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Synthetic Photochemistry. XLI.1) Photorearrangement of 5-Alkyl-1-hydroxy-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ones to 2-Alkyl-3-oxatricyclo[3.3.0.0^{2,8}]octane-4,6-diones

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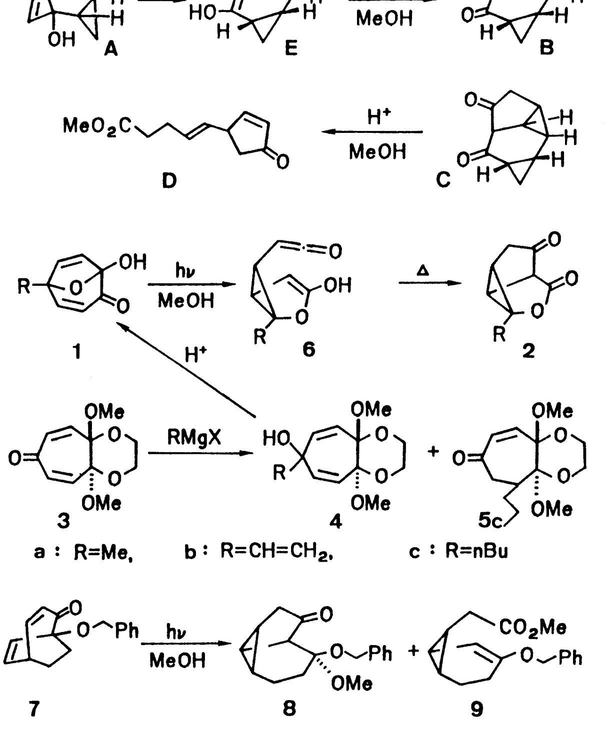
Synopsis. The irradiations of 5-alkyl-1-hydroxy-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ones, either in benzene or methanol by means of a high-pressure mercury lamp produced 2-alkyl-3-oxatricyclo[3.3.0.0^{2,8}]octane-4,6-diones. Although the intermediate ketenes could be detected by low-temperature NMR, no adduct was formed in protic solvents.

In the late 1960s, Kende2) and Chapman3) respectively studied photorearrangements of bicyclic dienones and trienones via ketene intermediates, which were detected and characterized by low-temperature IR and ^{1}H NMR spectroscopies. Many related works have been reported. Among them particularly interesting was a facile formation of a potential precursor of prostanoids by photolysing 1-hydroxytricyclo[3.3.2.0^{2,4}]deca-6,9-dien-8-one (**A**) to a methoxycarbonyl derivative (**B**) in methanol and a tetracyclic β-diketone (**C**) and a cyclopentenone (**D**) in a mixed solution of methanol and acetic acid via a ketene (**E**).4)

The photolysis of 5-alkyl-1-hydroxy-8-oxabicyclo-[3.2.1]octa-3,6-dien-2-ones (**1a**, R=CH_3; **1b**, R=CH=CH_2, and **1c**, R=C_4H_9) revealed a facile rearrangement to 2-alkyl-3-oxatricyclo[3.3.0.0^{2,8}]octa-4,6-diones (**2a**, **2b**, and **2c**), but no solvolysis occurred. The results will be briefly described herein.



Scheme 1.

The substrates, **1**, were prepared by Grignard reaction of *p*-tropoquinone bisacetal (**3**)5) followed by an acid hydrolysis of alcohols (**4a**, **4b**, and **4c**) to spontaneously give bicyclic acetals, **1**. In a preparation of **4c**, a by-product, conjugate addition product **5c**, was isolated.

Structural evidence for **1** was obtained from the ^{1}H and ^{13}C NMR spectra; e.g., four vinylic proton signals appeared as two AB-type doublets with J=9.5 and J=5.5 Hz, respectively. Accordingly, **1** can only be explained as the 8-oxabicyclo[3.2.1]octadienone derivative.

When **1a** was irradiated with a 400-W high-pressure mercury lamp in benzene, a single product (**2a**, 57%) was obtained. Its NMR spectrum showed no C=C bond, and its IR spectrum [1790 and 1740 cm^{-1}] showed $\nu_{C=O}$ bands due to γ-lactone and cyclopentanone, but the former was ca. 20 cm^{-1} higher than those of ordinary γ-lactones, suggesting a partial enol lactone character by the π-like cyclopropyl linkage. These allowed us to assign the structure as shown in Scheme 1. In addition, the irradiation of **1a** in methanol only gave **2a** in 49% yield.

Similar irradiations of **1b** and **1c** derivatives in methanol formed corresponding γ-lactones (**2b**, 55%, and **2c**, 81%), but no methanol adduct.

Although adducts were undetectable, the intermediary of the ketene was certain: When the photoreaction of **1a** was carried out in methanol-d_4 at −80 °C, its low-temperature ^{1}H NMR revealed a formation of a new compound **6a** as showing an olefinic proton signal ascribable to a ketene. Warming up the solution to room temperature confirmed the formation of **2a**-d_1, whose yield from **1a** was 93% according to the NMR, which diminished the signal (δ=2.72) of *exo*-H-7 as shown in Fig. 1. Therefore, **6a** must be the ketene.

An apparent contrast to the photolysis of **A**, which gave **C** only in a mixed solution of methanol and acetic acid, is noteworthy. Since we obtained **2** by irradiating **1** in methanol without acetic acid, the Uyehara's proposal, an involvement of acetic acid to form **C**, should not be operative in **1** to **2**. In view of a facile formation of tricyclic compounds, **2**, reinvestigations of the bicyclo[3.2.*n*]dienones is desirable to understand the generality of the process.

Indeed, an irradiation of 1-benzyloxybicyclo[3.2.2]-nona-3,6-dien-2-one (**7**) in methanol gave 5-benzyloxy-5-methoxytricyclo[4.3.0.0^{2,9}]nonan-7-one (**8**), in 64% yield, together with methyl [3-benzyloxybicyclo[4.1.0]-hept-2-en-7-yl]acetate (**9**), in 9% yield.

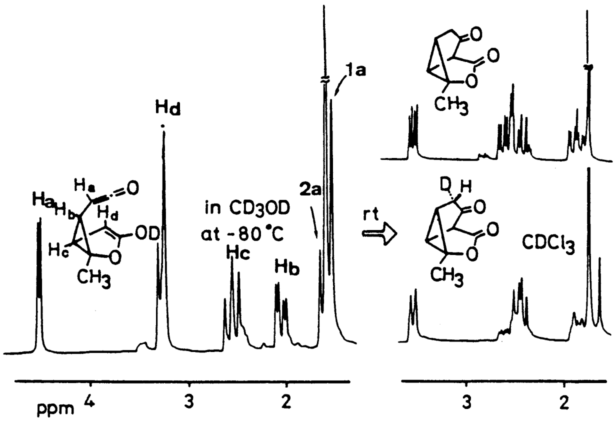


Fig. 1. Low-temperature NMR identification of ketene **6a**. A part of the doublet signal, Hd, overlapped with the solvent signal.

Nevertheless, a replacement of the carbon chain to the oxygen bridge in the vicinity of the hydroxyl group dramatically altered the course of the rearrangement to form cyclopropanes exclusively. The tricyclic derivatives, **2**, will be a good starting material for certain functionalized carbocycles since its rigid carbon skeleton will allow the introduction of various substituents via stereocontrolled reactions.

Experimental

Preparation of 4 (General Method). The starting materials, **4a**, **4b** and **4c**, were prepared from **3** by Grignard reaction. After the ordinary workup by hydrolysis and extraction with ether, the organic extracts were chromatographed on a silica-gel column to give **4** along with **5**.

4a [a colorless oil, 98%. Found: *m/z*, 242.1136. Calcd for $C_{12}H_{18}O_5$: M, 242.1152. ¹H NMR $\delta^{6)}$=1.37 (3H, s), 2.28 (1H, br s), 3.24 (3H, s), 3.28 (3H, s), 3.3—3.4 (4H, m), 5.40 (1H, d, J=12.5 Hz), 5.43 (1H, d, J=12.5 Hz), 5.73 (1H, dd, J=12.5, 2 Hz), and 5.83 (1H, dd, J=12.5, 2 Hz). ¹³C NMR δ=28.5, 49.1, 49.2, 58.6 (2C), 71.5, 96.4, 97.1, 126.8, 127.2, 137.2, and 139.0. IR ν: 3550, 1450, 1400, 1215, 1150, 1090, 1065, and 1000 cm⁻¹].

4b [a pale yellow oil, 69%. Found: *m/z*, 254.1149. Calcd for $C_{13}H_{18}O_5$: M, 254.1151. ¹H NMR δ=2.40 (1H, br s), 3.18 (3H, s), 3.27 (3H, s), 3.4—4.2 (4H, m), 5.12 (1H, dd, J=10.2, 1.5 Hz), 5.36 (1H, dd, J=17, 1.5 Hz), 5.22 (1H, d, J=12.5 Hz), 5.47 (1H, d, J=12.5 Hz), 5.65 (1H, dd, J=12.5, 2 Hz), 5.73 (1H, dd, J=12.5, 2 Hz), and 5.83 (1H, dd, J=17, 10.2 Hz). ¹³C NMR δ=49.1, 49.3, 58.5 (2C), 74.7, 97.4, 96.2, 113.8, 127.7, 127.9, 134.8, 136.7, and 139.8].

4c [a yellow oil, 48%. Found: C, 63.12; H, 8.46%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%. ¹H NMR δ=0.89 (3H, t, J=6 Hz), 1.1—1.5 (4H, m), 1.5—1.8 (2H, m), 2.18 (1H, br s), 3.22 (3H, s), 3.25 (3H, s), 3.3—4.2 (4H, m), 5.45 (1H, d, J=12.5 Hz), 5.47 (1H, d, J=12.5 Hz), 5.72 (1H, dd, J=12.5, 1.5 Hz), and 5.75 (1H, dd, J=12.5, 1.5 Hz). ¹³C NMR δ=14.0, 23.1, 25.8 (2C), 42.2, 49.2, 58.7 (2C), 73.5, 96.8 (2C), 127.8, 128.9, 136.7, and 138.1. IR ν: 3450, 1450, 1400, 1210, 1145, 1100, 1060, and 1000 cm⁻¹].

5c [a pale yellow oil, 23%. Found: C, 63.30; H, 8.60%. Calcd for $C_{15}H_{24}O_5$: C, 63.36; H, 8.51%. ¹H NMR δ=0.90 (3H, t, J=6 Hz), 1.1—1.6 (4H, m), 1.7—2.0 (2H, m), 2.1 (1H, br m), 2.62 (2H, d, J=8 Hz), 3.15 (3H, s), 3.29 (3H, s), 3.4—4.2 (4H, m), and 6.07 (2H, s). ¹³C NMR δ=14.2, 22.9, 30.9 (2C), 40.1, 45.3, 47.2, 49.2, 58.7, 59.1, 98.8, 100.4, 133.5, 141.2, and 202.7. IR ν: 1680, 1460, 1380, 1215, 1135, and 1090 cm⁻¹].

Hydrolysis of 4 to 1. An acetone solution containing 5% HCl (7 cm³) of **4** (100 mg) was stirred at room temperature for 30 min. After evaporation of the volatile material in vacuo, the residue was diluted with water and extracted with $CHCl_3$. Silica-gel column chromatography of the extract gave **1**.

1a [a pale yellow oil, 59%. Found: *m/z*, 152.0479. Calcd for $C_8H_8O_3$: M, 152.0474. ¹H NMR δ=1.63 (3H, s), 4.49 (1H, br s), 5.61 (1H, d, J=9.6 Hz), 6.16 (1H, d, J=5.4 Hz), 6.74 (1H, d, J=5.4 Hz), and 7.19 (1H, d, J=9.6 Hz). ¹³C NMR δ=21.4, 85.9, 107.4, 120.7, 133.7, 145.7, 158.1, and 193.2. IR ν: 3400, 1700, 1445, and 1305 cm⁻¹].

1b [a pale yellow oil, 20%. Found: *m/z*, 164.0468. Calcd for $C_9H_8O_3$: M, 164.0471. ¹H NMR δ=4.54 (1H, br s), 5.39 (1H, dd, J=10.5, 1 Hz), 5.50 (1H, dd, J=17.5, 1 Hz), 6.12 (1H, dd, J=17.5, 10.5 Hz), 5.64 (1H, d, J=9.6 Hz), 6.27 (1H, d, J=5.9 Hz), 6.76 (1H, d, J=5.9 Hz), and 7.26 (1H, d, J=9.6 Hz). IR ν: 3400, 1700, 1300, and 1180 cm⁻¹].

1c [a yellow oil, 82%. Found: *m/z*, 194.0939. Calcd for $C_{11}H_{14}O_3$: M, 194.0940. ¹H NMR δ=0.91 (3H, t, J=6 Hz), 2.1—2.7 (4H, m), 2.7—3.1 (2H, m), 4.65 (1H, br s), 5.60 (1H, d, J=9.5 Hz), 6.14 (1H, d, J=5.8 Hz), 6.70 (1H, d, J=5.8 Hz), and 7.19 (1H, d, J=9.5 Hz). ¹³C NMR δ=13.9, 22.9, 26.1, 34.5, 89.1, 107.4, 121.0, 133.7, 145.0, 157.7, and 193.5. IR ν: 3400, 1700, 1460, and 1370 cm⁻¹. UV $\lambda_{\max}^{\mathrm{MeOH}}$: 224 nm (ε=2800), 267 (630), and 376 (70)].

Photorearrangement of 1a. a) A benzene solution (2 cm³) of **1a** (65 mg) was irradiated with a high-pressure mercury lamp for 2 h under an N_2 atmosphere with cooling by water. After evaporation of the solvent, the residue was chromatographed on a silica-gel column to give **2a** [a colorless oil, 37.1 mg; 57%. Found: *m/z*, 152.0468. Calcd for $C_8H_8O_3$: M, 152.0471. ¹H NMR δ=1.72 (3H, s), 1.89 (1H, ddd, J=7.5, 6, 1.5 Hz), 2.40 (1H, dd, J=7.5, 5 Hz), 2.43 (1H, dd, J=19.5, 1.5 Hz), 2.72 (1H, ddd, J=19.5, 6, 2.5 Hz), and 3.54 (1H, dd, J=5, 2.5 Hz). ¹³C NMR δ=18.4, 25.3, 26.6, 32.9, 58.7, 69.9, 172.1, and 206.5. IR ν: 1790, 1740, 1440, 1410, and 1330 cm⁻¹].

b) An MeOH solution (2 cm³) of **1a** (44 mg) was irradiated under the similar conditions as above. Silica-gel column chromatography of the product gave **2a** [22 mg; 49%].

Photorearrangement of 1b. An MeOH solution (2 cm³) of **1b** (36.7 mg) was similarly irradiated to give **2b** [a pale yellow oil, 20.1 mg; 55%. Found: *m/z*, 164.0476. Calcd for $C_9H_8O_3$: M, 164.0471. ¹H NMR δ=2.15 (1H, ddd, J=7, 6, 2 Hz), 2.34 (1H, dd, J=7, 5 Hz), 2.50 (1H, dd, J=19.5, 2 Hz), 2.78 (1H, ddd, J=19.5, 6, 2.5 Hz), 3.58 (1H, dd, J=5, 2.5 Hz), 6.25 (1H, dd, J=10.5, 1.5 Hz), 6.44 (1H, dd, J=17, 1.5 Hz), and 6.83 (1H, dd, J=17, 10.5 Hz). IR ν: 1800, 1750, 1410, and 1215 cm⁻¹].

Photorearrangement of 1c. Similarly, an MeOH solution (2 cm³) of **1c** (36 mg) was irradiated to give **2c** [a pale yellow oil, 29.1 mg; 81%. Found: C, 67.75; H, 7.41%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%. ¹H NMR δ=0.92 (3H, t, J=6 Hz), 1.1—1.8 (4H, m), 1.8—2.1 (3H, m), 2.42 (1H, dd, J=19.5, 2 Hz), 2.43 (1H, dd, J=8, 5 Hz), 2.70 (1H, ddd, J=19.5, 6, 2.7 Hz), and 3.52 (1H, dd, J=5, 2.5 Hz). ¹³C NMR δ=13.9, 22.4, 24.4, 25.6, 27.9, 32.2, 32.8, 58.4, 73.4, 172.2, and 206.4. IR ν: 1800, 1740, 1460, 1410, 1195, 1140, and 1075 cm⁻¹].

Photorearrangement of 1a in Methanol-d_4. A CD_3OD solution (0.3 cm³) of **1a** (32 mg) was irradiated at −80 °C for 2 h to observe **6a** [¹H NMR (CD_3OD) at −80 °C δ=1.60 (3H, s), 2.05 (1H, dd, J=7.5, 3 Hz), 2.58 (1H, dd, J=7.5, 6.5 Hz), 3.30 (1H, d, J=6.5 Hz), and 4.56 (1H, d, J=3 Hz)]. An ordinary workup of the mixture via silica-gel column chromatography gave **2a**-d_1 [30 mg; 93%].

Diels-Alder Reaction of 2-Benzyloxytropone with Ethylene. A toluene solution (10 cm³) of 2-benzyloxytropone (1.80 g) saturated with ethylene at 40 bar was placed in an autoclave and heated at 160 °C for 24 h. The mixture was chromatographed to give **7** [colorless crystals, mp 67—68 °C, 890 mg; 44%. Found: C, 80.40; H, 6.79%. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71%. ^{1}H NMR δ=1.6—2.3 (4H, m), 3.30 (1H, m), 4.75 (2H, s), 5.82 (1H, dd, J=11.5, 0.5 Hz), 6.06 (1H, d, J=9 Hz), 6.48 (1H, dd, J=9, 7 Hz), 7.01 (1H, dd, J=11.5, 8.5 Hz), and 7.2—7.5 (5H, m), ^{13}C NMR δ=24.4, 27.8, 36.5, 66.9, 87.4, 127.4, 127.7 (2C), 128.4 (2C), 128.7, 130.8, 136.7, 139.4, 152.2, and 195.9. IR ν: 1675, 1660, 1630, 1215, 995, and 740 cm^{-1}].

Photolysis of 7 to 8 and 9. An MeOH solution (5 cm^3) of **7** (370 mg) was irradiated with a high-pressure Hg lamp through a Pyrex-glass filter for 6 h. The mixture was then chromatographed on silica-gel column to give **8** [colorless crystals, mp 45—48 °C, 268 mg; 64%. Found: C, 74.74; H, 7.53%. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40%. ^{1}H NMR δ=0.7—2.2 (7H, m), 2.28 (1H, dd, J=20, 2 Hz), 2.60 (1H, ddd, J=20, 6, 2 Hz), 3.02 (1H, dt, J=7, 2 Hz), 3.29 (3H, s), 4.48 (2H, s), and 7.2—7.5 (5H, m). ^{13}C NMR δ=14.3, 14.9, 17.0, 18.1, 27.8, 37.7, 48.7, 49.8, 62.6, 65.4, 100.1, 127.6 (2C), 128.6 (2C), 138.8, and 217.9. IR ν: 1740 and 1110 cm^{-1}] and **9** [a colorless oil, 36.9 mg; 9%. Found: C, 74.94; H, 7.42%. ^{1}H NMR δ=1.0—2.4 (9H, m,), 3.64 (3H, s), 4.70 (1H, d, J=4 Hz), 4.73 (2H, s), and 7.29 (5H, m). ^{13}C NMR δ=12.2, 13.9, 18.6, 20.1, 26.3, 29.3, 51.6, 68.7, 91.2, 127.6 (2C), 127.8, 128.6 (2C), 137.6, 157.2, and 174.6. IR ν: 1730, 1710, 1419, and 1170 cm^{-1}].

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