December, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 4397—4400 (1988)* 4397

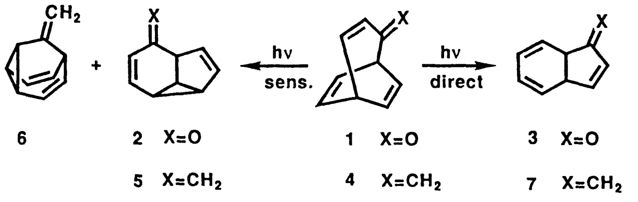
Synthetic Photochemistry. XLV.[1] Photoconversion of 2-Methylenehomobarrelenes to 9-Methylenebarbaralanes

Guan Rong TIAN,† Shigeru SUGIYAMA, Akira MORI, and Hitoshi TAKESHITA*
Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816

(Received April 27, 1988)

The photolysis of 4-methoxycarbonyl-2-oxatricyclo[6.2.2.0^{1,5}]dodeca-4,6,9,11-tetraen-3-one derivatives yielded 9-methylenebarbaralanes along with 5-methylenetricyclo[4.3.0.0^{2,9}]nonadiene and 1-methyleneindan derivatives. From the benzophenone-sensitization experiments, 9-methylenebarbaralane and 5-methylenetricyclo[4.3.0.0^{2,9}]nonadiene were formed via a triplet excited state, but 1-methyleneindan was formed via a singlet excited state.

Previously, the benzophenone-sensitized irradiation of bicyclo[3.2.2]nona-3,6,8-trien-2-one (homobarrelenone) (**1**) was shown to give a tricyclic ketone (**2**),[2] while direct photolysis afforded the dihydroindenone (**3**).[3] Furthermore, the acetone-sensitized photolysis of 2-methylenehomobarrelene (**4**) resulted in two isomeric products (**5** and **6**) and the direct irradiation of **4** gave methylenedihydroindene (**7**)[4,5] via a concerted [1,3] vinyl shift. Recently, we prepared 2-methylenehomobarrelenes (**8**) from cyclohepta[*b*]furan-2-one derivatives and 2,3-bis(methoxycarbonyl)-7-oxanorbornadiene by a high-pressure cycloaddition-thermal cycloreversion procedure.[6] In this paper we describe the photochemical behaviors of these 2-methylenehomobarrelenes as well as the reaction mechanism.

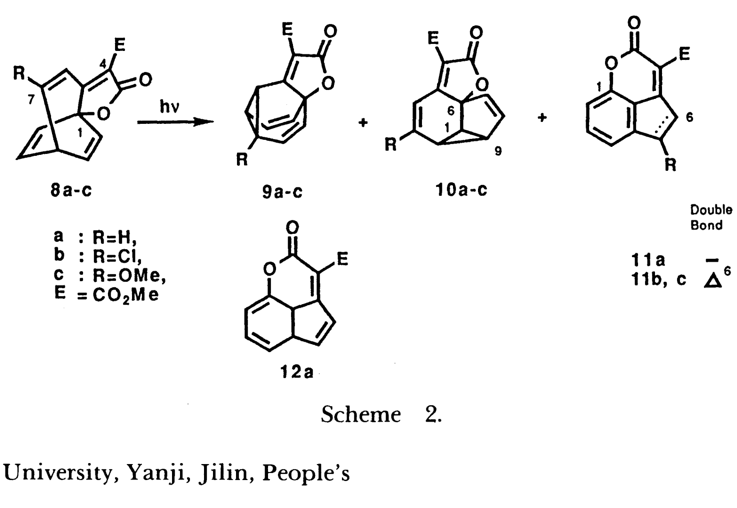


Scheme 1.

Photolysis of 2-Methylenehomobarrelenes. Upon UV-light irradiation by means of a 400-W high-pressure mercury lamp through a Pyrex-glass filter, 4-methoxycarbonyl-2-oxatricyclo[6.2.2.0^{1,5}]dodeca-4,6,9,11-tetraen-3-one (**8a**) furnished three photoproducts (**9a**—**11a**) in 19, 15, and 25% yields. The structures of these photolysates were determined to be derivatives of a barbaralylidene (type I), a tricyclo[4.3.0.0^{2,9}]nonadiene (type II), and an indanylidene (type III) according to spectral evidence. When the photolysis of **8a** was monitored by ^{1}H NMR spectroscopy, a new set of signals appeared at δ 3.66 (1H, dd, J=11.4, 2.2 Hz), 4.06 (1H, ddq, J=11.4, 4.0, 2.6 Hz), 5.47 (1H, dd, J=6.0, 2.2 Hz), 5.50 (1H, dd, J=9.5, 4.0 Hz), 5.88 (1H, ddd, J=9.5, 6.0, 2.6 Hz), 7.06 (1H, dd, J=5.5, 2.6 Hz), and 7.43 (1H, dd, J=5.5, 2.6 Hz) together with the signals of **9a**, **10a**, and **11a**. These new signals disappeared after silica-gel chromatography. From this evidence, the intermediary product was assigned to be a dihydroindene derivative (**12a**) which isomerized to an indan derivative (**11a**) upon being worked up.

Similarly, the products obtained from 7-chloro-4-methoxycarbonyl-2-oxatricyclo[6.2.2.0^{1,5}]dodeca-4,6,9,11-tetraen-3-one (**8b**) and 7-methoxy-4-methoxycarbonyl-2-oxatricyclo[6.2.2.0^{1,5}]dodeca-4,6,9,11-tetraen-3-one (**8c**) were type I (**9b** and **9c**), type II (**10b** and **10c**), and type III (**11b** and **11c**).

Mechanistic Considerations. In order to determine



Scheme 2.

---

† On leave from Yanbian University, Yanji, Jilin, People's Republic of China.

Table 1. Product Distributions of Photolysis in the Presence of 1,3-Pentadiene

Time/min	8a			9a			10a			11a+12a		
	A	B	C	A	B	C	A	B	C	A	B	C
15	85	84	86	3	3	3	4	3	3	9	10	8
30	75	73	74	4	5.5	5	6	6.5	6	15	15	15
45	71	67.5	69	6	6.5	6	7	8	7	16	18	17
60	62	58	61	7	10	8	8	10	9	23	22	22
105	45	43	44	10	12	15	13	15	13	32	30	28
175	29	26	30	15	16	14	17	20	18	39	38	38

Photolysis conditions: A, 0.29 mol dm^{-3} of **8a** in $CDCl_3$. B, 0.29 mol dm^{-3} of **8a** and 0.64 mol dm^{-3} of 1,3-pentadiene in $CDCl_3$. C, 0.29 mol dm^{-3} of **8a** and 1.42 mol dm^{-3} of 1,3-pentadiene in $CDCl_3$.

Table 2. Products Distributions of Photolysis in Acetone

Time/min	8a		9a		10a		11a+12a	
	A	D	A	D	A	D	A	D
10	89	—	—	—	4	—	8	—
25	79	78.5	3	2.5	5	5	12	14
55	65	66	4	4	9	7	22	22.5
115	45	45.5	6	10	14	14.5	35	30
175	28	31.5	9	13	17	18.5	45	37

Photolysis conditions: A, in $CDCl_3$. D, in acetone-d_6.

Table 3. Products Distributions of Benzophenone-Sensitized Photolysis

Time/min	8a		9a		10a		11a+12a	
	A	E	A	E	A	E	A	E
6	88	90	2	3	3	4	7	3
12	80	79	4	6	5	9	11	6
18	70	66	6	10	7	15	17	10
24	69	60	7	13	7	16	18	12
84	22	15	15	25	17	37	46	24

Photolysis conditions: A, 0.21 mol dm^{-3} of **8a** in $CDCl_3$. E, 0.21 mol dm^{-3} of **8a** and 0.24 mol dm^{-3} of benzophenone in $CDCl_3$.

the multiplicity of the excited state, reactions of **8a** with 1,3-pentadiene were traced by means of ^{1}H NMR spectroscopy. Distributions of photolysates, together with results of the photolyses in acetone and of the benzophenone-sensitized photolysis, are summerized in Tables 1—3 and Fig. 1.

As shown in Table 1, product distributions from **8a** were insensitive to the concentrations of 1,3-pentadiene, a triplet quencher. No quenching by 1,3-pentadiene indicates that a singlet state of **8a** can lead to photolysates. However, a triplet intermediate could not be ruled out, since the rate of the intramolecular rearrangements to photolysates could occur more rapidly than a diffusion controlled rate. Product distributions in acetone were almost similar to those in chloroform. The benzophenone-sensitized photolysis of **8a**, however, showed that the yields of **9a** and **10a** increased roughly twice and those of **11a** and **12a** decreased by roughly one half, with a small increasement of the consumption of **8a**. Therefore, **9a** and **10a** formed via a

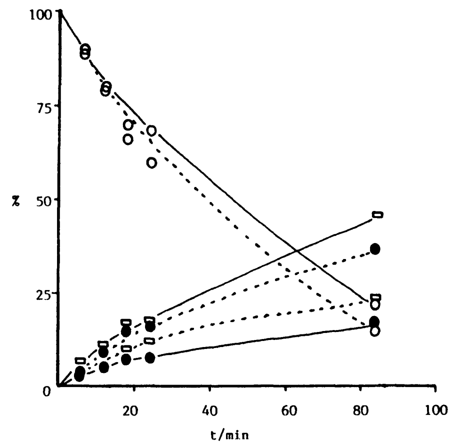
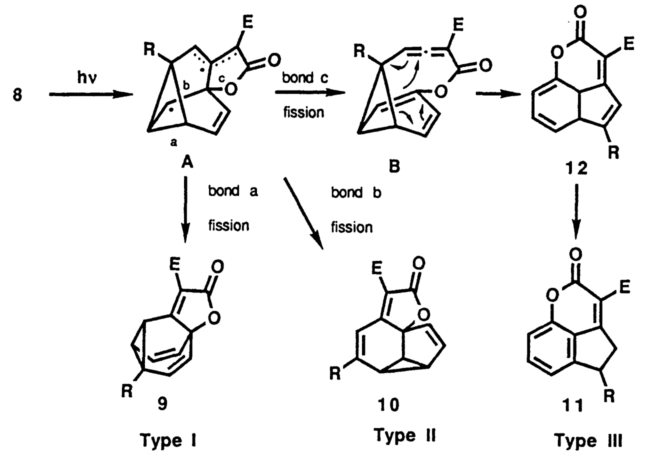


Fig. 1. Time-course of benzophenone-sensitized photolysis of **8a**.
——: in $CDCl_3$, ------: with benzophenone in $CDCl_3$.
○: **8a**, ●: **10a**, □: **11a**+**12a**.



Scheme 3.

triplet excited state and **11a** and **12a** via a singlet excited state.

The formation of photolysates can be explained by di-π-methane rearrangements,[7] as shown in Scheme 3. Bond-a fission in a diradical **A** gave type-I products, while bond-b fission gave type-II products. On the other hand, bond-c fission led to a tricyclic allene derivative (**B**); further, an electrocyclic [$4\pi s+2\pi a+2\sigma s$] path should give a dihydroindan derivative (**12**). Subsequent aromatization and a dehydrogenation of **12** gave type-III products.

These results are as same as those of the previously reported **4**[4,5] and **1**[2,3] in respect to not only the product distributions, but also the multiplicities of the concerned excited state.

Experimental

Elemental analyses were performed by Miss S. Hirashima, of Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured by a JEOL 270 H Spectrometer in a $CDCl_3$ solution, unless otherwise specified, and the chemical shifts expressed were in δ unit. The mass spectra were measured with a JEOL 01SG-2 Spectrometer at 70 eV. The IR spectra were taken in a $CHCl_3$ solution using a Jasco IR-A 102 Spectrometer. The UV spectra were measured by a Hitachi U-3200 Spectrophotometer.

Irradiation of 8. A $CHCl_3$ solution (1 cm^3) of **8** (**8a**, 160 mg; **8b**, 250 mg; **8c**, 223 mg) was irradiated for 3 h with a 400-W high-pressure mercury lamp through a Pyrex filter and the reaction was monitored by ^{1}H NMR spectroscopy. The solvent was evaporated and the residue was purified by a silica-gel column and HPLC to give products (**9**—**11**) and the recovered **8** (**8a**, 45.5 mg; **8b**, 116 mg; **8c**, 58 mg).

9a: Colorless crystals, mp 122—123 °C, 22 mg, 19%. Found: C, 67.96; H, 4.14%. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38%. ^{1}H NMR δ=3.0—3.1 (2H, m), 3.87 (3H, s), 4.01 (1H, t, J=7.0 Hz), 5.7 (2H, m), and 6.19 (2H, dm, J=8.8 Hz). ^{13}C NMR δ=22.0, 33.9 (2C), 52.1, 82.0, 112.0, 119.4 (2C), 128.5 (2C), 162.1, 167.3, and 176.2. IR ν: 1785, 1775, 1715, 1660, and 1440 cm^{-1}. UV (MeOH) λ_{max}: 234.0 (ε 11200) and 282.4 nm (4450). MS m/z (%) 230 (M$^+$, 30), 170 (33), 115 (base), and 91 (74).

10a: Colorless crystals, mp 155—157 °C, 17 mg, 15%. Found: C, 67.59; H, 4.28%. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38%. ^{1}H NMR δ=2.36 (1H, td, J=7.0, 4.4 Hz), 2.94 (1H, ddm, J=7.0, 5.9 Hz), 3.02 (1H, ddd, J=7.0, 5.9, 2.6 Hz), 3.88 (3H, s), 5.33 (1H, dm, J=5.5 Hz), 6.03 (1H, ddd, J=5.5, 2.6, 0.7 Hz), 6.34 (1H, dd, J=9.9, 4.4 Hz), and 7.24 (1H, d, J=9.9 Hz). ^{13}C NMR δ=29.5, 39.1, 43.5, 52.1, 89.6, 111.5, 123.7, 132.2, 133.7, 138.0, 161.8, 167.6, and 172.8. IR ν: 1780, 1715, 1630, and 1440 cm^{-1}. UV (MeOH) λ_{max}: 225.2 (ε 6300), 273.0 (7000), and 314.6 nm (8400). MS m/z (%) 230 (M$^+$, 24), 202 (32), 198 (65), 170 (55), 142 (40), 131 (33), 115 (base), 114 (40), 89 (32), and 76 (34).

11a: Colorless crystals, mp 172—173 °C, 29.1 mg, 25%. Found: C, 67.87; H, 4.29%. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38%. ^{1}H NMR δ=3.3—3.4 (2H, m), 3.5—3.6 (2H, m), 3.94 (3H, s), 7.10 (1H, d, J=7.7 Hz), 7.23 (1H, d, J=7.0 Hz), and 7.61 (1H, dd, J=7.7, 7.0 Hz). ^{13}C NMR δ=31.4, 33.1, 52.2, 110.8, 112.4, 120.3, 125.5, 135.9, 149.1, 151.9, 158.8, 164.5, and 171.5. IR ν:1755, 1740, and 1600 cm^{-1}. UV (MeOH) λ_{max}: 207.8 (ε 31400), 232.0 (8500 sh), 242.0 (4700 sh), and 309.4 nm (17150). MS m/z (%) 230 (M$^+$, 42), 199 (49), 198 (base), 170 (34), 115 (52), 114 (45), and 57 (36).

9b: Colorless crystals, mp 124—126 °C, 67 mg, 50%. Found: C, 59.38; H, 3.31%. Calcd for $C_{13}H_9O_4Cl$: C, 59.00; H, 3.43%. ^{1}H NMR δ=3.36 (1H, ddm, J=7.7, 6.2 Hz), 3.90 (3H, s), 4.29 (1H, d, J=7.7 Hz), 5.76 (1H, d, J=9.1 Hz), 5.87 (1H, dd, J=8.8, 6.2 Hz), 6.18 (1H, d, J=9.1 Hz), and 6.24 (1H, dd, J=8.8, 1.1 Hz). ^{13}C NMR δ=30.9, 43.5, 52.3, 53.3, 81.0, 113.2, 119.6, 123.3, 127.2, 129.2, 161.5, 166.6, and 170.3. IR ν: 1785, 1720, 1665, 1605, and 1440 cm^{-1}. UV (MeOH) λ_{max}: 227.6 (ε 12100) and 279.4 nm (5500).

10b: Colorless crystals, mp 109—110 °C, 23 mg, 17%. Found: C, 59.09; H, 3.19%. Calcd for $C_{13}H_9O_4Cl$: C, 59.00; H, 3.43%. ^{1}H NMR δ=2.53 (1H, t, J=7.7 Hz), 2.99 (1H, dd, J=7.7, 5.9 Hz), 3.10 (1H, ddd, J=7.7, 5.9, 2.9 Hz), 3.89 (3H, s), 5.39 (1H, dd, J=5.5, 0.7 Hz), 6.15 (1H, ddd, J=5.5, 2.9, 0.8 Hz), and 7.31 (1H, s). ^{13}C NMR δ=34.7, 38.6, 42.4, 52.3, 88.9, 111.6, 121.9, 133.1, 133.3, 143.8, 161.0, 167.1, and 171.5. IR ν: 1780, 1715, 1630, 1540, and 1440 cm^{-1}. UV (MeOH) λ_{max}: 226.0 (ε 5900) and 300.8 nm (9900). MS m/z (%) 266 (M$^+$+2, 9), 264 (M$^+$, 41), 236 (41), 206 (35), 204 (41), 197 (86), 178 (31), 149 (65), 126 (49), 114 (65), 113 (60), 102 (33), 87 (31), 75 (51), 73 (41), 63 (50), 62 (36), 59 (39), and 42 (base).

11b: Colorless crystals, mp 151 °C, 8.7 mg, 6%. Found: C, 59.70; H, 2.49%. Calcd for $C_{13}H_7O_4Cl$: C, 59.45; H, 2.69%. ^{1}H NMR δ=3.98 (3H, s), 7.03 (1H, s), 7.16 (1H, d, J=8.4 Hz), 7.26 (1H, d, J=7.0 Hz), and 7.51 (1H, dd, J=8.4, 7.0 Hz). ^{13}C NMR δ=52.9, 114.0, 116.7, 117.1, 118.2, 123.1, 134.1, 137.0, 148.8, 149.4, 152.4, 158.1, and 162.9. IR ν: 1760, 1730, 1665, 1620, 1495, and 1460 cm^{-1}. UV (MeOH) λ_{max}: 246.4 (ε 10600), 290.0 (10600), and 385.4 nm (8300). MS m/z (%) 264 (M$^+$+2, 20), 262 (M$^+$, 37), 233 (38), 231 (75), 204 (48), 159 (52), 147 (66), 85 (52), 73 (42), and 42 (base).

9c: Colorless crystals, mp 102—104 °C, 56.4 mg, 34%. Found: C, 64.72; H, 4.44%. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65%. ^{1}H NMR δ=3.35 (1H, ddm, J=8.1, 6.2 Hz), 3.55 (3H, s), 3.89 (3H, s), 4.12 (1H, d, J=8.1 Hz), 5.78 (1H, d, J=9.2 Hz), 5.82 (1H, dd, J=8.8, 6.2 Hz), 6.09 (1H, d, J=8.8 Hz), and 6.11 (1H, d, J=9.2 Hz). ^{13}C NMR δ=30.0, 44.5, 52.1, 57.9, 81.8, 82.0, 111.2, 119.2, 119.9, 123.6, 125.4, 162.0, 167.3, and 172.5. IR ν: 1780, 1715, 1655, and 1440 cm^{-1}. UV (MeOH) λ_{max}: 231.6 (ε 11600) and 290.4 nm (7000). MS m/z (%) 260 (M$^+$, 49), 228 (35), and 121 (base).

10c: Colorless crystals, mp 143—145 °C, 5 mg, 3%. Found: C, 64.62; H, 4.55%. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65%. ^{1}H NMR δ=2.31 (1H, t, J=7.7 Hz), 2.9 (2H, m), 3.81 (3H, s), 3.88 (3H, s), 5.35 (1H, d, J=5.9 Hz), 6.05 (1H, ddd, J=5.9, 2.2, 1.1 Hz), and 6.47 (1H, s). ^{13}C NMR δ=29.9, 36.0, 39.7, 51.8, 56.7, 89.1, 96.1, 117.5, 132.2, 134.6, 162.5, 166.3, 168.2, and 177.6. IR ν: 1770, 1705, 1610, and 1560 cm^{-1}. UV (MeOH) λ_{max}: 232.0 (ε 5600) and 329.8 nm (17000). MS m/z (%) 260 (M$^+$, 21), 73 (base), and 42 (78).

11c: Colorless crystals, mp 197 °C, 6.7 mg, 4%. Found: C, 64.80; H, 3.62%. Calcd for $C_{14}H_{10}O_5$: C, 65.11; H, 3.90%. ^{1}H NMR δ=3.97 (3H, s), 4.11 (3H, s), 6.08 (1H, s), 7.10 (1H, d, J=8.4 Hz), 7.19 (1H, d, J=7.3 Hz), and 7.41 (1H, dd, J=8.4, 7.3 Hz). ^{13}C NMR δ=52.5, 59.3, 96.1, 109.7, 116.8, 117.4, 118.1, 133.1, 134.2, 148.4, 155.5, 158.9, 164.5, and 174.8. IR ν: 1760, 1725, 1620, and 1540 cm^{-1}. UV (MeOH) λ_{max}: 209.8 (ε 30450), 245.6 (7100), 255.0 (7000), 264.6 (6400), 299.0 (10100), and 370.2 nm (10200). MS m/z (%) 258 (M$^+$, 52), 227 (base), 200 (43), 100 (48), and 74 (39).

References

1) Synthetic Photochemistry. XLIV. N. Kato, H. Takeshita, H. Kataoka, S. Ohbuchi, and S. Tanaka, *J. Chem. Soc., Perkin Trans. 1,* in press.

2) A. S. Kende and Z. Goldschmidt, *Tetrahedron Lett.*, **1970**, 783.

3) M. J. Goldstein and B. G. Odell, *J. Am. Chem. Soc.*, **89**, 6356 (1967).

4) Z. Goldschmidt and A. Worchel, *Tetrahedron Lett.*, **1973**, 3621.

5) Z. Goldschmidt and A. Worchel, *Tetrahedron Lett.*, **1973**, 3623.

6) G. R. Tian, S. Sugiyama, A. Mori, H. Takeshita, M. Higashi, and H. Yamaguchi, *Chem. Lett.*, **1988**, 941.

7) H. E. Zimmerman, *Acc. Chem. Res.*, **15**, 312 (1982).