The Photolysis and Thermolysis of 3-(Diphenylhydroxymethyl)-4-(diphenylmethylene)-2-cyclobuten-1-one and Its 2-Bromo Derivative[1]

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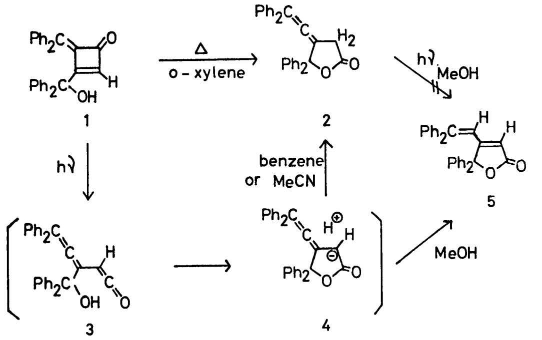
The photolysis of the title methylenecyclobutenone (**1**) and 2-bromomethylenecyclobutanone (**9**) in MeOH afforded 4,4-diphenyl-3-(2,2-diphenylvinyl)-2-buten-4-olide (**5**) and 3,3,5-triphenyl-1,3-dihydronaphtho[1,2-*c*]-furan-2-one (**11**) respectively. The photolysis of **1** and **9** in benzene, however, afforded 4,4-diphenyl-3-(diphenylvinylidene)-4-butanolide (**2**), and bromo-derivative of **5** (**8**) and **11** respectively. The thermolysis of **1** and **9** in *o*-xylene afforded **2** and 2-bromo derivative of **5**(**10**) respectively. The mechanisms of these reactions were discussed. The solvent effect on the photolysis of **1** and **9** was also discussed.

The photochemical conversion of cyclobutenedione into the bisketene intermediate *via* a Norrish Type I reaction is well established.[2,3] In order to compare the photolysis of methylenecyclobutenone with that of cyclobutenedione, we studied the photolysis of the title compounds (**1** and **9**) in benzene and MeOH; we found that all the reactions afford products which are probably derived from alleneketene intermediates (**3** and **12**) initially formed by Norrish Type I reactions of **1** and **9** respectively. It was also found that the thermolysis of **1** and **9** probably proceeds *via* the alleneketene intermediates, **3** and **12** respectively.

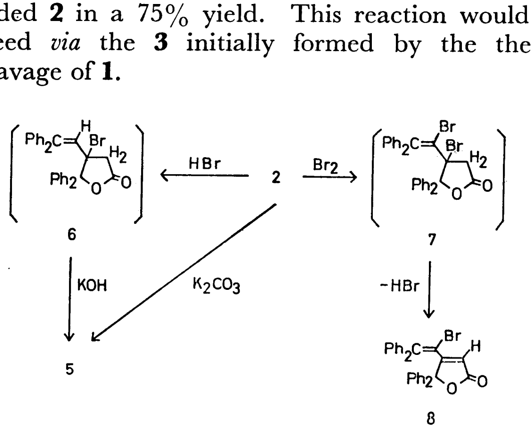
The irradiation of **1** in benzene for 1 h afforded 4,4-diphenyl-3-(diphenylvinylidene)-4-butanolide (**2**) in an 82% yield. The formation of **2** can be explained in terms of intramolecular esterification involving the alleneketene (**3**) as an intermediate produced by the α-cleavage of **1**. Such an easy lactonization has been demonstrated in the photochemical conversion of 3,4-bis (diphenylhydroxymethyl) cyclobut-3-ene-1,2-dione into 4,4,8,8-tetraphenyl-3,7-dioxabicyclo[3.3.0]octane-2,6-dione.[3]



Scheme 1.

In contrast with the photolysis of **1** in benzene, the photolysis of **1** in MeOH afforded 4,4-diphenyl-3-(2,2-diphenylvinyl)-2-buten-4-olide (**5**) in a 35% yield as the sole isolable product. This reaction would also proceed *via* **3**. It seems that the type of reaction product depends on whether the solvent used is polar or nonpolar. It is clear, however, that **5** was not derived from **2**, because the irradiation of **2** in MeOH did not give **5**, and **2** was recovered unchanged. Nevertheless, a polar solvent is not always sufficient for the formation of **5** in the photolysis of **1**; the photolysis of **1** in MeCN afforded **2**, but not **5**. The formation of **5** can be interpreted by assuming the ion pair (**4**) as an intermediate; it would easily be protonated in MeOH on its allene carbon.

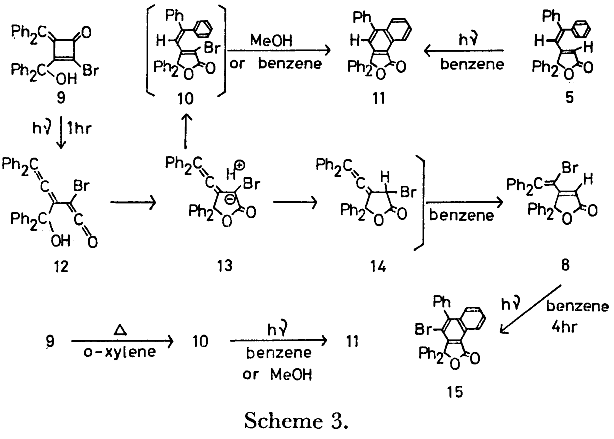
The heating of **1** in *o*-xylene under reflux for 5 h afforded **2** in a 75% yield. This reaction would also proceed *via* the **3** initially formed by the thermal α-cleavage of **1**.



Scheme 2.

The prototropic rearrangement of **2** into **5** occurred easily when **2** was treated with K_2CO_3 in MeOH. The conversion of **2** into **5** was also performed by the treatment of **2** with HBr, followed with KOH. The dehydrobromination of the Br_2-addition product of **2** (**7**) afforded the bromo-derivative of **5** (**8**).

The photolysis and thermolysis of the 2-bromo derivative of **1** (**9**) gave slightly different results from



Scheme 3.

those of **1**. The thermolysis of **9** under the same conditions as those used for **1** afforded the 3-bromo derivative of **5** (**10**) in a 46% yield. The photolysis of **9** in benzene under the same conditions as those used for **1** afforded **8** and 3,3,5-triphenyl-1,3-dihydronaphtho[1,2-*c*]furan-2-one (**11**) in 25 and 27% yields respectively, whereas the photolysis in MeOH afforded **11** in a 20% yield as the sole isolable product. All these reactions can be interpreted by assuming the ion pair (**13**) to be the intermediate which was produced by the intramolecular esterification of the alleneketene intermediate (**12**) initially formed by the α-cleavage of **9** similar to the case of **1**. The ion pair (**13**) would be more stabilized by an inductive effect of Br than would **4**.

In the thermolysis of **9**, **10** would be derived directly from **13**, but not from **14**; the latter probably affords **8**, because the average bond energy of C–H (99) is larger than that of C–Br (68 kcal/mol). The thermal stability of **2** supports this.

The formation of **8** and **11** in the photolysis of **9** in benzene can be interpreted by assuming **14** and **10** as intermediates; *i.e.*, the process involves the rearrangement of Br of **14** and an electrocyclic reaction, followed by the dehydrobromination of **10** to afford **8** and **11** respectively. Evidence for the intermediacy of **10** was obtained by the photolysis of **10** in benzene and MeOH, which affords **11** in 84 and 57% yields respectively. In a similar manner, the prolonged photolysis of **5** and **8** in benzene afforded **11** and its 4-bromo derivative (**15**) respectively. These reactions are similar to the photochemical conversion of stilbene into phenanthrene.[4,5] The exclusive formation of **11** in the photolysis of **9** in MeOH can be interpreted in the way employed for the interpretation of the solvent effect on the photolysis of **1**; *i.e.*, **13** would easily be protonated in MeOH on its allene carbon.

Experimental

All the melting points are uncorrected. The 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, $CHCl_3$, 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**[6] (0.6 g) in benzene (150 ml) was irradiated for 1 h. The crude crystals left after the evaporation of the solvent were recrystallized from MeOH to afford **2** as colorless needles; 0.49 g (82%); mp 112—113 °C. IR: 1790 (C=O), 1400 (CH_2), and 1205 cm^{-1} (lactone); λ_{max}: 270 nm (ε, 14500); NMR: 2.2—3.3 (m, Ph, 20H) and 6.35 τ (s, CH_2, 2H); MS: *m*/*e* (rel intensity) 414 (M^+, 72), 386 (M^+-CO, 17), and 204 ($386-Ph_2CO$, 100).

Found: C, 86.77; H, 5.31%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%.

Photolysis of 1 in MeOH. A solution of **1** (0.4 g) in MeOH (150 ml) was irradiated for 6 h. The oily material left after the evaporation of the solvent was dissolved in CCl_4, after which the solution was chromatographed on Al_2O_3. The crude crystals obtained from the fraction eluted with benzene were recrystallized from MeOH to afford **5** as pale yellow prisms; 0.14 g (35%); mp 148—150 °C. IR: 1755 (C=O), 1625 (C=C), and 1220 and 1180 cm^{-1} (lactone); λ_{max}: 327 nm (ε, 19100); NMR: 2.3—3.2 (m, Ph, 20H), 3.35 (s, =CH, 1H), and 4.85 τ (s, =CH, 1H); MS *m*/*e* (rel intensity): 414 (M^+, 7), 370 (M^+-CO_2, 84), 232 (M^+-Ph_2CO, 21), and 204 ($232-CO$, 100).

Found: C, 86.81; H, 5.15%. Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35%.

Thermolysis of 1 in o-Xylene. A solution of **1** (0.071 g) in *o*-xylene (10 ml) was heated under reflux in a nitrogen atmosphere for 5 h. The crude crystals left after the evaporation of the solvent were recrystallized to afford **2**; 0.053 g (75%).

Conversion of 2 into 5. *a*) When a mixture of **2** (0.056 g), K_2CO_3 (0.1 g) and MeOH (20 ml) was heated under reflux for 1 h, **5** was obtained after recrystallization from MeOH; 0.045 g (81%). *b*) Into a solution of **2** (0.097 g) in $CHCl_3$ (10 ml), HBr was bubbled for 10 min. The oily material left after the evaporation of the solvent was dissolved in 0.5% KOH–MeOH (20 ml), after which the solution was heated under reflux for 1 h. The recrystallization from MeOH of the crude crystals obtained by the dilution of the reaction mixture with water afforded **5**, 0.05 g (52%).

Preparation of 8. To a solution of **2** (0.092 g) in $CHCl_3$ (10 ml), Br_2 (0.05 g) was added. The oily material left after the evaporation of the solvent crystallized when treated with AcOEt (1 ml).

The recrystallization of the crude crystals from AcOEt afforded **8** as pale yellow prisms; 0.054 g (42%); mp 217—218 °C. IR: 1760 (C=O), 1605 (C=C), and 1265 and 1210 cm^{-1} (lactone); λ_{max}^{EtOH}: 248 (31600), 318 (6300), and 332 nm (ε, 5600); NMR: 2.3—3.2 (m, Ph, 18H), 3.6—3.8 (m, Ph, 2H), and 4.18 τ (s, =CH, 1H); MS *m*/*e* (rel intensity): 494 and 492 (M^+, each 16), 450 and 448 (M^+-CO_2, each 28), 413 (M^+-Br, 20), 369 ($413-CO_2$, 24), 292 ($369-Ph$, 28), 231 ($413-Ph_2CO$, 96), and 203 ($231-CO$, 100).

Found: C, 72.85; H, 4.16%. Calcd for $C_{30}H_{21}O_2Br$: C, 73.02; H, 4.25%.

Thermolysis of 9 in o-Xylene. A solution of **9** (0.318 g) in *o*-xylene (10 ml) was heated under reflux in a nitrogen atmosphere for 5 h. The crude crystals left after the evaporation of the solvent were recrystallized from AcOEt to afford **10** as pale yellow leaflets; 0.147 g (46%); mp 217—218 °C. IR: 1760 (C=O), 1610 (C=C), and 1230 cm^{-1} (lactone); λ_{max}^{EtOH}: 238 (17700) and 328 nm (ε, 13400); NMR: 2.0—3.0 (m, Ph, 18H), 3.3—3.6 (m, Ph, 2H), and 3.73 τ (s, =CH, 1H).

Found: C, 73.10; H, 4.18%. Calcd for $C_{30}H_{21}O_2Br$; C, 73.02; H, 4.25%.

Photolysis of 9 in Benzene. A solution of **9** (0.43 g) in benzene (150 ml) was irradiated for 1 h. The crude product left after the evaporation of the solvent was recrystallized from MeOH-$CHCl_3$ (1 : 1) (10 ml) to afford **8**; 0.108 g (25%). The evaporation of the solvent of the mother liquor left after the separation of **8** gave crude crystals, which were then recrystallized from MeOH–acetone to afford **11** as colorless prisms; 0.097 g (27%); mp 157—158 °C. IR 1750 (C=O) and 1180 and 1130 cm^{-1} (lactone); λ_{max}: 250 (31700) and 314 nm (ε, 9900).

NMR: 1.7—2.8 τ (m, Aromatic); MS *m*/*e* (rel intensity): 412 (M^+, 75), 368 (M^+-CO_2, 27), 335 (M^+-Ph, 73), and 307 ($335-CO$, 100).

Found: C, 87.31; H, 4.75%. Calcd for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89%.

Photolysis of 9 in MeOH. A solution of **9** (0.4 g) in MeOH (150 ml) was irradiated for 1 h. The crude crystals left after the evaporation of the solvent were recrystallized from MeOH–acetone to afford **11**: 0.082 g (25%).

Photolysis of 10 in Benzene and MeOH. A solution of **10** (0.102 g) in benzene (150 ml) was irradiated for 2 h. The crude crystals left after the evaporation of the solvent were recrystallized from MeOH–acetone to afford **11**; 0.072 g (84 %). When a solution of **10** (0.05 g) in MeOH (150 ml) was irradiated for 2 h, and then worked up as above, 0.024 g (57%) of **11** was obtained.

*Photolysis of **5** in Benzene.* A solution of **5** (0.167 g) in benzene (150 ml) was irradiated for 3 h. The recrystallization from MeOH–acetone of the crude crystals left after the evaporation of the solvent afforded **11**; 0.13 g (76%).

*Photolysis of **8** in Benzene.* A solution of **8** (0.1 g) in benzene (150 ml) was irradiated for 4 h. The crude crystals left after the evaporation of the solvent were recrystallized from MeOH–$CHCl_3$ to afford **15** as colorless needles; 0.06 g (60%); mp 276—279 °C. IR: 1765 (C=O) and 1200 and 1140 cm^{-1} (lactone); λ_{max}: 320 (10000) and 332 nm (ε, 8800); NMR: 1.8—2.8 τ (m, Aromatic); MS *m/e* (rel intensity): 492 and 490 (M^+, each 58), 448 and 446 (M^+-CO_2, each 20), 411 (M^+-Br, 14), 367 ($411-CO_2$, 100), and 290 (367−Ph, 58).

Found: C, 73.42; H, 3.71%. Calcd for $C_{30}H_{19}O_2Br$: C, 73.31; H, 3.87%.

References

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5) For the photochemical conversion of stilbene into phenanthrene, it has been reported that oxygen acts as a reagent of the dehydrogenation of the dihydrophenanthrene initially formed by the electrocyclic reaction of stilbene; F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Am. Chem. Soc.*, **84**, 4361 (1962). Therefore, in the photochemical conversions of **5** and **8** into **11** and **15** respectively, the oxygen which contaminates the nitrogen atmosphere seems to act as a reagent of dehydrogenation.

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