

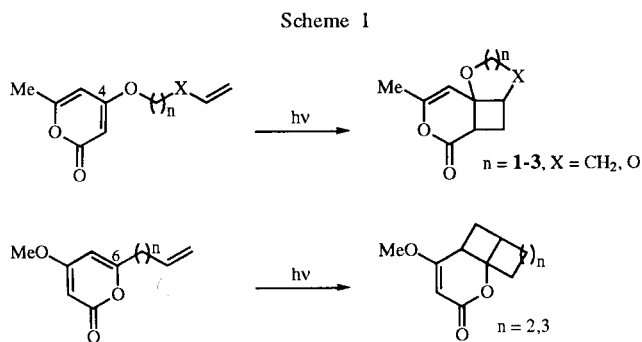
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4-( $\omega$ -Enyl)-2-pyrone **3** and two types of 4-( $\omega$ -dienyl)-2-pyrones **4-6**, **9** and **10** were prepared and the photochemical behavior was investigated. Photosensitized reaction of **3** afforded [2+2]-cycloadduct **11** site-specifically. On the other hand, **4** and **5** gave geometrical isomers, respectively. 2-Pyrones **6**, **9** and **10** possessing pendant furans gave no adduct. The reasons for the differences are described.

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2-Pyrone is not only an unsaturated  $\delta$ -lactone bearing a conjugated dienoate structure but also a heterocyclic compound showing aromaticity based on the pyrylium oxide betain structure. We previously reported that intramolecular photochemical reactions of 4-( $\omega$ -alkenyl)- and 6-( $\omega$ -alkenyl)-2-pyrones provided two types of oxatri-cyclic lactones, depending upon the number of methylene chains between the 2-pyrone ring and the olefinic moiety (Scheme 1) [1-2], together with the explanation of the cycloaddition mechanism [3]. In this paper we report the photochemical behavior of 4-( $\omega$ -enyl)- and 4-( $\omega$ -dienyl)-2-pyrones in order to make clear the reactivity.



All of the substrates required for this study were prepared as shown in Scheme 2. 2-Pyrones **3-5** were obtained via Wittig reactions of phosphonium bromide **2** with benzaldehyde, cinnamaldehyde and crotonaldehyde, respectively. 2-Pyrones **6**, **9** and **10** were prepared from 4-hydroxy-6-methyl-2-pyrone by way of a dehydrohalogenation reaction with the proper halogenated heterocycles.

A solution of a mixture of **3a** and **3b** (1:3) in acetonitrile in the presence of benzophenone as a sensitizer was irradiated under nitrogen to afford expected [2+2]-cycloadducts **11a** and **11b** in 25% and 15%, respectively (Scheme 3). On the other hand, similar photoirradiation of a mixture of **4a** and **4b** (2:1) (R = Ph) or **5a** and **5b** (5:2) (R = Me), having acyclic diene moieties, did not give [2+2]-cycloadducts but gave a mixture of **4a** and **4b**

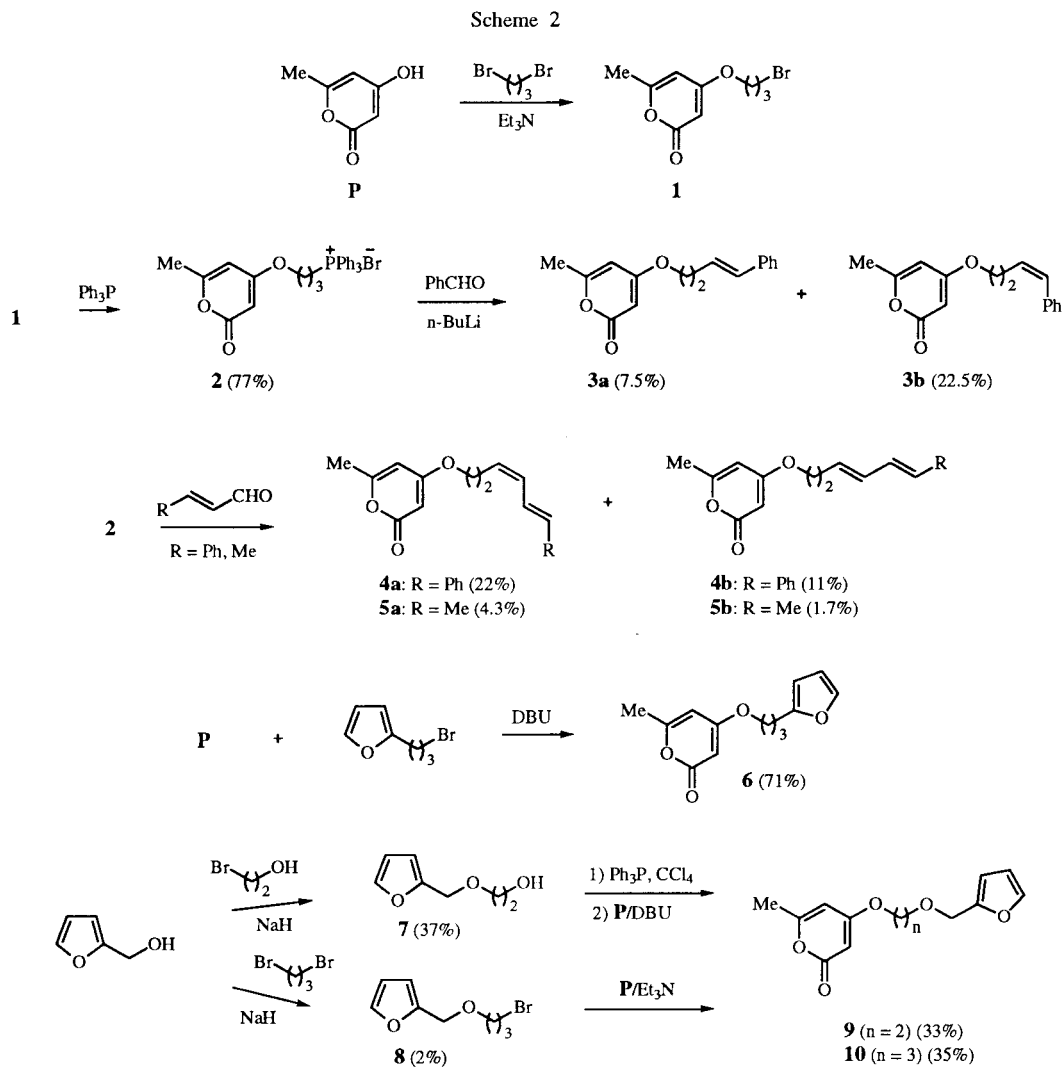
(2:5.4) or **5a** and **5b** (1:1), respectively. Photoreactions of **6**, **9** and **10** having cyclic diene moieties gave no cycloadducts in the presence of benzophenone and without one.

The structures of **11a** and **11b** were assigned as intramolecular [2+2]-cycloadducts from the spectroscopic data compared to the related compounds reported earlier [1]. The stereoisomers of **11a** and **11b** were deduced to be endo- and exo-6-phenyl derivatives, respectively, by noting the magnitude of the NOE for 6-H/7-H: **11a** showed the 5.8% enhancement but **11b** showed no enhancement.

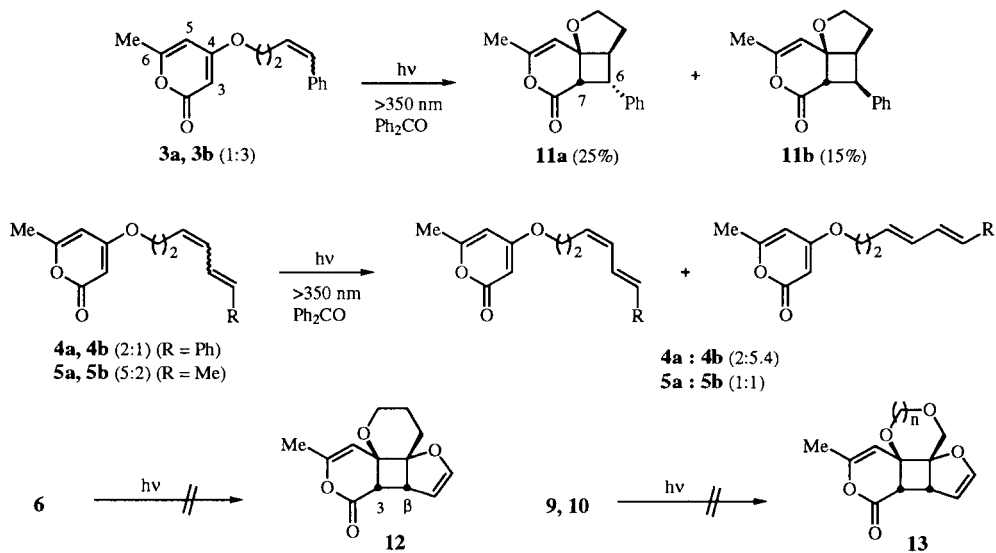
Irradiation of **4** (**4a**:**4b** = 2:1) with several sensitizers having triplet energies of 62-72 kcal/mole gave a mixture of **4a** and **4b** (ca 2:5) in acetonitrile. In the case of no sensitizer the isomer ratio became to 2:6. The same results were also obtained in methanol. Pirrung and co-worker have reported that the olefin has been activated by phenyl and vinyl substituents in the intramolecular photocycloadditions of cyclooctenones **14** to afford cycloadducts **15** (Scheme 4) [4]. On the other hand, Pattenden and co-workers have reported that geometrical isomerization has been caused by the vinyl group in the photoreaction of 2-(2,4-pentadienyl)-2-cyclopentenone [5]. Since **4** has uv absorption at 347 nm, the geometrical isomerization of **4** was considered to prior to the intramolecular cycloaddition owing to the direct diene excitation of the side chain or the energy transfer from the excited 2-pyrone to the diene moiety of the side chain. And the latter reason was deduced to be reasonable to the isomerization of **5**.

Each photoreactions of **6**, **9** and **10**, possessing pendant furans which prevent the geometrical isomerization of the side chain, were expected to afford novel tetracyclic lactones **12** and **13**, but gave no cycloadducts in the presence of sensitizer. West and co-workers have reported that 2-pyrones **16** having pendant furans have undergone intramolecular [4+4]- and [2+2]-cycloadditions to give **17** and **18**, respectively (Scheme 4) [6]. The initial bond formation is inferred to occur at C<sub>6</sub>-C $\alpha$  owing to the matching of the MO interaction [7] to give a biradical intermediate **A** which may lead to the adducts **17** and **18**. In the case of **6**, **9** and **10**, the orientations affording the two

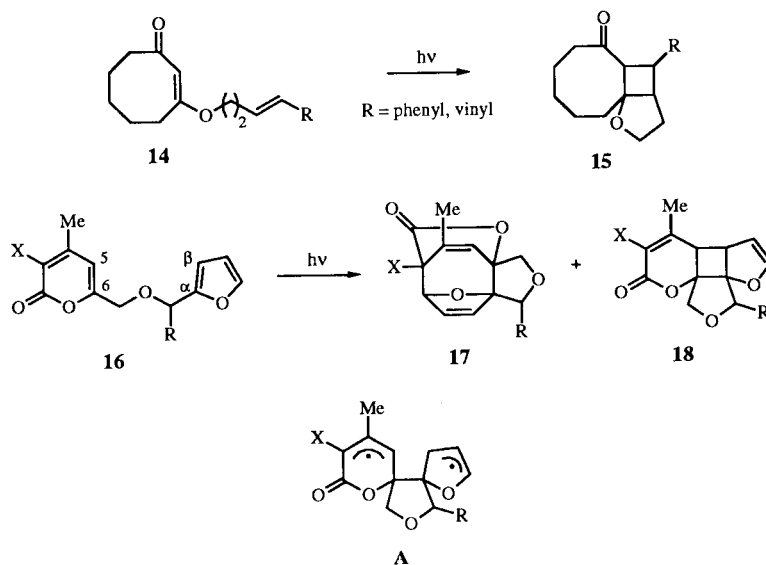
Scheme 2



Scheme 3



Scheme 4



types of the adducts **17** and **18** were difficult to construct from the HGS model consideration because of the steric unfitness. And the lack of cycloadducts **12** and **13** from the irradiation of **6**, **9** and **10** probably reflects that the initial bond formation at  $C_3-C_\beta$  is hard owing to the mismatching of the MO interaction [7] or reflects that the pendant furan being a diene acts as a triplet quencher.

## EXPERIMENTAL

All of the melting points were measured on a Yanagimoto Mel-temp apparatus and are uncorrected. The ir,  $^1\text{H}$  nmr, and mass spectra were recorded on JASCO A-3, JEOL JNM-GSX 400, and JEOL JMSOISG spectrometers, respectively. Photoirradiation was carried out in a Pyrex tube by using a Riko 400W high-pressure mercury lamp equipped with a merry-go-round apparatus. In the case of a photosensitized reaction, a UV 35 filter (Toshiba) which cuts off under 350 nm was used. All of the photoreactions were monitored by tlc on silica-gel plates.

4-(3-Bromopropoxy)-6-methyl-2-pyrone (**1**) [3] and 2-(3-bromopropyl)furan [8] were prepared according to the method described in the literature.

### 6-Methyl-4-(4-phenyl-3-butenyloxy)-2-pyrone (**3**).

1) A solution of **1** (14.3 g, 57.7 mmoles) and triphenylphosphine (18.2 g, 69.3 mmoles) in benzene (450 ml) was refluxed for 15 days. The resulting solid was filtered to give **2** (22.5 g, 77%), which was difficult to purify by recrystallization. Compound **2** had mp 105-107°; ir (potassium bromide): 1700, 1645, 1570, 1260  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  2.13, 4.14 (each m, 2H), 2.18 (s, 3H), 4.35 (t, 2H,  $J = 5.8$  Hz), 5.31, 5.88 (each s, 1H), 7.80 (m, 15H).

2) To a THF (100 ml) solution of **2** (7.10 g, 13.9 mmoles) was slowly added *n*-butyllithium (8.70 ml, 13.9 mmoles, 1.6 *M* solution in hexane) at 0° under a nitrogen atmosphere. The solution

was stirred at -78° for 0.5 hour and then benzaldehyde (1.8 g, 17 mmoles) was added. Stirring was continued for 5.5 days at room temperature. The filtrate of the reaction mixture was concentrated and the resulting oil was chromatographed on a silica gel using ethyl acetate-hexane 1:1 v/v mixture to afford 1.1 g (30%) of a mixture of **3a** (7.5%) and **3b** (22.5%), whose ratio was determined by  $^1\text{H}$  nmr. A mixture of **3a** and **3b** was obtained as an oil; ir (neat): 1730, 1650, 1570, 1250, 1040  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): **3a**:  $\delta$  2.20 (s, 3H), 2.69 (q, 2H,  $J = 6.8$  Hz), 4.06 (t, 2H,  $J = 6.8$  Hz), 5.41, 5.79 (each s, 1H), 6.19 (m, 1H), 6.51 (d, 1H,  $J = 15.6$  Hz), 7.32 (m, 5H); **3b**:  $\delta$  2.20 (s, 3H), 2.80 (q, 2H,  $J = 6.8$  Hz), 4.10 (t, 2H,  $J = 6.8$  Hz), 5.38, 5.76 (each s, 1H), 5.69 (m, 1H), 6.60 (d, 1H,  $J = 11.6$  Hz), 7.32 (m, 5H); ms:  $m/z$  (relative intensity) 256 ( $M^+$ , 2), 130 (100).

Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{O}_3$ : C, 74.99; H, 6.29. Found: C, 75.10; H, 6.20.

### 6-Methyl-4-(6-phenyl-3,5-hexadienyloxy)-2-pyrone (**4**).

To a THF (100 ml) solution of **2** (6.91 g, 13.6 mmoles) was slowly added *n*-butyllithium (8.50 ml, 13.6 mmoles) at 0° under a nitrogen atmosphere. The solution was stirred at -78° for 20 minutes and then cinnamaldehyde (2.23 g, 16.8 mmoles) was added. Stirring was continued for 10 days at room temperature. The filtrate of the reaction mixture was concentrated and the resulting oil was chromatographed on silica gel with ethyl acetate-hexane 1:2 v/v mixture to give 1.27 g (33%) of a mixture of **4a** (22%) and **4b** (11%). A mixture of **4a** and **4b** was obtained as an oil; ir (neat): 1720, 1655, 1570, 1255, 1150  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform): **4a**:  $\delta$  2.11 (s, 3H), 2.72 (dt, 2H,  $J = 7.7$ , 6.6 Hz), 3.96 (t, 2H,  $J = 6.6$  Hz), 5.38 (s, 1H), 5.49 (dt, 1H,  $J = 10.8$ , 7.7 Hz), 5.72 (s, 1H), 6.28 (dd, 1H,  $J = 11.2$ , 10.8 Hz), 6.56 (d, 1H,  $J = 15.5$  Hz), 7.01 (dd, 1H,  $J = 15.5$ , 11.2 Hz), 7.19-7.41 (m, 5H); **4b**:  $\delta$  2.15 (s, 3H), 2.56 (dt, 2H,  $J = 7.7$ , 6.6 Hz), 3.95 (t, 2H,  $J = 6.6$  Hz), 5.38 (s, 1H), 5.76 (s, 1H), 5.76 (dt, 1H,  $J = 15.4$ , 7.7 Hz), 6.28 (dd, 1H,  $J = 15.4$ , 10.8 Hz), 6.48 (d, 1H,  $J = 15.6$  Hz), 6.73 (dd, 1H,  $J = 15.6$ , 10.8 Hz), 7.19-7.41 (m, 5H); ms:  $m/z$  (relative intensity) 282 ( $M^+$ , 0.3), 165 (100).

Anal. Calcd. for  $\text{C}_{18}\text{H}_{18}\text{O}_3$ : C, 76.57; H, 6.43. Found: C, 76.38; H, 6.23.

6-Methyl-4-(6-methyl-3,5-hexadienyloxy)-2-pyrone (**5**).

To a THF (100 ml) solution of **2** (7.0 g, 14 mmoles) was slowly added *n*-butyllithium (8.7 ml, 14 mmoles) at 0° under a nitrogen atmosphere. The solution was stirred at -78° for 20 minutes and then crotonaldehyde (1.2 g, 17 mmoles) was added. Stirring was continued for 12 days at room temperature. The same workup mentioned above was carried out to give 0.17 g (6%) of a mixture of **5a** (4.3%) and **5b** (1.7%). A mixture of **5a** and **5b** was obtained as an oil; ir (neat): 1710, 1655, 1570, 1250, 1150 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): **5a**: δ 1.80 (d, 3H, J = 6.8 Hz), 2.20 (s, 3H), 2.62 (dt, 2H, J = 7.6, 6.8 Hz), 5.27 (dt, 1H, J = 10.8, 7.6 Hz), 5.37 (s, 1H), 5.76 (dq, 1H, J = 14.8, 6.8 Hz), 5.77 (s, 1H), 6.09 (dd, 1H, J = 12.0, 10.8 Hz), 6.30 (dd, 1H, J = 14.8, 12.0 Hz); **5b**: δ 1.75 (d, 3H, J = 6.8 Hz), 2.20 (s, 3H), 2.52 (dt, 2H, J = 7.6, 6.8 Hz), 3.95 (t, 2H, J = 6.8 Hz), 5.37 (s, 1H), 5.51 (dt, 1H, J = 15.2, 7.6 Hz), 5.66 (dq, 1H, J = 14.8, 6.8 Hz), 5.77 (s, 1H), 6.02 (dd, 1H, J = 14.8, 12.0 Hz), 6.11 (dd, 1H, J = 15.2, 12.0 Hz); ms: m/z (relative intensity) 220 (M<sup>+</sup>, 3), 165 (100).

*Anal.* Calcd. for C<sub>13</sub>H<sub>16</sub>O<sub>3</sub>: C, 70.89; H, 7.32. Found: C, 71.23; H, 7.55.

4-[3-(2-Furyl)-propoxy]-6-methyl-2-pyrone (**6**).

To a refluxing solution of 4-hydroxy-6-methyl-2-pyrone (**P**) (3.7 g, 30 mmoles) and DBU (4.5 g, 30 mmoles) in acetonitrile (170 ml) was slowly added 2-(3-bromopropyl)furan (4.6 g, 25 mmoles). After refluxing for 20 hours, the filtrate of the reaction mixture was concentrated and chromatographed using ethyl acetate-hexane 1:2 v/v mixture to give **6** (4.1 g, 71%). Compound **6** had mp 56-58°; ir (potassium bromide): 1713, 1647, 1563, 1256, 1148 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.11 (quint, 2H, J = 7.2 Hz), 2.21 (s, 3H), 2.79 (t, 2H, J = 7.2 Hz), 3.96 (t, 2H, J = 6.4 Hz), 5.36 (s, 1H), 5.77 (s, 1H), 6.01, 6.29, 7.32 (furan); ms: m/z (relative intensity) 234 (M<sup>+</sup>, 4), 108 (100).

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>: C, 66.65; H, 6.02. Found: C, 66.73; H, 6.12.

4-[5-(2-Furyl)-1,4-dioxapentyl]-6-methyl-2-pyrone (**9**).

1) To a suspension of furfuryl alcohol (15.0 g, 153 mmoles) and sodium hydride (7.36 g, 184 mmoles) under a nitrogen atmosphere was slowly added 2-bromoethanol (21.5 g, 172 mmoles) and then the solution was refluxed for 19 hours. After removing sodium bromide, the filtrate was concentrated and chromatographed using ethyl acetate-hexane 2:3 v/v mixture to afford **7** (8.0 g, 37%). Compound **7** was obtained as an oil; ir (neat): 3420, 1620, 1503, 1412, 1105, 1067 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.46 (bs, 1H), 3.58, 3.72 (each m, 2H), 4.50 (s, 2H), 6.33, 7.41 (furan).

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>O<sub>3</sub>: C, 59.14; H, 7.09. Found: C, 59.09; H, 6.97.

2) A solution of **7** (5.3 g, 37 mmoles) and triphenylphosphine (12 g, 45 mmoles) in carbon tetrachloride (40 ml) was refluxed for 70 minutes and during this reaction triethylamine was added to the solution in order not to become to acidity. After cooling the solution hexane (70 ml) was added and the resulting solid was filtered. To the concentrated filtrate was added an acetonitrile (40 ml) solution of **P** (4.7 g, 37 mmoles) and DBU (6.9 g, 45 mmoles). After refluxing the solution for 20 hours, the concentrated reaction mixture was submitted to repeated chromatography using ethyl acetate-hexane 1:2 v/v mixture to give **9**

(3.1 g, 33%). Compound **9** was obtained as an oil; ir (neat): 1723, 1713, 1651, 1566, 1252, 1150 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.20 (s, 3H), 3.80, 4.07 (each m, 2H), 4.54 (s, 2H), 5.37 (s, 1H), 5.82 (s, 1H), 6.36, 7.43 (furan); ms: m/z (relative intensity) 250 (M<sup>+</sup>, 11), 81 (100).

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>5</sub>: C, 62.39; H, 5.64. Found: C, 62.31; H, 5.64.

4-[6-(2-Furyl)-1,5-dioxahexyl]-6-methyl-2-pyrone (**10**).

1) To a suspension of furfuryl alcohol (6.0 g, 61 mmoles) and sodium hydride (3.2 g, 80 mmoles) under a nitrogen atmosphere was slowly added 1,3-dibromopropane (24.7 g, 122 mmoles) and then the solution was refluxed for 20 hours. After removing sodium bromide, the filtrate was concentrated and followed to be chromatographed using ethyl acetate-hexane 1:10 v/v mixture to afford **8** (0.25 g, 2%). Compound **8** was obtained as an oil; ir (neat): 1605, 1500, 1435, 1100 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.10 (quint, 2H, J = 6.1 Hz), 3.49 (t, 2H, J = 6.1 Hz), 3.59 (t, 2H, J = 6.1 Hz), 4.45 (s, 2H), 6.31, 6.34, 7.40 (furan).

2) To a refluxing solution of **P** (0.28 g, 2.2 mmoles) and triethylamine (0.24 g, 24 mmoles) in acetonitrile (2 ml) was slowly added bromide **8** (0.40 g, 1.8 mmoles). After refluxing for 11 hours, the filtrate of the reaction mixture was concentrated and chromatographed using ethyl acetate-hexane 2:3 v/v mixture to afford **10** (0.17 g, 35%). Compound **10** had mp 72-74°; ir (potassium bromide): 1709, 1694, 1651, 1570, 1254, 1150 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): δ 2.02 (quint, 2H, J = 6.4 Hz), 2.20 (s, 3H), 3.59, 4.02 (each d, 2H, J = 6.4 Hz), 4.44 (s, 2H), 5.39 (s, 1H), 5.75 (s, 1H), 6.31, 6.34, 7.40 (furan); ms: m/z 264 (M<sup>+</sup>, 34), 81 (100).

*Anal.* Calcd. for C<sub>14</sub>H<sub>16</sub>O<sub>5</sub>: C, 63.62; H, 6.10. Found: C, 63.76; H, 6.01.

10-Methyl-6-phenyl-2,9-dioxatricyclo[5.4.0.0<sup>1,5</sup>]undec-10-en-8-one (**11**).

A solution of a mixture of **3a** and **3b** (1:3) (0.20 g, 0.80 mmole) and benzophenone (0.23 g, 1.25 mmoles) in acetonitrile (100 ml, 7.8 mM) was irradiated under nitrogen atmosphere using a UV 35 filter for 17 hours at room temperature. The solvent was then removed *in vacuo* and the residue was chromatographed using ethyl acetate-hexane 1:20 v/v mixture to afford a mixture (80 mg, 40%) containing **11a** (25%) and **11b** (15%), whose ratio was determined by <sup>1</sup>H nmr. A mixture of **11a** and **11b** was obtained as an oil; ir (neat): 1760, 1705, 1225, 1060 cm<sup>-1</sup>; <sup>1</sup>H nmr (deuteriochloroform): **11a**: δ 1.92 (s, 3H, Me), 1.90, 2.13 (each m, 1H, 4-CH<sub>2</sub>), 3.12 (m, 1H, 5-H), 3.53 (dd, 1H, J = 11.6, 4.4 Hz, 6-H), 3.73 (d, 1H, J = 11.6 Hz, 7-H), 4.13, 4.28 (each m, 1H, 3-CH<sub>2</sub>), 5.07 (s, 1H, =CH), 7.28 (m, 5H, Ph); **11b** (separated signals from **11a**): δ 3.00 (m, 1H, 5-H), 3.65 (d, 1H, J = 6.6 Hz, 7-H), 5.03 (s, 1H, =CH); ms: m/z (relative intensity) 256 (M<sup>+</sup>, 6), 91 (100).

*Anal.* Calcd. for C<sub>16</sub>H<sub>16</sub>O<sub>3</sub>: C, 74.99; H, 6.29. Found: C, 74.68; H, 6.03.

Photoisomerization Reactions of **4** and **5**.

A 7.4 mM solution of a mixture of **4a** and **4b** (2:1) in acetonitrile was irradiated in the presence of three kinds of sensitizers using a UV 35 filter under nitrogen atmosphere. The concentration of a sensitizer was prepared as the triplet state of the sensitizer was produced to five or one hundred times when **4a** and **4b** absorbed the light one part at 360 nm [9]. 9 Hours irradiation in

the presence of benzophenone ( $E_T = 69$  kcal/mole) afforded a mixture of **4a** and **4b** (2:5.4). Same irradiation in the presence of Michler's ketone ( $E_T = 62$  kcal/mole), diphenylamine ( $E_T = 72$  kcal/mole) or without sensitizer gave a mixture of **4a** and **4b** in the ratio of 2:5.2, 2:4.8 and 2:6, respectively. The same irradiation in methanol in the presence of Michler's ketone or without it gave a mixture of **4a** and **4b** in the ratio of 2:6.8 and 2:4.6, respectively. Similarly, a 7.2 mM solution of a mixture of **5a** and **5b** (5:2) in acetonitrile was irradiated in the presence of benzophenone, Michler's ketone or without a sensitizer gave a mixture of **5a** and **5b** in the ratio of 1:1, 1:1 and 1:0.8, respectively.

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