Photoadducts of 4,6-Dimethyl- and 4-Methoxy-6-methyl-2-pyrones with Chloroethylenes and Their Dehydrochlorination

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Sensitized photoreactions of 2-pyrones with chloroethylenes gave two kinds of [2+2]cycloadducts, 2-oxabicyclo[4.2.0]oct-4-en-3-ones (**4**, **8**) and across the C_3–C_4 double bond in 2-pyrone, benzene derivatives, and/or cyclobutanecarboxylic acids: Their relative yields greatly depended upon the nature of the reactants. The dehydrochlorination of the cycloadducts **4** and **8** across the C_5–C_6 double bonds in the pyrones with triethylamine in ethanol gave 5-ethenyl-2-pyrones, whose structures were previously incorrectly assigned as oxocinones, via a symmetry-allowed ring opening of 2-oxabicyclo[4.2.0]octa-4,6-dien-3-ones. Some 5-ethenyl-2-pyrones possessing a chlorinated ethenyl group finally affords 5-ethynyl-2-pyrones by an anti-elimination of hydrogen chloride. The X-ray crystallographic analyses of 5-ethenyl- and 5-ethynyl-2-pyrones are also described.

Although much attention has been denoted to the thermal cycloaddition reactions of 2-pyrones,[1] the investigation of their photochemical ones has not been extended beyond our reports[2,3] except dimerization.[4] The sensitized photochemical reaction of 4,6-dimethyl-2-pyrone (**1**) with such electron-deficient olefins as acrylonitrile and methyl acrylate gave two stereoisomeric [2+2]cycloadducts, as major products, across the C_5–C_6 double bond in **1**,[2] while methyl 2-pyrone-5-carboxylate afforded two stereoisomeric [4+2]cycloadducts in the reaction with acrylonitrile under similar conditions.[3]

Hanifin and Cohen[5] have first reported the formation of an eight-membered oxygen heterocycle, oxacyclooctatrienone (oxocinone) ring system, by the pyrolysis of a 3-chlorocoumarin photodimer with the elimination of hydrogen chloride. It was demonstrated, however, that the pyrolysis of photochemical [2+2]-cycloadducts between 2,6-dimethyl-4-pyrone with acetylenes gave no expected monocyclic oxocinones, but instead the adducts underwent a symmetry-allowed bicyclic Claisen rearrangement followed by aromatization to substituted phenols.[6] Thus, it has not been known monocyclic oxocinone ring system up to date. If [2+2]cycloadducts are again formed in the photochemical reaction of such 2-pyrones bearing an electron-donating group as **1** with halogen-substituted olefins, the halogenated cycloadducts would be expected to give monocyclic oxocinones by dehydrohalogenation with a concurrent ring expansion.

The purpose of this work was to prepare halogenated [2+2]cycloadducts to 2-pyrones in hope that they would serve as useful intermediates in the preparation of monocyclic oxocinones. This paper describes the sensitized photochemical reaction of 4,6-dimethyl- (**1**) and 4-methoxy-6-methyl-2-pyrone (**2**) with chlorinated olefins, and the dehydrochlorination of [2+2]cycloadducts. The previously proposed structures for dehydrochlorinated products[7] are also revised.

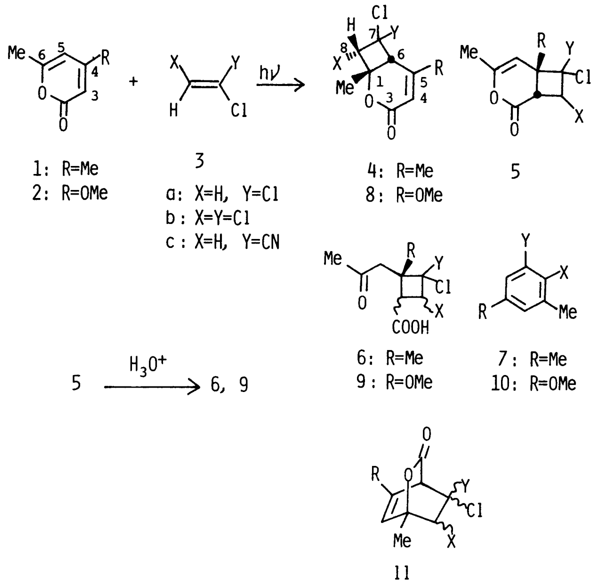
Results and Discussion

Photochemical Reactions. A solution of 4,6-dimethyl-2-pyrone (**1**) and 1,1-dichloroethylene (**3a**), trichloroethylene (**3b**), or 2-chloroacrylonitrile (**3c**), in the presence of benzophenone as a sensitizer, in acetonitrile was irradiated, through a Pyrex vessel, with a 400W high-pressure mercury lamp under nitrogen. As expected, [2+2]cycloadducts **4** were obtained in all reactions together with other products, **5**, **6** and/or **7**: Their relative yields greatly depended upon the nature of olefins (Table 1).

The products, **4a—c**, formed in all cases were assigned as regioselective [2+2]cycloadducts, 2-oxabicyclo-[4.2.0]oct-4-en-3-ones, across the C_5–C_6 double bond in **1**, and two isomers, **4c**-1 (major) and **4c**-2 (minor), which were formed in the reaction with **3c**, were deduced to be *endo*- and *exo*-7-cyano derivatives, respectively, on the basis of spectral data. Since two isomers, **4c**-1 and **4c**-2, as well as **4a** and **4b** did not change on treatment with basic alumina, which was used to infer the stereochemistry of ring junctions in photochemical [2+2]cycloadducts,[2,8] all the adducts **4** could be assigned as *cis*-fused. And, it seemed reasonable to assume that the configurations between hydrogens at 6- and 8-positions in all **4** are *cis*, because of showing a large value (2.0 Hz) of long range coupling.[9]

On the basis of comparison of spectral data of similar corresponding compounds,[2] the other products, **5**, **6**, and **7**, were easily assigned as the corresponding 3-oxabicyclo[4.2.0]oct-4-en-2-one, 2-acetonyl-2-methyl-1-cyclobutane carboxylic acids, and *m*-xylene derivatives, respectively (Scheme 1).

The photochemical reaction of 4-methoxy-6-methyl-2-pyrone (**2**) with **3a** under similar conditions gave the corresponding [2+2]cycloadduct **8a**, together with a cyclobutanecarboxylic acid **9a** as the major product. In the reaction with **3b**, **2** gave three products, [2+2]cycloadduct **8b**, cyclobutanecarboxylic acid **9b**, and 2,3-dichloro-5-methoxytoluene (**10b**). The results



Scheme 1.

Table 1. Photochemical Reaction of 2-Pyrones with Chlorinated Ethylenes[a]

2-Pyrone	Ethylene	Products (yield/%)
1	**3a**	**4a** (17), **5a** (34)
1	**3b**	**4b** (10), **6b** (5), **7b** (4)
1	**3c**	**4c** (23),[b] **7c** (13)
2	**3a**	**8a** (16), **9a** (56)
2	**3b**	**8b** (23), **9b** (8), **10b** (17)

a) A solution of 2-pyrone and ethylene was irradiated in the presence of benzophenone. b) Two stereoisomers, **4c**-1 and **4c**-2, were isolated in 17 and 6% yields.

are also given in Table 1.

The [2+2]cycloadducts, **8a** and **8b**, were again assigned as regio- and stereoselective adducts, like **4a** and **4b**, across the C_5–C_6 double bond in **2**, respectively.

The cyclobutanecarboxylic acids, **6** and **9**, correspond to hydrolyzed products of [2+2]cycloadducts **5** across the C_3–C_4 double bonds in **1** and **2**, respectively. In fact, the cycloadduct **5a** (R=Me, X=H, Y=Cl) was quantitatively hydrolyzed to **6a** at room temperature. On the other hand, it is evident that toluene derivatives, **7** and **10** are formed from [4+2]cycloadducts like **11** with the decarboxylation followed by dehydrochlorination (Scheme 1).

Dehydrochlorination of the 2-Oxabicyclo[4.2.0]oct-4-en-3-ones. Dehydrochlorination of the [2+2]cycloadducts, **4** and **8**, with triethylamine in ethanol under reflux afforded three types of dehydrochlorinated products depending upon the nature of substituents on the adducts as well as the reaction conditions.

The reaction of dichloro-substituted adduct **4a** with triethylamine for 30 h afforded a product **14a** with the elimination of two moles of hydrogen chloride, while trichloro- **4b** and monochloro-substituted adduct **4c** (a mixture of two isomers) gave high yields of mono-dehydrochlorinated products, **13b** and **13c**, under similar conditions for 15 h. Similar treatment of the dichloro-substituted adduct **8a** with triethylamine afforded a mono- **16a** and di-dehydrochlorinated product **17a** depending upon the reaction conditions (Table 2).

Table 2. Dehydrochlorination of [2+2]Cycloadducts

[2+2]Cycloadduct	Conditions[a] Time/h	Product Yield/%
4a	Et_3N 30	**14a** 41
4b	Et_3N 15	**13b** 97
4c[b]	Et_3N 15	**13c** 89
8a	Et_3N 2	**16a** 95
8a	Et_3N 38	**17a** 89
8b	Et_3N 1.5	**12b** 82
12b[c]	100 °C 2	**16b** 80

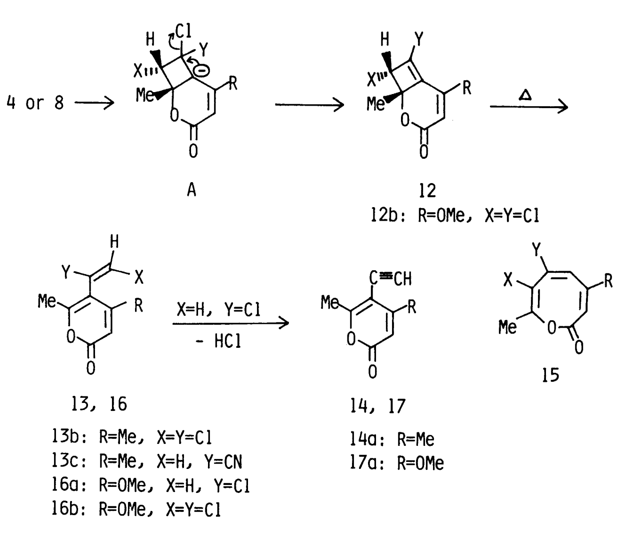
a) The reactions with Et_3N were carried out in EtOH under reflux. b) A mixture of **4c**-1 and **4c**-2 was used. c) Heated in DMSO.

The spectral data indicated that the products, **13b**, **13c**, **16a**, have similar structures each other. Although we have previously proposed the 2*H*-oxocin-2-one structures (**15**) for the compounds, **13b** and **13c**,[7] they should be now revised to 5-ethenyl-2-pyrones on the basis of further inspection of spectral data. In addition, **13b** was finally confirmed to be 5-(*trans*-1,2-dichloroethenyl)-4,6-dimethyl-2-pyrone by the X-ray crystallographic analysis.

The di-dehydrochlorinated products, **14a** and **17a**, could be assigned as the corresponding 5-ethynyl-2-pyrones, respectively, on the basis of spectral data, and finally of X-ray crystallographic analysis of **14a**.

The X-ray crystallographic data of **13b** and **14a** will be shown in the next section.

On the other hand, the reaction of trichloro-substituted adduct **8b** with triethylamine for 1.5 h afforded another type of mono-dehydrochlorinated product **12b**, which was easily converted into an isomeric 5-ethenyl-2-pyrone (**16b**) on heating at 100 °C for 2 h (Table 2).



Scheme 2.

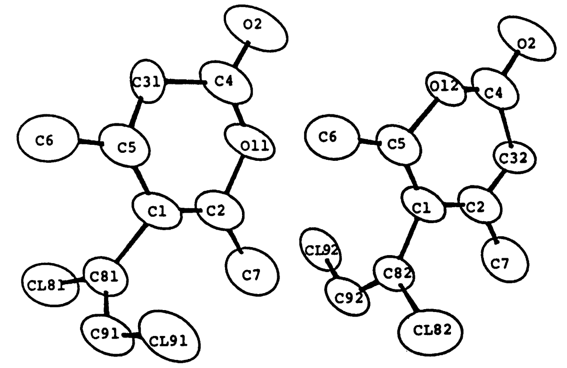


Fig. 1. Two possible molecules, **13b**, at a crystallographically equivalent site.

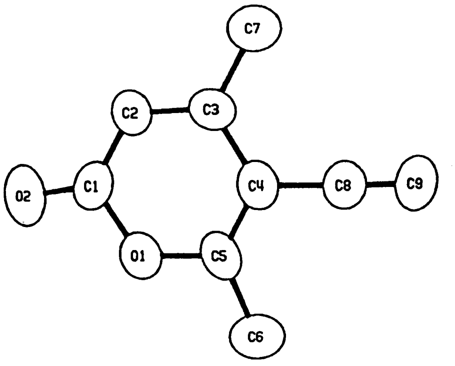


Fig. 2. Molecular structure of **14a**.

On the basis of spectral data the compound **12b** was deduced to be 7,8-dichloro-5-methoxy-1-methyl-2-oxabicyclo[4.2.0]octa-4,6-dien-3-one. Both its IR and ^{1}H NMR spectra are very similar to those of the starting [2+2]cycloadduct **8b**, except for an additional double bond absorption (1580 cm^{-1}) in the IR and a lack of a methine proton at 6-position in the ^{1}H NMR spectra. In the ^{13}C NMR spectrum, **12b** has two additional sp^2 carbons (δ 135.3 and 131.3) assigned to 6-and 7-C, accompanying lacks of sp^3 carbons (δ 53.5 and 85.3) in **8b**.

These dehydrochlorinations are summarized as follows; dichloro-**4a** → **14a**, trichloro-**4b** → **13b**, monochloro-**4c** → **13c**, dichloro-**8a** → **16a** → **17a**, trichloro-**8b** → **12b** → **16b**. The formation of **12b** from **8b** was effective in ethanol solvent, but not in benzene.

On the basis of the above results, the transformation sequence, **4** or **8** → **12** → **13** or **16** → **14** or **17**, can be illustrated as shown in Scheme 2. The elimination of a proton from **4** or **8** with triethylamine occurs at the 6-position but not at the 8-position, and generates an anionic intermediate A which is stabilized by the conjugated enone and by solvation in ethanol. Subsequent elimination of a chloride ion from A gives **12**, which then undergoes a symmetry-allowed ring opening to afford **13** or **16**. Finally, the chlorinated ethenyl-2-pyrones (**13**, **16**) (X=H, Y=Cl) give **14** and **17** by an anti-elimination of hydrogen chloride.

Table 3. Selected Bond Lengths (l/Å) and Angles (ϕ/°) in **13b** (Standard Deviations are in Parentheses)

O2-C4	1.21(7)	C2-O11-C4	129(6)
O11-C2	1.44(4)	C2-C1-C5	121(5)
O11-C4	1.23(6)	O11-C2-C1	113(3)
C1-C2	1.36(9)	O11-C4-C31	116(4)
C1-C5	1.38(9)	C1-C5-C31	129(3)
C1-C81	1.54(2)	C4-C31-C5	113(5)
C5-C31	1.24(6)	CL81-C81-C91	116(2)
C81-C91	1.30(2)	CL91-C91-C81	120(2)
C91-CL91	1.72(3)		
C4-C31	1.64(5)		

Table 4. Selected Bond Lengths (l/Å) and Angles (ϕ/°) in **14a** (Standard Deviations are in Parentheses)

O1-C1	1.395(7)	C1-O1-C5	122.4(5)
C1-O2	1.219(7)	O1-C1-C2	116.7(5)
C1-C2	1.403(9)	O2-C1-C2	128.2(7)
C2-C3	1.355(8)	C1-C2-C3	122.3(6)
C3-C7	1.498(9)	C2-C3-C4	118.3(6)
C3-C4	1.434(9)	C2-C3-C7	121.0(6)
C4-C5	1.347(9)	C3-C4-C5	120.5(6)
C4-C8	1.447(9)	C3-C4-C8	119.7(6)
C5-O1	1.370(7)	O1-C5-C4	119.7(6)
C5-C6	1.477(9)	C4-C5-C6	127.6(6)
C8-C9	1.185(8)	C4-C8-C9	178.5(8)

Table 5. Selected Tortional Angles (ϕ/°) in **13b**

C2-C1-C5-C31	1.9
C1-C81-C91-CL91	4.1
C2-C1-C81-C91	94.4
C2-C1-C5-C6	−179.0
C5-C1-C2-C7	−178.6
CL81-C81-C91-CL91	−178.7

X-Ray Crystal Structures of 5-Ethenyl- (13b) and 5-Ethynyl-2-pyrone (14a). The molecular structures of **13b** and **14a** are illustrated in Figs. 1 and 2, respectively. Bond lengths and angles for **13b** and **14a** are also listed in Tables 3 and 4, respectively.

The compound **13b** has some interesting and unusual features in its molecular geometry. The length of the bond C_1-C_{81} (1.54 Å) is fairly longer than that for a normal conjugated single bond (ca. 1.47 Å), while the double bond C_{81}-C_{91} is fairly short (1.30 Å) (Table 3). As shown in Fig. 1, the sp^2 face of the dichloroethenyl group (C_{81}-C_{91}-CL_{91}) is distorted against the 2-pyrone face (torsional angle of C_2-C_1-C_{81}-C_{91}=94.4°) (Table 5). The characteristic geometry can be easily explained on the basis of the steric repulsion between the 5-(1,2-dichloroethenyl) group and 4,6-dimethyl groups.

Experimental

General and Materials. All melting points were uncorrected. UV spectra were recorded on a Hitachi EPS-3 spectrometer and IR spectra were determined with JASCO A-3 spectrometer. ^{1}H and ^{13}C NMR spectra were measured for $CDCl_3$ solutions on a JEOL JNM-MH-100 (100 MHz) and JEOL FX-100 (25 MHz) spectrometers using TMS as the internal reference. Mass spectra were measured with a JEOL

JMS-01SG spectrometer. The X-ray diffraction data were obtained on an Enraf-Nonius CAD-4 automated four-circle diffractometer with a SDP program package. All the photoaddition and synthetic application reactions were monitored by the use of GC, which was performed at 170 °C (column temp) on a Yanagimoto G80 instrument using a column of Silicone SE-30 (10%)/Chromosorb W (AW). Wakogel C200 was used for preparative column chromatography.

4,6-Dimethyl-2-pyrone (**1**)[10] and 4-methoxy-6-methyl-2-pyrone (**2**)[11] were prepared according to methods previously descrived in the literature.

Photoreaction of 1 with 3a. A solution of **1** (3.0 g, 24 mmol), **3a** (23 ml, 240 mmol), and benzophenone (0.5 g, 2.7 mmol) as a sensitizer in 200 ml of acetonitrile under nitrogen atmosphere was irradiated with a Riko immersion-type 400W high-pressure mercury lamp through a Pyrex vessel at 0—5 °C for 2.5 h. The solvent was removed by the use of a rotary evaporator. The residue was chromatographed on a silica-gel column with benzene-acetone (40 : 1) gave 1.81 g (34%) of **5a** (R=Me, X=H, Y=Cl), and with (20 : 1) gave 0.90 g (17%) of **4a**. Adding one drop of water to 11 mg of **5a** and left 10 d at room temperature to give 12 mg (100%) of **6a**. Compound **5a** was detected by GC analysis at 1.8 min when **4a** was at 2.6 min.

4a: Colorless oil; IR (neat) 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.62 (3H, s, Me), 2.06 (3H, br. s, Me), 3.24 (1H, dd, J_{gem}=16.0, $J_{8,6}$=2.0 Hz, 8-*exo*-H), 3.40 (1H, d, J_{gem}=16.0 Hz, 8-*endo*-H), 3.62 (1H, br. s, 6-H), 6.14 (1H, br. s, 4-H); MS *m/z* (220 M$^+$, 0.3%), 105 (base peak).

Found: C, 49.34; H, 4.56%. Calcd for $C_9H_{10}O_2Cl_2$: C, 48.90; H, 4.56%.

5a: Colorless plates from hexane; mp 78—79 °C; IR (KBr) 1765 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.43, 2.04 (each 3H, s, Me), 3.22 (3H, m, 1-H, 8-CH$_2$), 5.12 (1H, br. s, 5-H); MS *m/z* 220 (M$^+$, 2%), 82 (base peak).

Found: C, 48.80; H, 4.56%. Calcd for $C_9H_{10}O_2Cl_2$: C, 48.89; H, 4.53%.

6a: Colorless solid from acetone; mp 115—116 °C; IR (KBr) 1720, 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.58, 2.15 (each 3H, s, Me), 2.82, 3.10 (each 1H, d, J_{gem}=18.5 Hz, 5-CH$_2$), 3.08—3.3 (2H, m, 1-, 4-H), 10.20 (1H, br. s, COOH); MS *m/z* 238 (M$^+$, 0.3%), 82 (base peack).

Found: C, 45.39; H, 5.08%. Calcd for $C_9H_{12}O_3Cl_2$: C, 45.21; H, 5.06%.

Photoreaction of 1 with 3b. A solution of **1** (5.0 g, 40 mmol), **3b** (28 ml, 310 mmol), and benzophenone (1.6 g, 9 mmol) in 200 ml of acetonitrile was irradiated for 28 h. The solvent was then removed to give 1.0 g (10%) of **4b**. The residue was chromatographed with benzene to afford 0.11 g (4%) of 4,5-dichloro-*m*-xylene (**7b**). The continued elution with benzene-acetone (5 : 1) gave 0.51 g (5%) of **6b**.

4b: Colorless needles from benzene; mp 192—193 °C; IR (KBr) 1722 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.55 (3H, s, Me), 2.03 (3H, d, Me), 3.48 (1H, d, $J_{6,8}$=2.0 Hz, 6-H), 4.76 (1H, d, $J_{8,6}$=2.0 Hz, 8-H), 6.00 (1H, br. s, 4-H); MS *m/z* 219 (M-Cl, 6%), 124 (base peak).

Found: C, 42.27; H, 3.52%. Calcd for $C_9H_9O_2Cl_3$: C, 42.30; H, 3.57%.

6b: Colorless needles from benzene-acetone (5 : 1); mp 132—135 °C; IR (KBr) 1738, 1698 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.60, 2.16 (each 3H, s, Me), 2.82, 3.14 (each 1H, d, J_{gem}=19.0 Hz, CH$_2$), 3.02 (1H, d, $J_{1,4}$=10.0 Hz, 1-H), 4.90 (1H, d, $J_{4,1}$=10.0 Hz, 4-H), 10.0 (1H, br. s, COOH); MS *m/z* 272 (M$^+$, 0.1%), 148 (base peak).

Found: C, 39.76; H, 4.13%. Calcd for $C_9H_{11}O_3Cl_3$: C, 39.53; H, 4.03%.

Photoreaction of 1 with 3c. A solution of **1** (3.0 g, 24 mmol), **3c** (9.5 ml, 120 mmol), and benzophenone (0.5 g, 2.7 mmol) in 200 ml of acetonitrile was irradiated for 1.5 h and the solvent was then removed. The chromatography of the residue with benzene gave 0.41 g (13%) of 3,5-dimethylbenzonitrile (**7c**). The continued elution with benzene-acetone (10 : 1) afforded 1.16 g of a mixture between **4c**-1 (17%) and **4c**-2 (6%), from which both of them were isolated by repeated chromatography.

4c-1: Colorless plates from diethyl ether; mp 100—102 °C; IR (KBr) 2250, 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.64 (3H, s, Me), 2.10 (3H, br. s, Me), 2.92 (1H, dd, J_{gem}=14.0, $J_{8,6}$=2.0 Hz, 8-*exo*-H), 3.36 (1H, d, J_{gem}=14.0 Hz, 8-*endo*-H), 3.36 (1H, br.s, 6-H), 6.12 (1H, br.s, 4-H); MS *m/z* 212 (M$^+$+1, 11%), 96 (base peak).

Found: C, 56.76; H, 4.88; N, 6.65%. Calcd for $C_{10}H_{10}NO_2Cl$: C, 56.75; H, 4.76; N, 6.62%.

4c-2: Colorless plates from diethyl ether; mp 110—113 °C; IR (KBr) 2250, 1720 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.64 (3H, s, Me), 2.05 (3H, br. s, Me), 3.10 (1H, d, J_{gem}=14.0 Hz, 8-*endo*-H), 3.30 (1H, dd, J_{gem}=14.0, $J_{8,6}$=2.0 Hz, 8-*exo*-H), 3.68 (1H, br. s, 6-H), 6.35 (1H, br. s, 4-H); MS *m/z* 212 (M$^+$+1, 3%), 96 (base peak).

Found: C, 56.69; H, 4.78; N, 6.48%. Calcd for $C_{10}H_{10}NO_2Cl$: C, 56.75; H, 4.76; N, 6.62%.

Photoreaction of 2 with 3a. A solution of **2** (7.0 g, 50 mmol), **3a** (48 ml, 500 mmol), benzophenone (1.0 g, 5.4 mmol), and acetonitrile (500 ml) was irradiated at 0—5 °C for 4 h, the same work-up as mentioned above to give 7.2 g (56%) of **9a** from concentration and 1.7 g (16%) of **8a** from column chromatography with benzene-acetone (10 : 1). The precursor of **9a** was detected by GC analysis at 3.0 min when **8a** was at 5.5 min.

8a: Colorless leaflets from acetone-hexane (1 : 3); mp 98—99 °C; IR (KBr) 1700 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.66 (3H, s, Me), 3.20 (1H, dd, J_{gem}=15.0, $J_{8,6}$=2.0 Hz, 8-*exo*-H), 3.36 (1H, d, J_{gem}=15.0 Hz, 8-*endo*-H), 3.68 (1H, d, $J_{6,8}$=2.0 Hz, 6-H), 3.80 (3H, s, OMe), 5.36 (1H, s, 4-H); MS *m/z* 236 (M$^+$, 2%), 112 (base peak).

Found: C, 45.63; H, 4.22%. Calcd for $C_9H_{10}O_3Cl_2$: C, 45.60; H, 4.25%.

9a: Colorless prisms from acetone; mp 121—122 °C; IR (KBr) 1730, 1705 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=2.18 (3H, s, Me), 2.76 (2H, d, $J_{4,1}$=8.5 Hz, 4-CH$_2$), 3.19 (2H, s, 5-CH$_2$), 3.40 (3H, s, OMe), 3.44 (1H, t, $J_{1,4}$=8.5 Hz, 1-H), 10.5 (1H, br. s, COOH); MS *m/z* 237 (M$-$H$_2$O+1, 0.2%), 98 (base peak).

Found: C, 42.39; H, 4.76%. Calcd for $C_9H_{12}O_4Cl_2$: C, 42.54; H, 4.74%.

Photoreaction of 2 with 3b. A solution of **2** (5.1 g, 36 mmol), **3b** (38 ml, 430 mmol), benzophenone (2.0 g, 11 mmol), and acetonitrile (450 ml) was irradiated for 10 h and then removed the solvent to afford 2.3 g (23%) of **8b**. The column chromatography of the filtrate with benzene gave 1.2 g (17%) of 2,3-dichloro-5-methoxytoluene (**10b**) and with benzene-acetone (1 : 1) gave 0.9 g (8%) of **9b**. The precursor of **9b** was detected by GC analysis at 2.1 min when **8b** was at 11.0 min.

8b: Colorless plates from diethyl ether-hexane (2 : 1); mp 210—212 °C; IR (KBr) 1715 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.60

(3H, s, Me), 3.26 (1H, d, $J_{6,8}$=2.0 Hz, 6-H), 3.81 (3H, s, OMe), 4.77 (1H, d, $J_{8,6}$=2.0 Hz, 8-*exo*-H), 5.35 (1H, s, 4-H); MS *m/z* 270 (M^+, 0.2%), 112 (base peak).

Found: C, 39.87; H, 3.33%. Calcd for $C_9H_9O_3Cl_3$: C, 39.81; H, 3.34%.

9b: Colorless plates from chloroform-hexane (1 : 1); mp 156—157 °C; IR (KBr) 1720, 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s, Me), 3.12, 3.40 (each 1H, d, J_{gem}=19.0 Hz, CH_2), 3.42 (1H, d, $J_{4,1}$=10.0 Hz, 4-H), 3.43 (3H, s, OMe), 4.61 (1H, d, $J_{1,4}$=10.0 Hz, 1-H), 8.14 (1H, br.s, COOH); MS *m/z* 273 ($M-H_2O+1$, 0.1%), 98 (base peak).

Found: C, 37.33; H, 3.83%. Calcd for $C_9H_{11}O_4Cl_3$: C, 37.50; H, 3.80%.

Dehydrochlorination of 4a. A mixture of **4a** (0.28 g, 1.3 mmol), triethylamine (0.6 ml, 4.4 mmol), and ethanol (5 ml) was refluxed for 30 h. After concentration the residue was extracted with benzene to give 0.08 g (41%) of **14a**.

14a: Colorless prisms from chloroform; mp 139—140 °C; UV (MeOH) 309 (ε 3000), 245 nm (5000); IR (KBr) 3260, 2250, 1744 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.24, 2.44 (each 3H, s, Me), 3.40 (1H, s, 8-H), 6.04 (1H, s, 3-H); ^{13}C NMR ($CDCl_3$) δ=19.2, 20.9 (each q, Me), 75.9 (s, 7-C), 85.3 (d, 8-C), 102.6 (s, 5-C), 110.7 (d, 3-C), 156.3 (s, 4-C), 160.6 (s, 2-C), 166.8 (s, 6-C); MS *m/z* 148 (M^+, 87%), 120 (base peak).

Found: C, 73.04; H, 5.58%. Calcd for $C_9H_8O_2$: C, 72.99; H, 5.44%.

Dehydrochlorination of 4b. A mixture of **4b** (0.26 g, 1.0 mmol), triethylamine (0.2 ml, 1.5 mmol), and ethanol (5 ml) was refluxed for 15 h. After concentration the residue was extracted with diethyl ether to give 0.21 g (97%) of **13b**.

13b: Colorless prisms from hexane; mp 130—132 °C; UV (MeOH) 296 (ε 5930), 237 nm (6040); IR (KBr) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.13 (3H, d, Me), 2.25 (3H, s, Me), 6.05 (1H, br. s, 3-H), 6.60 (1H, s, 8-H); ^{13}C NMR ($CDCl_3$) δ=17.9, 19.3 (each q, Me), 111.5 (d, 3-C), 113.5 (s, 5-C), 120.8 (d, 8-C), 127.3 (s, 7-C), 154.5 (s, 4-C), 161.1, 161.2 (each s, 2-, 6-C); MS *m/z* 218 (M^+, 29%), 43 (base peak).

Found: C, 49.46; H, 3.67%. Calcd for $C_9H_8O_2Cl_2$: C, 49.32; H, 3.65%.

Dehydrochlorination of 4c. A mixture of **4c**-1 and **4c**-2 (4 : 1 mix. 0.32 g, 1.5 mmol), triethylamine (0.4 ml, 3.0 mmol), and ethanol (5 ml) was refluxed for 15 h. After concentration the residue was column chromatographed using benzene to afford 0.23 g (89%) of **13c**.

13c: White crystal; mp 63—64 °C; UV (MeOH) 296 (ε 7200), 214 nm (7700); IR (KBr) 2250, 1740, 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.20, 2.30 (each 3H, s, Me), 5.96, 6.42 (each 1H, $=CH_2$), 6.06 (1H, br. s, 3-H), ^{13}C NMR ($CDCl_3$) δ=18.4, 20.3 (each q, Me), 111.8 (d, 3-C), 113.1, 116.1 (each s, 5-, 7-C), 116.8 (s, CN), 138.3 (t, 8-C), 154.4 (s, 4-, 6-C), 160.7 (s, 2-C); MS *m/z* 175 (M^+, 44%), 147 (base peak).

Found: C, 68.42; H, 5.19; N, 8.00%. Calcd for $C_{10}H_9NO_2$: C, 68.56; H, 5.17; N, 8.00%.

Dehydrochlorination of 8a. The refluxing of a mixture of **8a** (0.5 g, 2.1 mmol) and triethylamine (0.9 ml, 6.3 mmol) in 10 ml of ethanol for 2 h, followed by extraction with diethyl ether to give 0.4 g (95%) of **16a**. On the other hand, a mixture of **8a** (0.28 g, 1.2 mmol), triethylamine (0.8 ml, 6.0 mmol), and ethanol (5 ml) was refluxed for 38 h, and the same work-up as mentioned above afforded 0.17 g (89%) of **17a**.

16a: Colorless prisms from chloroform; mp 110—112 °C; UV (MeOH) 283 (ε 6500), 228 nm (8000); IR (KBr) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.28 (3H, s, Me), 3.84 (3H, s, OMe), 5.40, 5.74 (each 1H, d, J_{gem}=1.5 Hz, $=CH_2$), 5.46 (1H, s, 3-H); ^{13}C NMR ($CDCl_3$) δ=17.9, 56.4 (each q, Me), 87.5 (d, 3-C), 112.7 (s, 5-C), 121.1 (t, 8-C), 130.7 (s, 7-C), 161.2 (s, 2-C), 163.1 (s, 6-C), 168.7 (s, 4-C); MS *m/z* 200 (M^+, 84%), 165 (base peak).

Found: C, 53.94; H, 4.54%. Calcd for $C_9H_9O_3Cl$: C, 53.88; H, 4.52%.

17a: Colorless needles from chloroform-diethyl ether (1 : 1); mp 140—141 °C; UV (MeOH) 290 (ε 4300), 240 nm (7900); IR (KBr) 3300, 1745, 1723 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.42 (3H, s, Me), 3.37 (1H, s, 8-H), 3.87 (3H, s, OMe), 5.44 (1H, s, 3-H); ^{13}C NMR ($CDCl_3$) δ=19.2, 56.6 (each q, Me), 73.5 (s, 7-C), 85.3 (d, 8-C), 87.2 (d, 3-C), 97.7 (s, 5-C), 162.3 (s, 2-C), 167.9 (s, 6-C), 169.3 (s, 4-C); MS *m/z* 164 (M^+, base peak).

Found: C, 65.79; H, 4.93%. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91%.

Dehydrochlorination of 8b. The refluxing of a mixture of **8b** (0.82 g, 3.0 mmol) and triethylamine (1.6 ml, 12 mmol) in 30 ml of ethanol for 1.5 h and washing the residue with water to give the water-insoluble product **12b** (0.58 g, 82%). A solution of **12b** (15 mg, 0.06 mmol) in 0.3 ml of DMSO-d_6 was heated in the NMR sample tube at 100 °C for 2 h to give 11 mg (80%) of **16b**.

12b: Colorless prisms from chloroform; mp 124—126 °C; UV (MeOH) 281 nm (ε 2100); IR (KBr) 1720, 1670, 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.61 (3H, s, Me), 3.81 (3H, s, OMe), 4.80 (1H, s, 8-H), 5.28 (1H, s, 4-H); ^{13}C NMR ($CDCl_3$) δ=21.7, 56.6 (each q, Me), 67.3 (d, 8-C), 78.3 (s, 1-C), 96.1 (d, 4-C), 131.3, 135.3 (each s, 6-, 7-C), 159.2 (s, 3-C), 164.6 (s, 5-C); MS *m/z* 234 (M^+, 2%), 199 (base peak).

Found: C, 46.07; H, 3.42%. Calcd for $C_9H_8O_3Cl_2$: C, 45.99; H, 3.43%.

16b: Colorless prisms from diethyl ether-hexane (2 : 1); mp 124—127 °C; UV (MeOH) 284 (ε 3020), 228 nm (6200); IR (KBr) 1710 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.24 (3H, s, Me), 3.84 (3H, s, OMe), 5.48 (1H, s, 3-H), 6.57 (1H, s, 8-H); ^{13}C NMR ($CDCl_3$) δ=18.6, 56.5 (each q, Me), 87.7 (d, 3-C), 107.5 (s, 5-C), 120.1 (d, 8-C), 126.4 (s, 7-C), 160.5 (s, 2-C), 163.7 (s, 6-C), 169.5 (s, 4-C); MS *m/z* 234 (M^+, 16%), 199 (base peak).

Found: C, 46.08; H, 3.42%. Calcd for $C_9H_8O_3Cl_2$: C, 45.99; H, 3.43%.

X-Ray Analyses of Compounds 13b and 14a. Compounds **13b** and **14a** were recrystallized from diethyl ether-hexane (1 : 1) and diethyl ether solutions as colorless prisms, respectively. Crystal size: **13b** 0.56×0.35×0.42 mm^3, **14a** 0.56×0.35×0.21 mm^3. All data sets were measured by the ω—2θ scan method on a CAD4 diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å). SDP Program package[12] with the tables of atomic scattering factors[13] was used.

13b: Triclinic, space group $P\bar{1}$, a=7.405(4) Å, b=7.408 (4) Å, c=10.133(3) Å, α=71.44(7)°, β=71.44(7)°, γ=81.36(7)°, V=498.8(4) Å^3, d (calcd)=1.458 g cm^{-3} for z=2, μ (Mo $K\alpha$)= 11.90 cm^{-1}; 2911 unique reflections, solution by direct method (MULTAN 82),[14] and refined by least-squares method with full matrix, R=0.050, R_w=0.050, unit weights, for 172 variables and 1308 reflections with $I \geq 3.0 \times \sigma$ (I). All non-H atoms anisotropic with H atoms isotropic.

14a: Monoclinic, space group $P2_1/n$, a=9.854(12) Å, b=11.444(1) Å, c=20.439(2) Å, β=85.14(5)°, V=2297(3) Å^3, d (calcd)=1.285 g cm^{-3} for Z=4 (12 molecules), μ (Mo $K\alpha$)=0.846

cm^{-1}; 4158 unique reflections, solution by direct method (MULTAN 82),[14] and refined by least-squares method with full matrix, R=0.106, R_w=0.106, unit weights, for 298 variables and 2076 reflections with $I \geqq 3.0 \times \sigma(I)$. All non-H atoms anisotropic with H atoms isotropic. The unsymmetric unit consists of three identical molecules of **14a**. Crystal data, positional and thermal parameters, bond distances and angles as well as ORTEP drawings[15] and structure factors for compounds **13b** and **14a** are kept in the office of the Chemical Society of Japan (Document No. 8721).

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