Site-selective Photocycloadditions of 2-Pyrones with Electron-poor Olefins and the Derivation from the Cycloadducts

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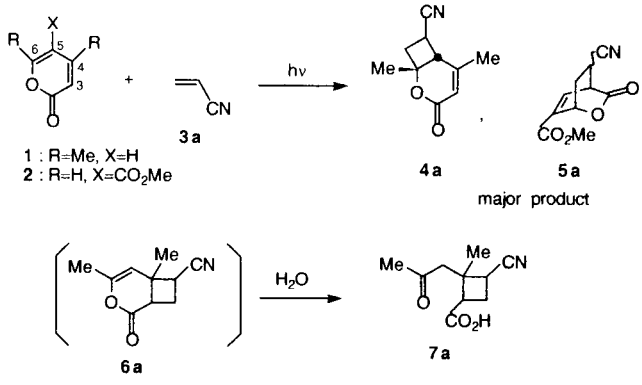
Received October 2, 1992

Photosensitized cycloaddition of 4,6-dimethyl-2-pyrone (**1**) with methacrylonitrile (**3b**) afforded two types of [2+2]cycloadducts, **4b** and **6b**, across the C_5-C_6 and C_3-C_4 double bonds in **1**, respectively. Photosensitized reactions of **1** with dimethyl maleate and dimethyl cyclobutene-1,2-dicarboxylate gave [2+2]cycloadducts **4d**, **4e** across the C_5-C_6 double bond, in addition to [4+2]cycloadduct **9d** or bicyclo[4.2.0]octadiene **10e**. The photoreactions of methyl 2-pyrone-5-carboxylate (**2**) with **3b** and 2-chloroacrylonitrile (**3c**) gave [4+2]cycloadducts **5b**, **5c** in addition to [2+2]cycloadducts **11b** and **11c** across the C_5-C_6 double bond in **2**. The photocycloaddition mechanism was explained from results calculated by means of PM3-CI method. Namely, the site- and/or regio-selective products, **4**, **5**, **8**, **9** and **10** were thought to come from the same site-selective radical intermediates in the case of electron-poor olefins. Pyrolysis and/or hydrolysis of the cycloadducts **4e**, **5b**, **5c** gave 5,6-dihydro-2-pyrone **12** or benzene derivatives.

J. Heterocyclic Chem., **30**, 419 (1993).

We previously reported that the photocycloaddition reactions of 2-pyrones with olefins gave [2+2]- and/or [4+2]cycloadducts, peri-selectively, and the cycloaddition mechanism was proposed [1-5]. Thus, sensitized photocycloadditions of 4,6-dimethyl-2-pyrone (**1**) with acrylonitrile (**3a**) afforded mainly [2+2]cycloadduct **4a** across the C_5-C_6 double bond in **1**, while methyl 2-pyrone-5-carboxylate (**2**) gave [4+2]cycloadduct **5a** (Scheme 1) and then the reaction mechanism was considered using MO method. As carboxylic acid **7a**, which was inferred to form from the hydrolysis of the photocycloadduct **6a**, was obtained in addition to **4a**, the cycloaddition of electron-poor olefin to the position of C_3-C_4 double bond in **1** was also suggested [1]. The site-selectivity is also interesting point.

Scheme 1



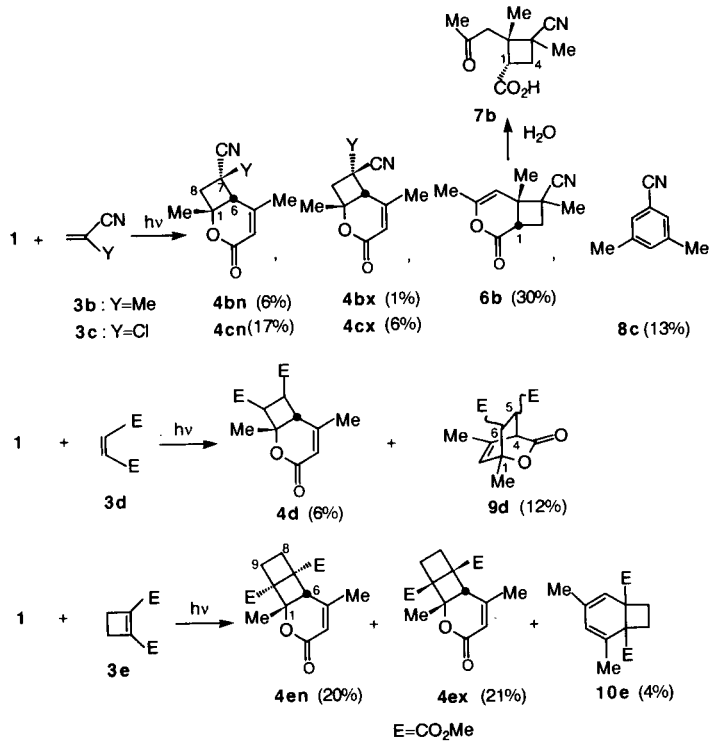
We describe herein the sensitized photoreactions of 2-pyrones **1**, **2** with electron-poor olefins in order to clarify the peri-selectivity more in detail, along with the derivation from the cycloadducts.

Photochemical Reactions.

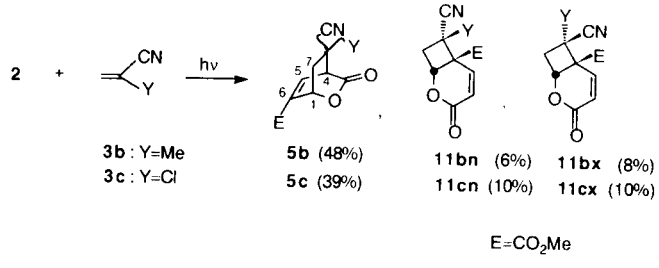
A solution of **1** and methacrylonitrile (**3b**) in acetonitrile in the presence of benzophenone as a sensitizer was irradiated with a 400W high-pressure mercury lamp through a Pyrex filter. After removal of the solvent the residue was chromatographed on silica gel to afford two kinds of [2+2]cycloadducts **4bn**, **4bx** and another type of [2+2]cycloadduct **6b** in 6%, 1% and 30% yields, respectively (Scheme 2). Photosensitized reaction of **1** with 2-chloroacrylonitrile (**3c**) gave [2+2]cycloadducts **4cn**, **4cx** and benzene derivative **8c** in our early report [2]. Compound **8c** is a product *via* eliminations of carbon dioxide and hydrogen chloride from the [4+2]cycloadduct. Photoreaction of **1** with dimethyl maleate (**3d**) afforded [2+2]cycloadduct **4d** (6%) and [4+2]cycloadduct **9d** (12%), and that of **1** with dimethyl cyclobutene-1,2-dicarboxylate (**3e**) afforded [2+2]cycloadducts **4en** (27%), **4ex** (21%), and bicyclo[4.2.0]octadiene **10e** (4%). Similarly, 2-pyrone **2** reacted with **3b** and **3c** to give [4+2]cycloadducts **5b** (48%), **5c** (39%), and [2+2]cycloadducts **11bn** (6%), **11bx** (8%) and **11cn** (10%), **11cx** (10%), respectively (Scheme 3).

The structures of **4b**, **4d**, **4e**, **11b**, and **11c** were assigned as [2+2]cycloadducts across the C_5-C_6 double bond in the 2-pyrone ring from the spectroscopic evidence compared to the related compounds reported earlier [2][6]. Another type of [2+2]cycloadduct **6b** was characterized as possessing strong carbonyl absorption at 1765 cm^{-1} in the ir spectrum for a γ,δ-unsaturated lactone. And the ^1H nmr spectrum showed higher-field chemical shift at δ 5.16 compared to that of compound **4b** (δ 5.94 for **4bn**, δ 6.20 for **4bx**). In addition, **6b** underwent hydrolysis to afford cyclobutanecarboxylic acid **7b** quantitatively. On the other

Scheme 2



Scheme 3

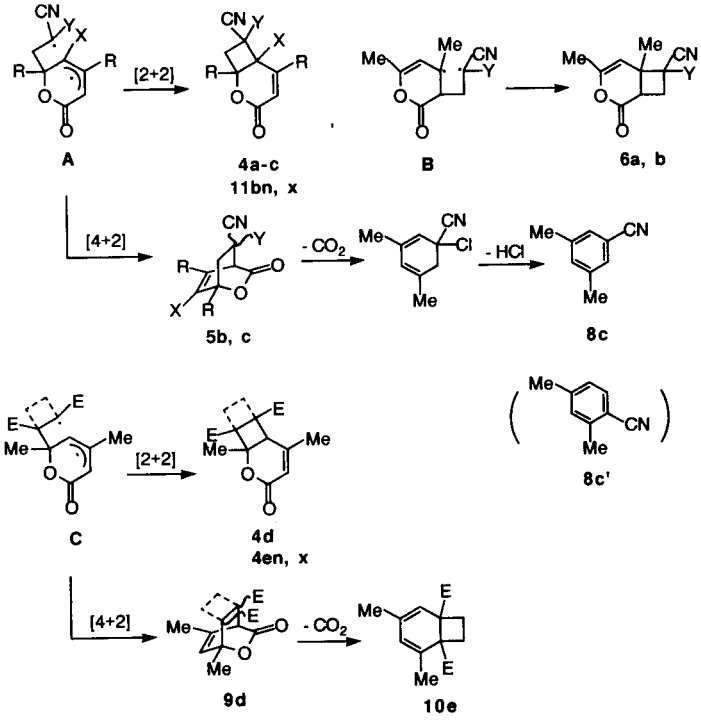


hand, the structures of **5b**, **5c** and **9d** were deduced as [4+2]cycloadducts from the spectroscopic data compared to the similar skeleton reported earlier [6][7]. Compound **10e** was assigned as dimethyl 2,4-dimethylbicyclo[4.2.0]-octa-2,4-diene-1,6-dicarboxylate from the ^{1}H nmr spectral data showing two olefinic protons at δ 6.19 and 5.72 for cyclohexadiene system. It was considered that **10e** was formed by the elimination of carbon dioxide from the [4+2]cycloadduct. These [4+2]cycloadducts were not obtained from the thermal reaction. If the thermal [4+2]-cycloaddition occur **8c'** will be obtained from the regio-isomer of **5c**.

On the basis of these results as shown in Schemes 2 and 3, photocycloaddition reactions of 2-pyrones with electron-poor olefins were confirmed to be site and peri-selective. Namely, the increase of the electron-deficiency at the olefin part lead to [2+2]cycloaddition across the 5,6-position in the 2-pyrone and [4+2]cycloaddition.

We next describe the photocycloaddition mechanism by using PM3-CI method [5]. It is reasonable to consider the mechanism of the cycloadditions of 2-pyrones **1**, **2** with cyanoethylenes **3b**, **3c**, and with dicarboxylates **3d**, **3e** is

Scheme 4



similar to that of reactions between 2-pyrones with acrylonitrile (**3a**), and with maleic anhydride (**3f**), respectively. The reasonable processes *via* biradical intermediates **A**, **B**, **C** in Scheme 4 are inferred from the narrow gaps (ΔE) of energies and the large coefficients (Ci, Cr) between two substrates in Figure 1 [5], and are quantitatively confirmed by large two-center frontier orbital interactions in Table 1 [5]. As the interactions, $(CiCr)^2/\Delta\epsilon$ (in γ^2/eV) have

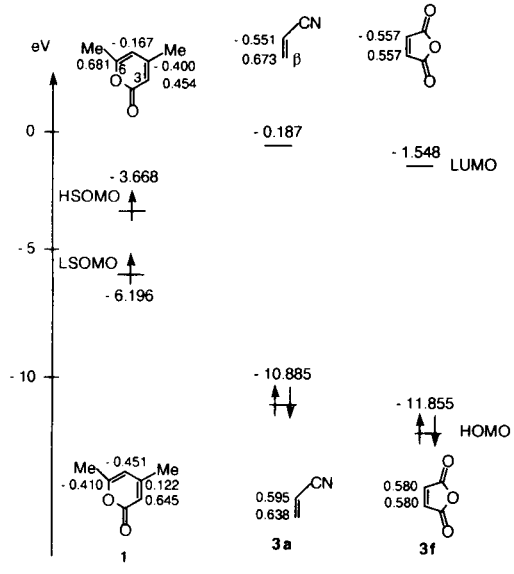


Figure 1 Estimated energies and coefficients of triplet 2-pyrones and ground-state olefins by means of PM3-CI method [5]

Table 1 Estimated Frontier Orbital Interactions between 2-Pyrones **1**, **2** and Olefins **3** by the PM3-CI Calculation (γ^2/ev)

		3a		maleic anhydride(3f)	
Position		6-β	3-β	6-β	3-β
$(CiCr)^2/\Delta\epsilon$	1	0.060 [a]	0.057 [b]	0.068	0.025
	2	0.060	0.039		

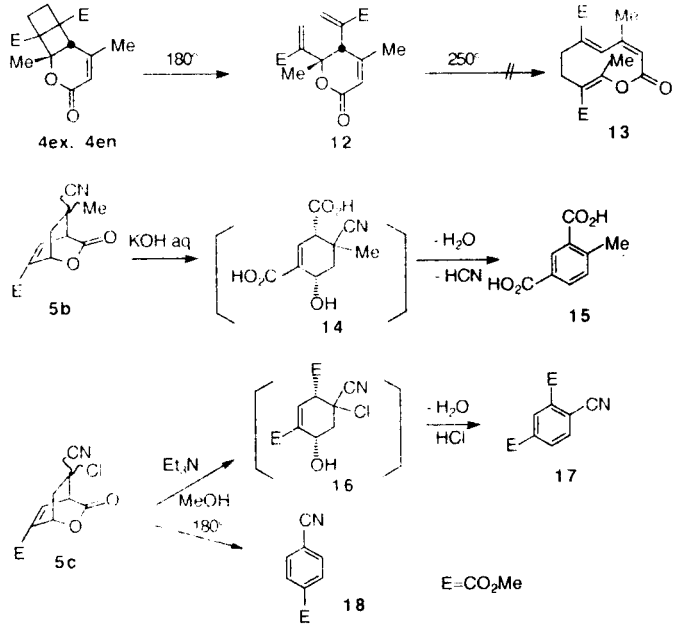
a) left: HSOMO(**1**)-LUMO(**3a**) interaction.
b) right: LSOMO(**1**)-HOMO(**3a**) interaction

a tendency to be larger between C_6 (**1** or **2**) and C_β (**3**), intermediates **A** and **C** occur by way of HSOMO (**1** or **2**) - LUMO (**3**) interaction. In the reaction of **1** with **3a**, the C_6 (**1**, HSOMO) - C_β (**3a**, LUMO) interaction is nearly equal to the C_3 (LSOMO) - C_β (HOMO) interaction, so intermediate **B** was thought to be generated. The reaction of **1** with **3b** was also estimated as similar as the case of **3a**. In the case of **3c** which has lower energy levels of LUMO and HOMO, it is considered that the [2+2]cycloadduct across the 3,4-position in the 2-pyrone was hardly obtained because of the wide energy gap of LSOMO (2-pyrone)-HOMO (olefin) interaction. The formation of **5** was also considered from the MO analysis.

Derivation from the Cycloadducts.

At first, [2+2]cycloadducts **4ex**, **4en** are equivalent to 5,6-dihydro-5,6-dialkenyl-2-pyrone **12** which is expected to give ten-member lactone **13** by the Cope rearrangement. So a solution of **4ex** in benzene was heated at 180° to give expected compound **12** in 97% yield, which did not afford ten-member lactone **13** at 250° (Scheme 5). Similar reaction of **4en** also gave **12** quantitatively. The structure of **12** was mainly considered from the ^{1}H- and ^{13}C-nmr spectral data showing five olefinic protons and nine sp^2-carbons, respectively. It is assumed that the Cope rearrangement of **12** was disturbed by the steric hindrance of the methyl group in **13**. Although [4+2]cycloadducts **5b**, **5c** were considered to be equivalent to stereo-controlled cyclohexene **14**, **15** the hydrolysis of **5b** and the methanolysis of **5c** gave benzene derivatives **15** and **17**, respectively. And the pyrolysis of **5c** also afforded **18**.

Scheme 5



EXPERIMENTAL

All the melting points were measured on a Yanagimoto Meltemp apparatus and are uncorrected. The ir and mass spectra were recorded on JASCO A-3, and JEOL JMSOISG spectrometers, respectively. The ^{1}H and ^{13}C nmr spectra were measured on JEOL JMN-MH 100 (100 MHz) and JEOL FX-100 (25 MHz) spectrometers using TMS as an internal reference. All the photoreactions were monitored by the use of gc, which was performed on a Yanagimoto G80 instrument using a column of Silicon SE-30 (10%)/Chromosorb W (AW) or tlc on silica gel plates.

4,6-Dimethyl-2-pyrone (**1**) [8], methyl 2-pyrone-5-carboxylate (**2**) [9] and dimethyl cyclobutene-1,2-dicarboxylate (**3e**) [10] were pre-

pared according to methods previously described in the literature.

1,5,7-Trimethyl-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-endo-7-carbonitrile (**4bn**), 1,5,7-Trimethyl-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-exo-7-carbonitrile (**4bx**), 4,6,7-Trimethyl-2-oxo-3-oxabicyclo-[4.2.0]oct-4-ene-7-carbonitrile (**6b**) and 2-Acetonyl-3-cyano-2,3-dimethylcyclobutane-1-carboxylic Acid (**7b**).

A solution of 4,6-dimethyl-2-pyrone (**1**) (3.0 g, 24 mmoles), methacrylonitrile (**3b**) (16.2 g, 240 mmoles) and benzophenone (0.5 g, 2.8 mmoles) in acetonitrile (200 ml) was irradiated under nitrogen for 1.5 hours at room temperature. The solvent was then removed *in vacuo* and the residue was chromatographed using benzene-acetone 20:1 v/v mixture to afford **4bn** (0.29 g, 6.4%), **4bx** (0.05 g, 1%) and **6b** (1.37 g, 30%). Adding one drop of water to **6b** (20 mg, 1.0 mmole) and left 10 days at room temperature to give **7b** (21 mg, 100%).

Compound **4bn** had mp 97-100°; ir (potassium bromide): 2240, 1700, 1650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.52, 1.68, 1.98 (each s, 3H, Me), 2.30, 2.96 (each d, 1H, 8-CH_2, J = 14.0 Hz), 2.76 (s, 1H, 6-H), 5.94 (bs, 1H, 4-H); ms: m/z (relative intensity) 191 (M^+, 2), 96 (100).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81; N, 7.33. Found: C, 68.83; H, 6.84; N, 7.33.

Compound **4bx** had mp 87-91°; ir (potassium bromide): 2240, 1693, 1650 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.48, 1.69, 2.04 (each s, 3H, Me), 2.48, 2.86 (each d, 1H, 8-CH_2, J = 14.0 Hz), 3.36 (s, 1H, 6-H), 6.20 (bs, 1H, 4-H); ms: m/z (relative intensity) 191 (M^+, 0.3), 96 (100).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81; N, 7.33. Found: C, 68.80; H, 6.86; N, 7.39.

Compound **6b** had mp 84-86° (hydroscopic); ir (potassium bromide): 2240, 1765 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.61, 1.56, 2.02 (each s, 3H, Me), 2.32, 2.78 (each dd, 1H, 8-CH_2, $J_{8,1} = J_{8',1} = 9.5$, $J_{8,8'} = 11.0$ Hz), 3.18 (t, 1H, 1-H, $J_{1,8} = 9.5$ Hz), 5.16 (bs, 1H, 5-H); ms: m/z (relative intensity) 191 (M^+, 5), 82 (100).

Anal. Calcd. for $C_{11}H_{13}NO_2 \cdot 2/9H_2O$: C, 67.69; H, 6.81; N, 7.33. Found: C, 67.70; H, 6.94; N, 7.05.

Compound **7b** had mp 84-86°; ir (potassium bromide): 2240, 1712, 1700 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.40, 1.52, 2.20 (each s, 3H, Me), 2.12, 2.96 (each dd, 1H, 4-CH_2, $J_{1,4} = J_{1,4'} = 8.0$, $J_{4,4'} = 12.0$ Hz), 2.82 (t, 1H, 1-H, J = 8.0 Hz), 3.06 (s, 2H, CH_2Ac), 10.0 (bs, 1H, CO_2H); ms; m/z (relative intensity) 209 (M^+, 0.2), 44 (100).

Anal. Calcd. for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70. Found: C, 63.15; H, 7.28; N, 6.56.

Dimethyl 1,5-Dimetyl-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-7,8-dicarboxylate (**4d**) and Dimethyl 1,8-Dimethyl-3-oxo-2-oxabicyclo-[2.2.2]oct-7-ene-5,6-dicarboxylate (**9d**).

A solution of **1** (3.0 g, 24 mmoles), dimethyl maleate and benzophenone (1.0 g, 5.5 mmoles) in acetone (200 ml) was irradiated for 5 hours at -10 to -25°. The solvent was removed at room temperature and the residue was chromatographed using benzene-acetone 10:1 v/v mixture to give **4d** (0.40 g, 6%) and **9d** (0.78 g, 12%).

Compound **4d** had mp 158-161°; ir (potassium bromide): 1720, 1705 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.63, 1.91 (each s, 3H, Me), 2.91 (dd, 1H, 8-H, $J_{8,7} = 8.0$, $J_{8,6} = 1.5$ Hz), 3.44 (dd, 1H, 6-H, $J_{6,7} = 8.0$, $J_{6,8} = 1.5$ Hz), 3.54 (t, 1H, 7-H, $J_{7,6} = J_{7,8} = 8.0$ Hz), 3.74 (s, 6H, Me), 5.77 (bs, 1H, 4-H); ms: m/z (relative intensity) 268 (M^+, 0.2), 124 (100).

Anal. Calcd. for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.31; H, 6.07.

Compound **9d** had mp 109-112° dec; ir (potassium bromide): 1750, 1725 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.63 (s, 3H, Me), 1.91 (d, 3H, Me, J = 2.0 Hz), 3.08 (d, 1H, 6-H, $J_{6,5} = 4.5$ Hz), 3.57 (dd, 1H, 5-H, $J_{5,4} = 3.0$, $J_{5,6} = 4.5$ Hz), 3.69-3.76 (m, 7H, CO_2Me, 4-H), 5.91 (bs, 1H, =CH); ms: m/z (relative intensity) 268 (M^+, 0.2), 165 (100).

Anal. Calcd. for $C_{13}H_{16}O_6$: C, 58.20; H, 6.01. Found: C, 58.20; H, 6.20.

Dimethyl 1,5-Dimethyl-3-oxo-2-oxatricyclo[4.4.0.$0^{7,10}$]dec-4-ene-endo-7,endo-10-dicarboxylate (**4en**), Dimethyl 1,5-Dimethyl-3-oxo-2-oxabicyclo[4.4.0.$0^{7,10}$]dec-4-ene-exo-7,exo-10-dicarboxylate and Dimethyl 2,4-Dimethylbicyclo[4.2.0]oct-2,4-diene-1,6-dicarboxylate (**10e**).

A solution of **1** (2.2 g, 18 mmoles), dimethyl cyclobutene-1,2-dicarboxylate (**3e**) (6.1 g, 36 mmoles) and benzophenone (0.90 g, 5.0 mmoles) in acetonitrile (200 ml) was irradiated at 0-10° for 2 hours. The solvent was removed and the resulting residue was chromatographed using benzene-acetone 10:1 v/v mixture to give **4en** (1.0 g, 20%), **4ex** (1.1 g, 21%) and **10e** (0.17 g, 4%).

Compound **4en** was obtained as an oil; ir (neat): 1720, 1700, 1653 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.60, 1.83, 3.72, 3.82 (each s, 3H, Me), 2.36, 3.03 (each m, 2H, CH_2), 6.03 (s, 1H, 4-H); ^{13}C nmr (deuteriochloroform): δ 20.7, 21.3, 22.3, 25.4, 45.0, 48.1, 52.0, 52.7, 59.3, 79.3, 117.1, 153.5, 162.6, 170.7, 171.5; ms: m/z (relative intensity) 294 (M^+, 2), 96 (100). High-resolution ms Calcd. for $C_{15}H_{18}O_6$: 294.1102. Found: 294.1100.

Compound **4ex** had mp 138-139°; ir (potassium bromide): 1720, 1700, 1655 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.63, 1.86, 3.66, 3.72 (each s, 3H, Me), 2.40, 3.00 (each m, 2H, CH_2), 5.86 (s, 1H, 4-H); ms: m/z (relative intensity) 294 (M^+, 10), 124 (100).

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.22; H, 6.17. Found: C, 60.97; H, 6.18.

Compound **10e** was obtained as an oil; ir (neat): 1740, 1718, 1640 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.96, 2.01 (each s, 3H, Me), 2.72 (m, 4H, 7-CH_2, 8-CH_2), 3.47 (s, 6H, Me), 5.72, 6.19 (each bs, 1H, =CH); ^{13}C nmr (deuteriochloroform): δ 21.1, 21.9, 24.3, 28.3, 49.6, 51.9, 52.0, 52.6, 57.9, 84.8, 116.8, 150.5, 162.8, 169.7, 169.9; ms: m/z (relative intensity) 250 (M^+, 10), 190 (100). High-resolution ms Calcd. for $C_{14}H_{18}O_4$: 250.1204. Found: 250.1206.

Methyl 8-Cyano-8-methyl-3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (**5b**), Methyl endo-7-Cyano-exo-7-methyl-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-6-carboxylate (**11bn**) and Methyl exo-7-Cyano-endo-7-methyl-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-6-carboxylate (**11bx**).

A solution of methyl 2-pyrone-5-carboxylate (**2**) (3.0 g, 20 mmoles), **3b** (8.2 ml, 100 mmoles) and benzophenone (1.0 g, 5.5 mmoles) in benzene (200 ml) was irradiated at room temperature for 6 hours. After evaporation of the solvent, the resulting solid was filtered and recrystallized from benzene to give **5b** (2.1 g, 48%). The filtrate was chromatographed using benzene-acetone 5:1 v/v mixture to afford **11bn** (0.27 g, 6%) and **11bx** (0.35 g, 8%).

Compound **5b** had mp 178-179°; ir (potassium bromide): 2230, 1772, 1717, 1634 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.65, 3.83 (each s, 3H, Me), 2.30 (m, 2H, CH_2), 3.76 (d, 1H, 4-H, $J_{4,5} = 7.0$

Hz), 5.76 (m, 1H, 1-H), 7.50 (dd, 1H, 5-H, $J_{5,4}$ = 7.0, $J_{5,1}$ = 2.5 Hz); ms: m/z (relative intensity) 222 (M^+, 0.1), 118 (100).

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33. Found: C, 59.54; H, 5.07; N, 6.21.

Compound **11bn** had mp 74-76°; ir (potassium bromide): 2230, 1738, 1725, 1640 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.48, 3.82 (each s, 3H, Me), 2.56, 2.78 (each dd, 1H, 8-CH_2, $J_{8,1}$ = 8.0, $J_{8,8'}$ = 12.5 Hz), 5.39 (td, 1H, 1-H, $J_{1,8}$ = $J_{1,8'}$ = 8.0, $J_{1,5}$ = 2.0 Hz), 6.30 (d, 1H, 4-H, $J_{4,5}$ = 10.0 Hz), 7.04 (dd, 1H, 5-H, $J_{5,1}$ = 2.0, $J_{5,4}$ = 10.0 Hz); ms: m/z (relative intensity) 221 (M^+, 0.2), 126 (100).

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33. Found: C, 59.97; H, 5.14; N, 6.27.

Compound **11bx** had mp 114-115°; ir (potassium bromide): 2230, 1734, 1728, 1640 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.54, 3.84 (each s, 3H, Me), 2.29, 2.90 (each dd, 1H, 8-CH_2, $J_{8,1}$ = 8.0, $J_{8',1}$ = 8.5, $J_{8,8}$ = 12.0 Hz), 5.50 (td, 1H, 1-H, $J_{1,5}$ = 2.0, $J_{1,8}$ = 8.0, $J_{1,8'}$ = 8.5 Hz), 6.30 (d, 1H, 4-H, $J_{4,5}$ = 10.0 Hz), 6.78 (dd, 1H, 5-H, $J_{5,1}$ = 2.0, $J_{5,4}$ = 10.0 Hz); ms: m/z (relative intensity) 222 (M + 1, 0.2), 126 (100).

Anal. Calcd. for $C_{11}H_{11}NO_4$: C, 59.73; H, 5.01; N, 6.33. Found: C, 59.50; H, 5.03; N, 6.52.

Methyl 8-Chloro-8-cyano-3-oxo-2-oxabicyclo[2.2.2]oct-5-ene-6-carboxylate (**5c**), Methyl exo-7-Chloro-endo-7-cyano-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-6-carboxylate (**11cn**) and Methyl endo-7-Chloro-exo-7-cyano-3-oxo-2-oxabicyclo[4.2.0]oct-4-ene-6-carboxylate (**11cx**).

A solution of **2** (3.0 g, 20 mmoles), **3c** (8.5 g, 100 mmoles) and benzophenone (1.0 g, 5.5 mmoles) in benzene (200 ml) was irradiated at room temperature for 5 hours. After evaporation of the solvent, the resulting residue was chromatographed using benzene-acetone 10:1 v/v mixture to afford **5c** (1.8 g, 39%) and a mixture of **11cn** (0.45 g, 10%) and **11cx** (0.45 g, 10%) whose yields were determined from the ^1H nmr spectrum.

Compound **5c** had mp 132-135°; ir (potassium bromide): 2245, 1776, 1729, 1636 cm^{-1}; ^1H nmr (deuteriochloroform): δ 2.89 (m, 2H, 7-CH_2), 3.87 (s, 3H, Me), 4.24 (d, 1H, 4-H, $J_{4,5}$ = 6.0 Hz), 5.80 (m, 1H, 1-H), 7.41 (dd, 1H, 5-H, $J_{5,1}$ = 2.0, $J_{5,4}$ = 6.0 Hz); ms: m/z (relative intensity) 210 (M-OMe, 4), 118 (100).

Anal. Calcd. for $C_{10}H_8NO_4Cl$: C, 49.71; H, 3.34; N, 5.80. Found: C, 49.64; H, 3.38; N, 5.76.

Mixture of **11cn** and **11cx**; ir (potassium bromide): 2250, 1740, 1720 cm^{-1}; ^1H nmr (deuteriochloroform): **11cn** δ 3.0-3.5 (m, 2H, 8-CH_2), 3.94 (s, 3H, Me), 5.48 (m, 1H, 1-H), 6.40 (d, 1H, 4-H, $J_{4,5}$ = 10.0 Hz), 7.07 (dd, 1H, 5-H, $J_{5,4}$ = 10.0, $J_{5,1}$ = 2.0 Hz); **11cx** δ 3.0-3.5 (m, 2H, 8-CH_2), 3.94 (s, 3H, Me), 5.48 (m, 1H, 1-H), 6.40 (d, 1H, 4-H, $J_{4,5}$ = 10.0 Hz), 6.92 (dd, 1H, 5-H, $J_{5,4}$ = 10.0, $J_{5,1}$ = 2.0 Hz); ms: m/z (relative intensity) 210 (M-OMe, 12), 118 (100).

Anal. Calcd. for $C_{10}H_8NO_4Cl$: C, 49.71; H, 3.34; N, 5.80. Found: C, 49.63; H, 3.36; N, 5.87.

5,6-Bis(1-methoxycarbonylethenyl)-5,6-dihydro-4,6-dimethyl-2-pyrone (**12**).

A benzene (2 ml) solution of **4ex** (176 mg, 0.60 mmole) in a sealed tube was heated at 180° for 7.5 hours. After evaporation of the solvent, the residual oil was chromatographed using benzene-acetone 10:1 v/v to give **12** (170 mg, 97%). Similar heating of **4en** for 2 hours gave **12** quantitatively.

Compound **12** was obtained as an oil; ir (neat): 1725 cm^{-1}; ^1H nmr (deuteriochloroform): δ 1.78, 1.97 (each s, 3H, Me), 3.71 (s, 6H, CO_2Me), 4.15 (bs, 1H, 5-H), 5.96 (bs, 1H, 3-H), 5.60, 6.18, 6.29, 6.35 (each bs, 1H, $=CH_2$); ^{13}C nmr (deuteriochloroform): δ 22.2, 26.5, 47.0, 52.0, 52.4, 83.5, 116.4, 128.0, 129.6, 136.8, 140.5, 158.2, 163.4, 165.5, 167.0; ms: m/z (relative intensity) 295 (M + 1, 100).

Anal. Calcd. for $C_{15}H_{18}O_6$: C, 61.22; H, 6.17. Found: C, 61.34; H, 6.23.

Hydrolysis of Methanolysis of **5b** and **5c**.

A mixture of **5b** (192 mg, 0.87 mmole) and 5% potassium hydroxide aqueous solution (5 ml) was refluxed for 1 hour. After neutralization of the solution with hydrochloric acid, resulting solid was recrystallized from ethanol to give 4-methylisophthalic acid **15** (130 mg, 83%). A solution of **5c** (240 mg, 1.0 mmole) and triethylamine (200 mg, 2.0 mmoles) in methanol (10 ml) was refluxed for 2 hours. After filtration of the solid, the filtrate was concentrated to give **17** (136 mg, 62%).

Compound **17** had mp 162-164°; ir (potassium bromide): 2240, 1732, 1725 cm^{-1}; ^1H nmr (deuteriochloroform): δ 4.00, 4.04 (each s, 3H, Me), 7.93, 8.32, 8.77 (Aromatic protons); ms: m/z (relative intensity) 219 (M^+, 25), 188 (100).

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