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Synthetic Photochemistry. LVI.1) Photorearrangement of Dimethyl 2-Oxohomobarrelene-6,7-dicarboxylates

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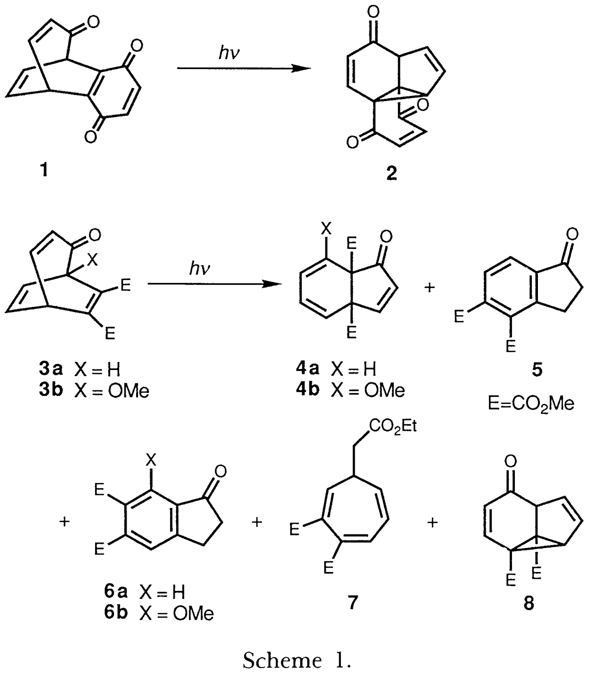
The direct irradiation of dimethyl 2-oxohomobarrelene-6,7-dicarboxylates in chloroform gave indanone derivatives. A benzophenone-sensitized reaction gave a new tricyclic compound, dimethyl 5-oxotricyclo-$[4.3.0.0^{2,9}]$nona-3,7-diene-1,2-dicarboxylate, the formation of which was quenched by isoprene.

Bicyclo[3.2.2]nona-3,6,8-trien-2-ones (homobarrelenones) are interesting molecules with regard to the photochemical reactivity, since they have a transannular conjugated tri-π-methane chromophore, in which one of the double bonds is conjugated with a carbonyl group. The photochemical reactivity of these transannularly delocalized π-systems has attracted much attention and, indeed, the photochemical reactions for parent homobarrelenone2) and benzo and dibenzo derivatives3,4) as well as 2-methylenehomobarrelenes5) have already been investigated. However, the reactions of the homobarrelenones with substituents were limited, since their preparation was somewhat difficult.

We recently developed a new synthetic method for producing homobarrelenones, the Diels–Alder cycloaddition of tropones to dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate and subsequent fragmentation.6) Furthermore, we could synthesize quinone-fused homobarrelenones, e.g., tricyclo$[6.3.2.0^{2,7}]$trideca-2(7),4,10,12-tetraene-3,6,9-trione (**1**) via a high-pressure Diels–Alder reaction of tropone with *p*-benzoquinone followed by dehydrogenation. We have verified that **1**, upon UV-irradiation, exclusively gave tetracyclo$[6.5.0.0^{1,9}.0^{5,9}]$trideca-2,6,11-triene-4,10,13-trione (**2**).7) This photochemical reaction of **1** has been shown to be different with regard to the product distribution to that of the parent homobarrelenone. It is therefore worth investigating other homobarrelenone derivatives having different chromophores. Herein, we describe the photorearrangement of dimethyl 2-oxohomobarrelene-6,7-dicarboxylate (**3**) with some mechanistic aspects.

When dimethyl 2-oxohomobarrelene-6,7-dicarboxylate (**3a**)8) was irradiated in chloroform by means of a 100-W high-pressure mercury lamp, four products (**4a**, **5**, **6a**, **7**) were obtained in 24, 2.3, 16, and 3.8% yields, respectively. The major product, **4a**, was identified as dimethyl 7-oxobicyclo[4.3.0]nona-2,4,8-triene-1,6-dicarboxylate by an ^{1}H NMR spectral comparison with an authentic sample, which has already been isolated from the thermal reaction of **3a**.8) While the minor product, **5**, could not be separated completely from **3a**, its ^{1}H NMR spectrum was identical with that of authentic dimethyl 1-oxoindan-4,5-dicarboxylate.8) The structure of **6a** was determined to be isomeric dimethyl 1-oxoindan-5,6-dicarboxylate, since aromatic proton signals appeared separately at δ=7.74 and 8.19 as singlets. Compound **7** had an ethoxycarbonyl group instead of the ketonic carbonyl group in the ^{13}C NMR spectrum, and its UV spectrum indicated a cycloheptatriene derivative. Since the signals for four olefinic protons and six olefinic carbons were recognized, **7** was deduced to be ethyl 3,4-bis(methoxycarbonyl)-2,4,6-cycloheptatrienylacetate. Evidently, **7** was formed via a ketene intermediate.

The irradiation of **3a** in chloroform in the presence of benzophenone afforded five products, four of which were the same as those characterized by direct irradiation. The structure of a new tricyclic compound (**8**) was determined as depicted on the basis of ^{1}H and ^{13}C NMR spectral analyses; the NMR spectral data for a common unsaturated ring moiety of **8** and **2**7) were almost superimposable on each other.



Scheme 1.

On the other hand, dimethyl 1-methoxy-2-oxohomobarrelene-6,7-dicarboxylate (**3b**) was irradiated under similar conditions; two products (**4b** and **6b**) were obtained in 41 and 42.4% yields, respectively.

The structure of **4b** was elucidated to be dimethyl 5-methoxy-7-oxobicyclo[4.3.0]nona-2,4,8-triene-1,6-dicarboxylate according to the NMR spectral similarity with **4a**. **6b** was identified to be dimethyl 7-methoxy-1-oxoindan-5,6-dicarboxylate, since no NOE was observed between the aromatic proton signal and the methoxyl signal. The irradiation of **3b** in the presence of benzophenone resulted in the formation of the same products (**4b** and **6b**) as those produced by direct irradiation.

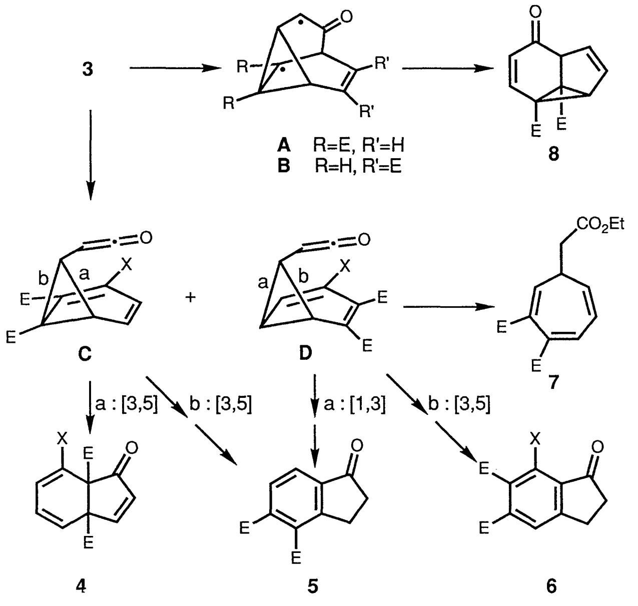
When the benzophenone-sensitized photoreaction of **3a** was monitored by the ^{1}H NMR spectra, as shown in Fig. 1, the consumption of **3a** was accelerated and the ratios of **3a**/**4a** increased.

In parallel, a quenching effect of the photoreaction of **3a** was analyzed by using isoprene. As shown in Table 1, compound **8** was undetectable and the product distribution was similar to that produced by direct irradiation. These results clearly show that **8** was formed via the triplet excited state and that the other products (indanones and **7**) were formed via singlet excited state, as illustrated in Scheme 2. The pathway to **8** can be explained in terms of di-π-methane rearrangements[2] of the diradical, **A**, which must be more stable than the alternative diradical, **B**, since both radical moieties of **A** were stabilized by the adjacent carbonyl groups.

Table 1. Product Distributions of Photoreactions of 3a

Solvent (Additive)	Yield/% **4a**	**5**	**6a**	**7**	**8**	Recovered **3a**
Chloroform	24	2.3	16	3.8	0	21
Chloroform (Benzophenone)	16	4.3	7.5	2.4	13	10
Chloroform (Isoprene)	28	1.9	13	3.7	0	24

Ketene intermediates, **C** and **D**, as has already been proposed regarding indanone formation in the thermal reaction of **3a**,[8,9] would be involved in photorear-



Scheme 2.

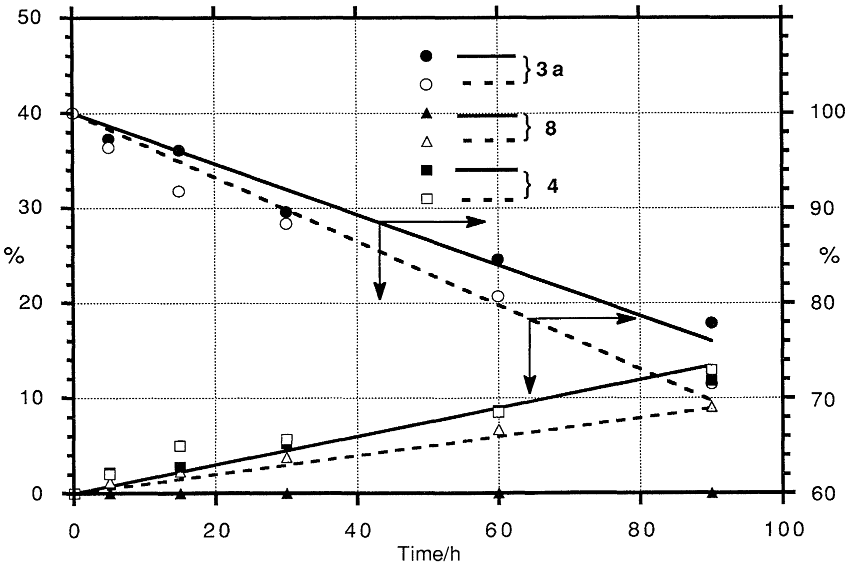


Fig. 1. Time-course of benzophenone-sensitized photorearrangement of **3a**. ——: in CDCl$_3$, -----: with benzophenone in CDCl$_3$. ● and ○: **3a**, ▲ and △: **8**, ■ and □: **4**.

rangements of **3**. The [3,5] shifts of bond a in **C** and bond b in **D** give **4** and **6**, respectively. Two paths, [3,5] shift of bond b in **C** and [1,3] shift of bond a in **D**, were equally possible to give **5** and were undistinguishable. In **3b**, the methoxyl group at C-1 assisted the [3,5] shifts of bond a in **C** and bond b in **D** to give **4b** and **6b**. The selective bridging between the enone part and the ethene part with substituents in the thermal reaction of **3** could be explained by a molecular orbital consideration.[9] However, according to the present photoreaction of **3**, both ketene intermediates were equally reactive and no selectivity of the bridging was observed.

In conclusion, the present study confirmed that the photoreaction of homobarrelenones having electron-withdrawing substituents, **3**, was different from the other electron-withdrawing homobarrelenone, **1**. Though the photoisomerization of **1** exclusively gave **2**, **3** afforded various products. The different product distributions between these two fundamental derivatives may be attributable to a difference in the primary excitation part; **3** absorbs light at the α,β-unsaturated keto group, while **1** does so at the ene-dione chromophore.

Experimental

Elemental analyses were performed by Miss S. Hirashima and Miss T. Mizoguchi of the Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured by means of a JEOL FX 100 Model and JEOL GSX 270 H Model spectrometer in a CDCl$_3$ solution (unless otherwise specified); The chemical shifts are expressed in units of δ. The mass spectra were measured with a JEOL O1SG-2 spectrometer. The IR spectra were taken as KBr disks or as a liquid film inserted between NaCl plates using a JASCO IR-A 102 spectrometer. The UV spectra were measured by using a Hitachi U-3200 spectrophotometer.

Irradiation of 3a. a) A CHCl$_3$ solution (3 cm^3) of **3a** (101 mg) in a Pyrex vessel was irradiated by means of a 100-W high-pressure mercury lamp for 5 h. The solvent was removed and the mixture was purified by silica-gel column chromatography and HPLC to give 18.8 mg (24%) of **4a**, 1.8 mg (2.3%) of **5**, 12.5 mg (16%) of **6a**, and 3.4 mg (3.8%) of **7** together with 21.6 mg (21%) of recovered **3a**.

4: Colorless crystals, mp 78.5—79.0 °C (lit,[8] mp 79.5—80.5 °C); ^{1}H NMR δ=3.70 (3H, s), 3.71 (3H, s), 5.65 (1H, dt, J=9.2, 1.1 Hz), 6.02 (1H, ddd, J=9.2, 5.5, 1.1 Hz), 6.09 (1H, ddd, J=9.5, 5.5, 1.1 Hz), 6.18 (1H, dt, J=9.5, 1.1 Hz), 6.55 (1H, d, J=5.8 Hz), and 7.95 (1H, d, J=5.8 Hz).

5: Not isolated as a pure form (lit,[8] mp 114—115 °C); ^{1}H NMR δ=2.7—2.8 (2H, m), 3.2 (2H, m), 3.94 (3H, s), 3.97 (3H, s), 7.86 (1H, d, J=7.7 Hz), and 7.89 (1H, d, J=7.7 Hz).

6a: Colorless crystals, mp 59—60 °C; ^{1}H NMR δ=2.7—2.8 (2H, m), 3.2 (2H, m), 3.93 (3H, s), 3.95 (3H, s), 7.74 (1H, s), and 8.19 (1H, s); ^{13}C NMR δ=26.0, 36.5, 52.6, 53.0, 125.1, 127.0, 129.9, 130.3, 138.5, 157.9, 166.5, 168.1, and 205.1; IR(KBr) 2956, 1741, 1714, 1618, 1274, 1201, and 1074 cm^{-1}; MS m/z (%) 248 (M$^+$, 26), 217 (100), and 189 (8).

Found: m/z 248.0684 (M$^+$). Calcd for C$_{13}$H$_{12}$O$_5$: 248.0684 (M).

7: A pale yellow oil; ^{1}H NMR δ=1.27 (3H, t, J=7.0 Hz), 2.3—2.4 (1H, m), 2.78 (2H, dd, J=7.0, 1.1 Hz), 3.72 (3H, s), 3.80 (3H, s), 4.20 (2H, q, J=7.0 Hz), 5.67 (1H, dd, J=9.8, 5.1 Hz), 6.31 (1H, d, J=6.6 Hz), 6.31 (1H, ddd, J=9.8, 6.6, 1.5 Hz), and 7.69 (1H, dd, J=5.9, 1.1 Hz); ^{13}C NMR δ=14.2, 35.4, 37.0, 52.3 (2C), 60.8, 125.8, 128.0, 132.5, 133.7, 136.6, 138.0, 166.8, 167.4, and 171.3; IR (oil) 2984, 2952, 1729, 1260, 1208, and 742 cm^{-1}; UV (MeOH) 220 nm (ε: 12800 sh) and 270 (4900); MS m/z (%) 294 (M$^+$, 8), 262 (100), 248 (18), and 189 (39).

Found: m/z 294.1101 (M$^+$). Calcd for C$_{15}$H$_{18}$O$_6$:1 294.1102 (M).

b) A CHCl$_3$ solution (3 cm^3) of **3a** (97.5 mg) and benzophenone (72.8 mg) was irradiated as mentioned above for 5 h to give 14.2 mg (16%) of **4a**, 3.8 mg (4.3%) of **5**, 6.6 mg (7.5%) of **6a**, 2.5 mg (2.4%) of **7**, and 11.5 mg (13%) of **8** together with 9.9 mg (10%) of recovered **3a**.

8: A colorless oil; ^{1}H NMR δ=3.71 (3H, s), 3.81 (3H, s), 3.9 (1H, m), 3.98 (1H, d, J=2.2 Hz), 5.73 (1H, dd, J=5.5, 2.2 Hz), 5.92 (1H, ddd, J=5.5, 2.2, 1.1 Hz), 6.22 (1H, dd, J=10.3, 0.7 Hz), and 6.69 (1H, d, J=10.3 Hz); ^{13}C NMR δ=39.5, 51.5, 52.7, 53.2, 55.1, 59.4, 129.7, 130.1, 134.7, 137.6, 168.4, 168.9, and 195.8; IR(oil) 3454, 2956, 1732, 1695 and 1268 cm^{-1}; UV (MeOH) 214 nm (ε: 9100), 251 (4100), 303 (1500 sh), and 336 (1100 sh); MS m/z (%) 248 (M$^+$, 46), 220 (38), 216 (100), and 188 (34).

Found; m/z 248.0685 (M$^+$). Calcd for C$_{13}$H$_{12}$O$_5$: 248.0684 (M).

c) A CHCl$_3$ solution (3 cm^3) of **3a** (102 mg) was irradiated as mentioned above for 5 h in the presence of isoprene (47.8 mg) to give 22.1 mg (28%) of **4a**, 1.5 mg (1.9%) of **5**, 10.2 mg (13%) of **6a**, and 3.4 mg (3.7%) of **7** together with 24.3 mg (24%) of **3a**.

d) A CHCl$_3$ solution (3 cm^3) of **3a** (134.5 mg) and benzophenone (100 mg) was irradiated by means of 400 W high-pressure lamp for 5 h to give 14.7 mg (11%) of **4a**, 3.3 mg (2%) of **6a**, 40.5 mg (22%) of **7**, and 14 mg (10%) of **8**.

Irradiation of 3b. a) A CHCl$_3$ solution (2 cm^3) of **3b** (50 mg) was irradiated for 5 h under similar conditions. The solvent was removed and the mixture was purified by a silica-gel column chromatography and HPLC to give 20.5 mg (41%) of **4b** and 21.2 mg (42.4%) of **6b**.

4b: Colorless needles, mp 128—130 °C; ^{1}H NMR δ=3.69 (6H, s), 3.70 (3H, s), 5.27 (1H, d, J=6.6 Hz), 5.53 (1H, J=9.5 Hz), 6.12 (1H, dd, J=9.5, 6.6 Hz), 6.58 (1H, d, J=5.9 Hz), and 7.47 (1H, J=5.9 Hz); ^{13}C NMR δ=52.9, 53.2, 56.1, 62.8, 94.1, 115.4, 123.0, 123.3, 133.9, 151.8, 159.3, 167.8, 170.7, and 197.8; IR(KBr) 1746, 1732, 1592, 1436, 1263, 1231, 1189, and 1049 cm^{-1}; UV (MeOH) 211 nm (ε: 13380) and 282 (4770); MS m/z (%) 278 (M$^+$, 38), 219 (100), 191 (66), 175 (67), 160 (25), and 132 (28).

Found: m/z 278.0789. Calcd for C$_{14}$H$_{14}$O$_6$: 278.0789 (M).

6b: Colorless needles, mp 148—149 °C; ^{1}H NMR δ=2.76 (2H, m), 3.17 (2H, m), 3.92 (3H, s), 3.95 (3H, s), 4.03 (3H, s), and 7.80 (1H, s); ^{13}C NMR δ=25.8, 37.1, 52.8, 53.0, 63.5, 123.0, 129.0, 131.7, 134.2, 155.4, 158.0, 165.1, 167.0, and 202.8; IR(KBr) 1743, 1711, 1453, 1302, 1272, 1231, 1194, 1150, and 1078 cm^{-1}; UV (MeOH) 206 nm (ε: 24360), 258 (12200), and 316 (2730); MS m/z (%) 278 (M$^+$, 54), 247 (100), 233 (54), and 160 (68).

Found: C, 60.40; H, 5.41%. Calcd for C$_{14}$H$_{14}$O$_6$: C, 60.46; H, 5.04%.

b) A CHCl$_3$ solution (2 cm^3) of **3b** (150 mg) and benzophenone (100 mg) was irradiated for 3 h. A similar work-up gave 51.5 mg (34.3%) of **4b** and 50.3 mg (33.5%) of **6b**.

Kinetics. A $CDCl_3$ solution (0.6 cm^3) of **3a** (72.6 mg) and a $CDCl_3$ solution (0.6 cm^3) of **3a** (73.7 mg) and benzophenone (51.2 mg) were irradiated using a "Merry-Go-Round" apparatus. The reaction was monitored by means of the ^1H NMR spectra. The results are summarized in Fig. 1.

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