation of the solvent were recrystallized from MeOH to afford **5** as colorless prisms; 0.03 g (31%); mp 135—136 °C. IR: 1940 (C=C=C), 1720 (C=O), and 1240 cm^{-1} (ester); λ_{max}: 252 nm (ε, 18800); NMR: 2.5—3.4 (m, Ph, 20H), 4.57 (s, CH, 1H), and 6.34τ (s, Me, 3H); MS *m/e* (rel intensity): 416 (M^+, 25), 385 (M^+—OMe, 56), 357 (385—CO, 66), and 167 ($Ph_2\overset{+}{C}H$, 100).

Found: C, 86.37; H, 5.73%. Calcd for $C_{30}H_{24}O_2$: C, 86.51; H, 5.81%.

*Photolysis of **1** under Oxygen Atmosphere.* A solution of **1** (0.1 g) in benzene (250 ml) was irradiated under oxygen atmosphere for 15 h. The crude crystals remaining after evaporation of the solvent were recrystallized from MeOH to afford **5**; 0.01 g (10%).

*Conversion of **5** into **6**.* Bromine (0.03 g) was added at room temperature to a solution of **5** (0.1 g) in $CHCl_3$ (10 ml). The crude crystals remaining after evaporation of the solvent were recrystallized from AcOEt to afford **6** as colorless prisms; 0.1 g (86%); mp 150 °C. IR: 1760 (C=O), 1630 (C=C), and



1140 cm^{-1} (lactone); λ_{max}: 245 nm (ε, 9600); NMR: 2.4—2.8 (m, Ph, 20H) and 4.38τ (s, CH, 1H).

Found: C, 72.42; H, 4.41%. Calcd for $C_{29}H_{21}O_2Br$: C, 72.35; H, 4.40%.

Hydrolysis of ***5***. A solution of **5** (0.1 g) in 5% KOH–MeOH (20 ml) was heated under reflux for 5 h. The crude crystals formed after the decomposition of the reaction mixture with water were recrystallized from hexane–CH_2Cl_2 to afford **7** as colorless needles; 0.09 g (93%); mp 185—186 °C. IR: 2620 (CO_2H), 1940 (C=C=C), and 1670 cm^{-1} (C=O); λ_{max}: 243 (19200) and 253 nm (ε, 19200); NMR: −1.33 (s, CO_2H, 1H), 2.6—3.1 (m, Ph, 20H), and 4.61 τ (s, CH, 1H).

Found: C, 86.49; H, 5.42%. Calcd for $C_{29}H_{22}O_2$: C, 86.54; H, 5.51%.

References

1) H. Nozaki, M. Nakano, and K. Kondo, *Tetrahedron*, **22**, 477 (1966).

2) F. Toda and E. Todo, *Chem. Lett.*, **1974**, 1279.