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Synthetic Photochemistry LV.[1] Characterization of the Lumiketone-Type Photoproducts, Bicyclo[3.2.0]hept-3-en-2-ones, from 2,6-Cycloheptadien-1-ones[2]

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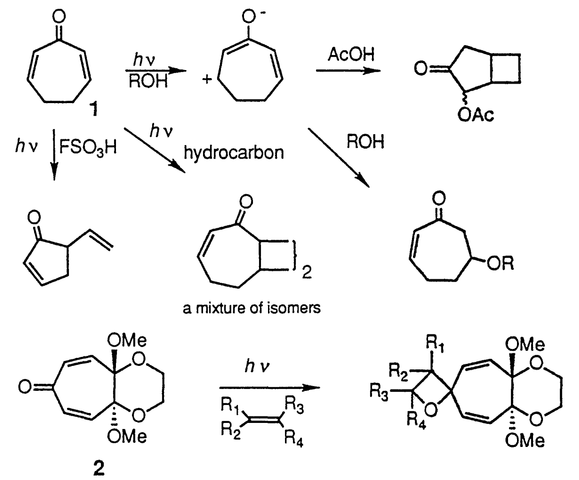
Unlike the parent 2,6-cycloheptadien-1-one, the UV-light irradiation of polysubstituted 2,6-cycloheptadien-1-ones gave bicyclo[3.2.0]hept-3-en-2-ones, lumiketone-like products, which subsequently photoisomerized to bicyclo[2.2.1]hept-2-en-7-ones. The reaction of cycloheptadienones to lumiketones was proven to proceed via a triplet excited state from both sensitization and quenching experiments.

The photorearrangement of 2,5-cyclohexadien-1-ones to bicyclo[3.1.0]hex-3-en-2-ones, lumiketones, has been extensively investigated from synthetic and mechanistic points of view.[3] The limitation of this photorearrangement has not yet been explored beyond the cyclohexadienone chromophore, and it is not known whether this is operative or not in the 2,6-cycloheptadien-1-one system, a homologous cross-conjugated system. Previously, upon irradiation of unsubstituted 2,6-cycloheptadien-1-one (**1**), formations of solvent-dependent photoproducts, i.e., a mixture of the head-to-head and the head-to-tail [2+2] cyclodimers in hexane, methanol adducts in methanol, bicyclo[3.2.0]heptan-3-ones in acetic acid,[4] and a 5-vinyl-2-cyclopenten-1-one in fluorosulfuric acid,[5] were reported. Herein, we wish to report the first occurrence of similar lumiketone-type products from several substituted 2,6-cycloheptadien-1-ones.



Scheme 1.

In connection to these, we have already reported that the reactions between *trans*-2,3,4a,9a-tetrahydro-4aα,9aβ-dimethoxy-7*H*-cyclohepta[1,4]dioxin-7-one (**2**), a cross conjugated cycloheptadienone having a cyclic acetal structure, and olefins exclusively yielded oxetane derivatives upon UV irradiation.[6] Without olefin, the irradiation of **2** afforded no photoproduct.

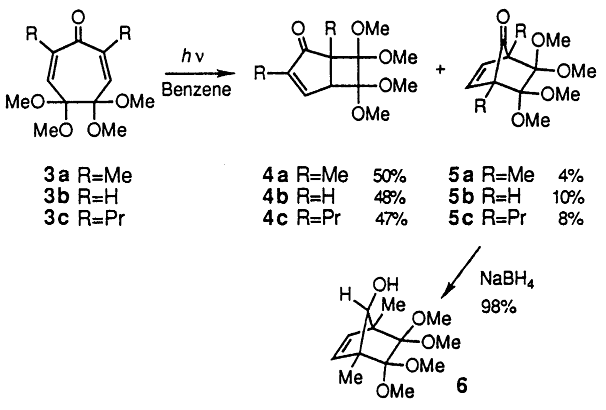
Results and Discussion

When a benzene solution of 4,4,5,5-tetramethoxy-2,7-dimethyl-2,6-cycloheptadien-1-one (**3a**)[7,8] was irradiated for 1 h by means of a 400-W high-pressure mercury lamp, two products (**4a** and **5a**) were isolated in 50 and 4% yields, respectively. Both of the products showed in their ^{13}C NMR spectra a carbonyl carbon signal, two olefinic carbon signals, and four sp^3-carbon signals, including two acetal carbons. The IR spectrum of the major product **4a** showed $\nu_{C=O}$ at 1710 cm^{-1}, which is appropriate for the cyclopentenone chromophore. All of these data are consistent with the proposed structure of **4a** to be 6,6,7,7-tetramethoxy-1,3-dimethylbicyclo[3.2.0]hept-3-en-2-one, a lumiketone-like product.

Since the second product **5a** revealed the presence of a symmetry element in the ^{13}C NMR spectrum and a strained carbonyl group at 1780 cm^{-1} in the IR spectrum, **5a** is 5,5,6,6-tetramethoxy-1,4-dimethylbicyclo[2.2.1]hept-2-en-7-one. A reduction of **5a** with sodium borohydride gave an alcohol (**6**) whose ^{13}C NMR spectrum retained the symmetry element. Furthermore, its ^{1}H NMR spectrum showed a doublet signal (J=12.8 Hz) of a methine proton on the carbon bearing a hydroxyl group at δ=3.06, which was coupled with the hydroxyl hydrogen. This indicates a tight intramolecular hydrogen bonding with a methoxyl group. The ^{1}H NMR signal for the methine proton appeared at a rather high field, suffering a shielding effect from the double bond. Therefore, the hydroxyl group is cis to the ethano bridge with tetramethoxyl groups.

Further irradiation of **4a** for 1 h gave **5a** in 33% yield. Similarly, **3b** and **3c** yielded corresponding photoproducts (**4b**; 48%, **4c**; 47%, **5b**; 10%, and **5c**, 8%).

It has been established that the photoreaction of cyclohexadienones to lumiketones proceeds via a triplet excited state by sensitized and quenching experiments.[3] In the present case, the direct irradiation of **3a**, a sensitized reaction with benzophenone, and a quenching experiment with isoprene were investi-



Scheme 2.

gated. A product identified by its ^{1}H NMR spectrum was **4a** in each experiment. The amount of **3a** was traced by the ^{1}H NMR spectrum using toluene as an internal standard (Fig. 1). The rate enhancement, measured by the decrease in **3a**, was ca. 1.5 when the reaction was carried out in the presence of benzophenone, a sensitizer. Although the quenching with isoprene was not so effective, it is evident that the triplet excited state was involved in the reaction of **3** to a lumiketone.

As has been verified in the photoreaction of cyclohexadienones,[3] a zwitterion (**7**) would be involved in the photoreaction of **3**. A subsequent rearrangement of **7** to bicyclo[3.2.0]hept-3-en-2-ones, the lumiketones, is a symmetry-allowed [1,4] sigmatropic shift. Further, a [1,3] sigmatropic shift[9] of the lumiketones should give symmetrical molecules, bicyclo[2.2.1]heptenones, as has been verified. An occurrence of the [1,3] sigmatropic shift should be characteristic for the cycloheptadienones; a photochemical [1,3] sigmatropic rearrangement of bicyclo[3.2.0]hept-3-en-2-one (**8**) gave bicyclo[2.2.1]hept-2-en-7-one (**9**) via a nonconcerted, biradical pathway and methyl cyclohexenecarboxylate derivative (**10**) via a concerted process.[10] In the cyclohexadienone derivatives, however, such a sigmatropic shift must lead to energetically disfavored strained bicyclo[2.1.1]hex-2-en-5-ones.

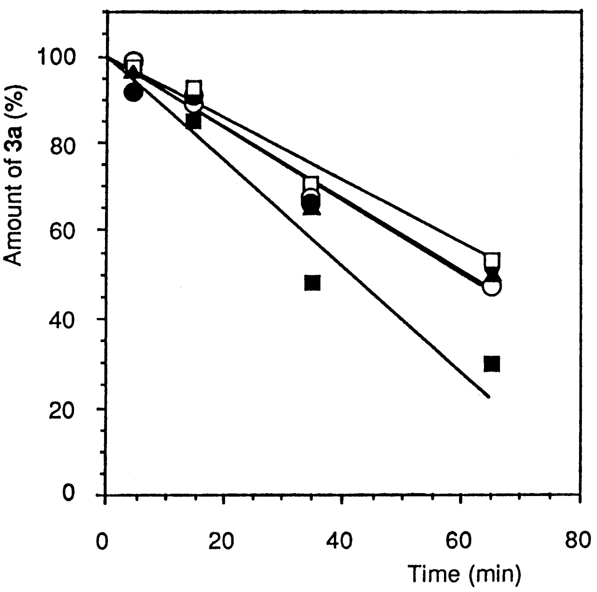
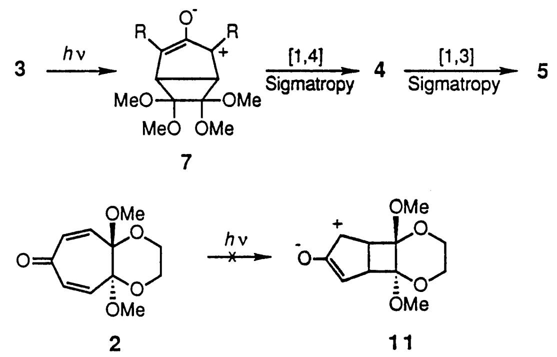
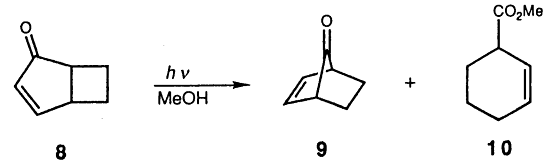


Fig. 1. Time-course of the benzophenone-sensitization and the isoprene-quenching expriments of **3a**: ○; 2.7 mg of **3a** in 0.6 cm^3 of benzene-d_6 (sample 1), ■; sample 1 and 70 mg of benzophenone, ▲; sample 1 and 7 mg of isoprene, ●; sample 1 and 14 mg of isoprene, and □; sample 1 and 28 mg of isoprene.



Scheme 3.



Scheme 4.

The inert nature of the intramolecular photorearrangement in **2** might be due to a severe ring strain in the trans-fused zwitterion (**11**). The different modes of photochemical changes revealed in **3** vs. **1** and **2** could be explained in terms of the substituent effect; the bulky substituents on C_4 and C_5 should inhibit an intermolecular approach to a double bond to form a [2+2] cyclodimer. Furthermore, the polysubstituted nature of **3** made the rates of the conformational change slow to decrease a self-quenching of the excited molecules.[11] The thermodynamic parameters of this interesting conformational change for **3** have been analyzed.[12]

In conclusion, the present results constitute the first observation of the lumiketone formation from cross-conjugated cycloheptadienones, which subsequently cause [1,3] sigmatropic isomerization to bicyclo[2.2.1]hept-2-en-7-one. The latter step has been never detected in the cyclohexadienone series, of which the expected products, bicyclo[2.1.1]hexenones, might be too strained to be formed.

Experimental

Elemental analyses were performed by Miss S. Hirashima and Miss T. Mizoguchi, of Institute of Advanced Material Study, Kyushu University. NMR spectra were measured by a JEOL FX 100 Model and a JEOL GSX 270 H Model spectrometers in a $CDCl_3$ solution (unless otherwise specified); chemical shifts are expressed in the unit δ. Mass spectra were measured with a JEOL 01SG-2 spectrometer. IR spectra were taken using a Jasco IR-A 102 spectrometer. UV spectra were measured by a Hitachi U-3200 spectrophotometer.

Photoreaction of 3a. A benzene solution (2.5 cm^3) of **3a** (177 mg) was irradiated for 1 h through a Pyrex filter by means of a 400 W high-pressure mercury lamp. The reaction mixture was purified by a HPLC (Microporasil, AcOEt-hexane) to give 88.7 mg (50%) of **4a** and 6.5 mg (4%) of **5a**.

4a: Colorless crystals, mp 69—70 °C. ^{1}H NMR δ=1.27 (3H, s), 1.84 (3H, dd, J=1.6, 1.5 Hz), 2.81 (1H, dq, J=2.9, 1.6 Hz), 3.24 (3H, s), 3.32 (3H, s), 3.38 (3H, s), and 7.16 (1H, dq, J=2.9, 1.5 Hz); ^{13}C NMR δ=10.9, 14.7, 49.9, 51.0, 51.2, 51.8 (2C), 53.7, 104.6, 104.7, 145.3, 152.0, and 209.2; IR (KBr) 3050—2850, 1710, 1640, 1450, 1270, and 1205 cm^{-1}; UV (MeOH) 227 nm (ε=5550); MS m/z (%) 256 (M$^+$, 24), 241 (53), 182 (28), 181 (27), 148 (46), 133 (100), 106 (51), 78 (21), and 60 (34).

Found: C, 61.10; H, 7.85%. Calcd for $C_{13}H_{20}O_5$: C, 60.92; H, 7.87%.

5a: Colorless crystals, mp 106—108 °C. ^{1}H NMR δ=1.32 (6H, s), 3.40 (6H, s), 3.47 (6H, s), and 6.25 (2H, s); ^{13}C NMR δ=9.8 (2C), 52.0 (2C), 52.5 (2C), 60.3 (2C), 106.9 (2C), 136.0 (2C), and 204.5; IR (KBr) 3050—2850, 1780, 1440, 1380, 1210, 1185, 1120, 1090, 1070, and 1025 cm^{-1}; UV (MeOH) 202 (ε=3500) and 227 nm (680 sh); MS m/z (%) 256 (M$^+$, 6), 241 (100), 213 (72), 182 (31), 148 (28), 139 (46), 133 (69), 105 (46), 78 (26), and 60 (26).

Found: 61.04; H, 7.99%. Calcd for $C_{13}H_{20}O_5$: C, 60.90; H, 7.87%.

Photoreaction of 3b. A $CDCl_3$ solution (0.3 cm^3) of **3b** (10.5 mg) was irradiated for 20 min. A HPLC purification gave 5 mg (48%) of **4b** and 1 mg (10%) of **5b**.

4b: Colorless crystals, mp 65—66 °C. ^{1}H NMR δ=3.00 (1H, d, J=7 Hz), 3.33 (3H, s), 3.34 (3H, s), 3.38 (3H, s), 3.4 (1H, underneath the signals of MeO groups), 3.42 (3H, s), 6.37 (1H, dd, J=5.5, 1.5 Hz), and 7.61 (1H, dd, J=5.5, 2.9 Hz); ^{13}C NMR δ=46.9, 49.2, 50.8, 51.1, 51.3, 51.8, 104.4, 105.3, 138.6, 159.2, and 205.5; IR ($CHCl_3$) 3050—2800, 1710, 1580, 1440, and 1340 cm^{-1}; UV (MeOH) 236 nm (ε=3100).

Found: C, 58.06; H, 7.13%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

5b: Colorless crystals, mp 77—78 °C. ^{1}H NMR δ=3.27 (2H, dd, J=2.6, 2.2 Hz), 3.35 (6H, s), 3.43 (6H, s), and 6.56 (2H, dd, J=2.6, 2.2 Hz); ^{13}C NMR δ=51.2 (2C), 51.6 (2C), 56.7 (2C), 106.4 (2C), 130.6 (2C), and 199.5; IR ($CHCl_3$) 3100—2800, 1780, 1600, and 1430 cm^{-1}.

Found: C, 58.09; H, 7.08%. Calcd for $C_{11}H_{16}O_5$: C, 57.88; H, 7.07%.

Photoreaction of 3c. A $CDCl_3$ solution (0.3 cm^3) of **3c** (6 mg) was irradiated for 10 min to give 2.8 mg (47%) of **4c** and 0.5 mg (8%) of **5c**.

4c: Colorless oil. ^{1}H NMR δ=0.8—1.2 (8H, m), 1.4—1.6 (2H, m), 1.6—1.8 (1H, m), 1.9—2.1 (1H, m), 2.1—2.3 (2H, m), 2.97 (1H, dt, J=3.5, 1.5 Hz), 3.23 (3H, s), 3.31 (3H, s), 3.36 (3H, s), 3.38 (3H, s), and 7.15 (1H, dt, J=3.5, 1.5 Hz); ^{13}C NMR δ=13.6, 14.4, 17.3, 20.9, 27.3, 30.3, 47.8, 49.9, 51.2, 51.9, 52.1, 58.9, 104.6, 104.7, 150.4, 152.1, and 208.5; IR ($CHCl_3$) 3050—2800, 1700, 1460, 1260, and 1195 cm^{-1}; MS m/z (%) 312 (M$^+$, 7), 297 (42), 269 (22), 149 (23), 133 (100), 105 (48), 91 (22), and 59 (46).

Found: C, 65.27; H, 9.04%. Calcd for $C_{17}H_{28}O_5$: C, 65.27; H, 9.03%.

5c: Colorless oil. ^{1}H NMR δ=0.93 (6H, t, J=7.0 Hz), 1.2—1.4 (4H, m), 1.6—1.8 (2H, m), 1.8—2.0 (2H, m), 3.39 (6H, s), 3.46 (6H, s), and 6.41 (2H, s); ^{13}C NMR δ=14.9 (2C), 18.4 (2C), 25.8 (2C), 52.0 (2C), 52.6 (2C), 64.3 (2C), 107.6 (2C), 133.2 (2C), and 205.6; IR (oil) 3100—2800, 1785, 1460, and 1175 cm^{-1}; MS m/z (%) 312 (M$^+$, 8), 297 (63), 281 (21), 269 (53), 195 (20), 149 (25), 133 (100), 105 (94), 91 (33), 79 (29), 77 (28), and 59 (57).

Found: C, 65.70; H, 9.22%. Calcd for $C_{17}H_{28}O_5$: C, 65.36; H, 9.03%.

A $NaBH_4$-Reduction of 4a. A dry MeOH solution (2 cm^3) of **4a** (8 mg) and $NaBH_4$ (7 mg) was stirred at room temperature monitoring with TLC. The solvent was evaporated and the residue was diluted by 5% aqueous HCl. The aqueous phase was extracted with $CHCl_3$ and the extract was purified by SiO_2 chromatography to give 7.8 mg (98%) of **6**.

6: Colorless crystals, mp 80—82 °C. ^{1}H NMR δ=1.28 (6H, s), 3.06 (1H, d, J=12.8 Hz), 3.35 (6H, s), 3.47 (6H, s), 3.69 (1H, d, J=12.8 Hz, D_2O exchangeable), and 5.86 (2H, s); ^{13}C NMR δ=13.6 (2C), 51.5 (2C), 51.6 (2C), 57.0 (2C), 90.5, 109.8 (2C), and 136.7 (2C); IR ($CHCl_3$) 3520, 3050—2800, 1440, and 1420 cm^{-1}.

Found: C, 60.27; H, 8.39%. Calcd for $C_{13}H_{22}O_5$: C, 60.44; H, 8.59%.

Photoconversion of 4a. A $CDCl_3$ solution of **4a** (81 mg) was irradiated for 1 h. The mixture was purified by a HPLC to give 25.9 mg (33%) of **5a** and 3.2 mg of **4a**.

Photoconversion of 4b. Similarly, irradiation of **4b** (17 mg) gave 7 mg (44%) of **5b** and 1 mg of **4b**.

Photoconversion of 4c. Similarly, irradiation of **4c** (17 mg) gave 9 mg (53%) of **5c**.

Sensitization and Quenching Experiments for 3a. A benzene-d_6 solution (4 cm^3) of **3a** (18 mg) and an internal standard (toluene) was degassed with N_2 for several min. The solutions used for these experiments contained 2.7 mg of **3a** in 0.6 cm^3 of benzene-d_6 (sample 1), sample 1 and 70 mg of benzophenone (sample 2), sample 1 and 7 mg of isoprene (sample 3), sample 1 and 14 mg of isoprene (sample 4), and sample 1 and 28 mg of isoprene (sample 5). Irradiation was carried out with a 100 W high-pressure mercury lamp using a merry-go-round apparatus. An amount of **3a** was analyzed by its ^{1}H NMR spectra.

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