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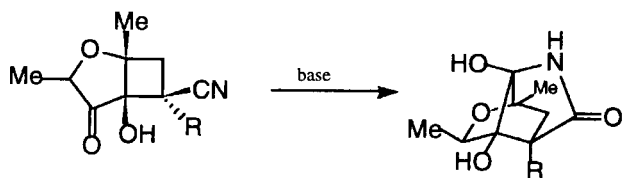
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Dehydrochlorination of chlorinated 5-hydroxy-2-oxabicyclo[3.2.0]heptan-4-ones, **3a-c**, which were obtained from the photo[2+2]cycloadditions between 4-hydroxy-3(2*H*)-furanone **1** and chloroethylenes, with triethylamine gave 2-ethenyl-3(2*H*)-furanones **4a,b** or 2-(2-cyanoethyl)-3(2*H*)-furanone **4c**. 2-Oxabicyclo[3.2.0]hept-6-en-4-ones **7** being [2+2]cycloadducts between **1** and acetylenes gave 2,3-dihydro-3-oxooxepin derivatives **8** by electrocyclic rearrangement.

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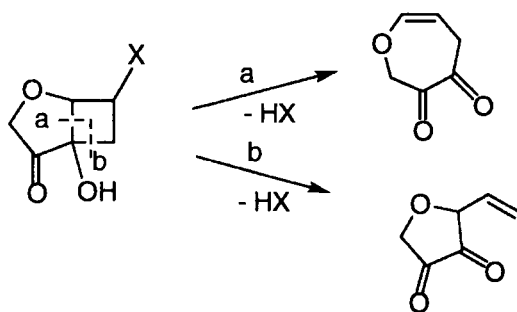
Although photochemical [2+2]cycloaddition reactions of 3(2*H*)-furanones with alkenes, which give an oxabicyclo[3.2.0]heptanone ring system, have been reported [1], little attention has been given to the ring-transformation reaction, except for the derivations of dioxabicyclo[3.3.0]octanone [2] and oxabicyclo[4.3.0]nonanones [3]. We previously reported a ring-transformation reaction of 5-hydroxy-4-oxo-2-oxabicyclo[3.2.0]heptane-6-carbonitriles, which were obtained from photocycloaddition reaction between 4-hydroxy-3(2*H*)-furanone **1** and cyanoethylenes, to give tricyclic  $\gamma$ -lactams (Scheme 1) [4]. Since

Scheme 1



[2+2]cycloadducts of **1** with chloroethylenes have a hydroxyl group on the cyclobutane ring, a ring-transformation *via* type-a bond fission of the strained cyclobutane may be expected to afford functionalized seven-membered ring ethers using a base as shown in Scheme 2. Medium-sized ring ethers occur widely in nature, particularly in marine natural products [5].

Scheme 2



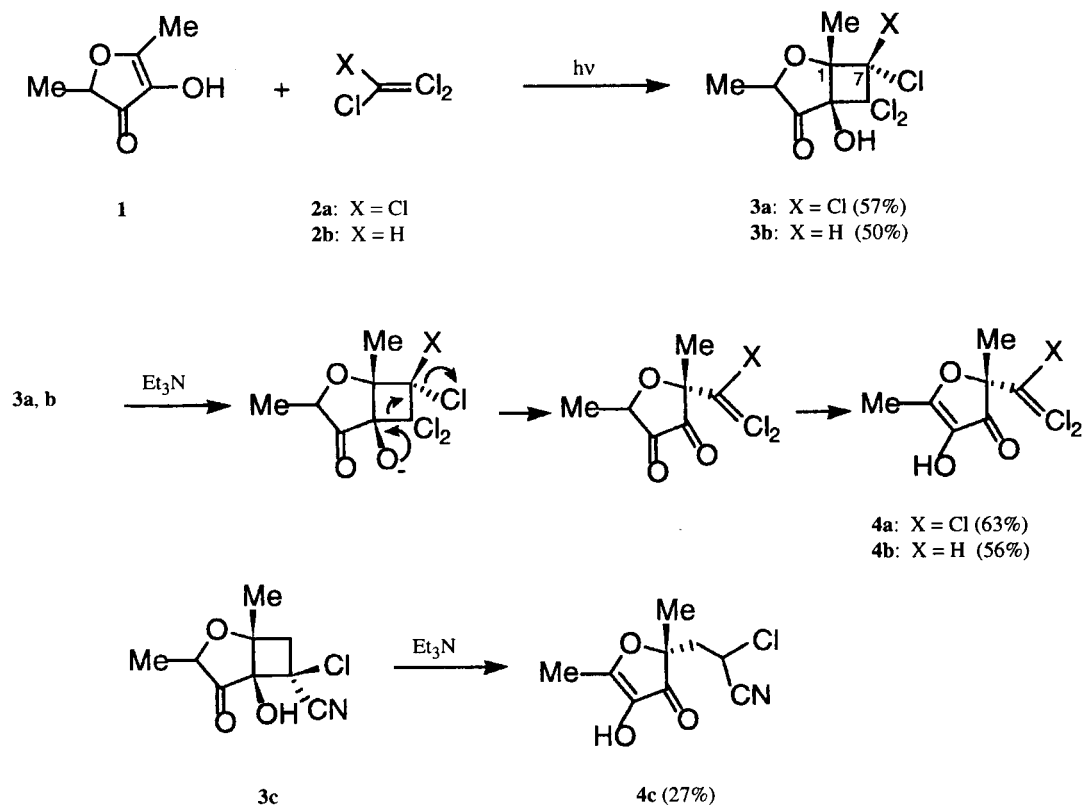
In this paper, ring-transformation reactions of the [2+2]cycloadducts of **1** with chloroethylenes or acetylenes are described.

A solution of **1** and tetrachloroethylene (**2a**) in acetonitrile 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 [2+2]cycloadduct **3a** in 57% yield. Similar photoreaction of **1** with trichloroethylene (**2b**) gave **3b** in 50% yield (Scheme 3). The regio- and stereochemistry of **3b** was confirmed by noting the magnitude of the NOE between 1-Me and 7-H. A solution of **3a** and triethylamine was refluxed in acetonitrile to give **4a** in 63% yield. Similar treatment of **3b** and **3c** [4] afforded **4b** (56%) and **4c** (27%), respectively, as shown in Scheme 3. The structures of **4a,b** and **4c** were assigned as 2-ethenyl-3(2*H*)-furanones and 2-(2-cyanoethyl)-3(2*H*)-furanone, respectively, from the spectral data compared to that of **1**.

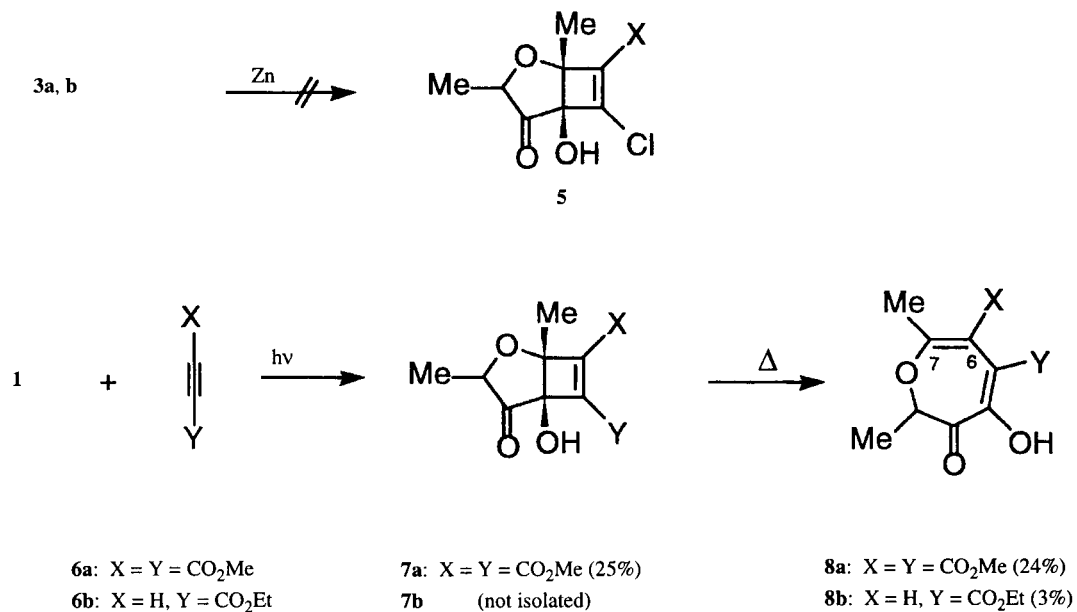
Since the treatment of 5-hydroxy-2-oxabicyclo[3.2.0]heptane-4-ones with base did not give seven-membered ring ethers but gave 2-ethenyl-3(2*H*)-furanones *via* type-b bond fission of the cyclobutane ring (Scheme 2), we set about to make cyclobutenes **5** and **8** whose compounds were expected to undergo ring opening reaction by electrocyclic rearrangements. At first dechlorination of the [2+2]cycloadducts **3a,b** with zinc dust in refluxing toluene for 4 days did not afford cyclobutene **5**.

A solution of **1** and dimethyl acetylenedicarboxylate (**5a**) in acetonitrile was irradiated. After removal of the solvent the residue was chromatographed on silica gel to give [2+2]cycloadduct **7a** in 25% yield. Similar photoreaction of **1** with ethyl propiolate (**6b**) did not give [2+2]cycloadduct **7b** but gave a ring-opened compound **8b** in 3% yield (Scheme 4). Thermal reaction of **7a** at 150° afforded **8a** in 24% yield, but photoirradiation to **7a** gave no product using low- and high-pressure mercury lamps. The products **7a,b** were assigned as 2,3-dihydro-3-oxooxepin carboxylates on the basis of spectral data. For example, **8b**, ethyl 2,7-dimethyl-2,3-dihydro-4-

Scheme 3



Scheme 4



hydroxy-3-oxooxepin-5-carboxylate, showed one olefinic proton at  $\delta$  7.09 in the  $^1\text{H}$  nmr and four  $\text{sp}^2$  carbons derived from  $\text{C}=\text{C}$  bond at  $\delta$  121.6, 133.5, 145.7, and 147.3 in the  $^{13}\text{C}$  nmr. In addition, NOE enhancement was observed between 6-H and 7-Me.

## EXPERIMENTAL

All of the melting points were measured on a Yanagimoto Mel-temp apparatus and are uncorrected. The ir and mass spectra were recorded on JASCO A-3 and JEOL JMSOISG spectrometers, respectively. The  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were measured on JEOL JNM-GSX 400 spectrometer. All the photoreactions were monitored by tlc on silica gel plates.

6,6,7,7-Tetrachloro-5-hydroxy-1,3-dimethyl-2-oxabicyclo[3.2.0]heptan-4-one (**3a**) and 6,6,7-Trichloro-5-hydroxy-1,3-dimethyl-2-oxabicyclo[3.2.0]heptan-4-one (**3b**).

A solution of 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**1**) (4.00 g, 31.3 mmoles) and tetrachloroethylene (51.9 g, 313 mmoles) in acetonitrile (200 ml) was irradiated under nitrogen for 14 hours at room temperature. The solvent was then removed *in vacuo* and the residue was chromatographed using ethyl acetate-hexane 1:5 v/v mixture to afford **3a** (5.24 g, 57%), which was recrystallized from a 1:1 v/v mixture of hexane-carbon tetrachloride. A similar photoreaction of **1** (4.00 g, 31.3 mmoles) with trichloroethylene (41.1 g, 313 mmoles) for 12 hours and the same work up gave **3b** (4.03 g, 50%).

Compound **3a** had mp 81-83°; ir (potassium bromide): 3400, 1810  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.25 (d, 3H, 3-Me,  $J = 6.4$  Hz), 1.50 (s, 3H, 1-Me), 3.41 (s, 1H, OH), 4.58 (q, 1H, 3-H,  $J = 6.4$  Hz); ms:  $m/z$  293 (M+1).

*Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{O}_3\text{Cl}_4$ : C, 32.69; H, 2.74. Found: C, 32.63; H, 2.71.

Compound **3b** had mp 79-81°; ir (potassium bromide): 3450, 1800  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.24 (d, 3H, 3-Me,  $J = 6.4$  Hz), 1.33 (s, 3H, 1-Me), 3.31 (s, 1H, OH), 4.25 (q, 1H, 3-H,  $J = 6.4$  Hz), 4.64 (s, 1H, 7-H); ms:  $m/z$  259 (M+1).

*Anal.* Calcd. for  $\text{C}_8\text{H}_9\text{O}_3\text{Cl}_3$ : C, 37.03; H, 3.50. Found: C, 37.09; H, 3.52.

2-Trichloroethenyl-4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**4a**), 2-(2,2-Dichloroethenyl)-4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**4b**) and 2-(2-Chloro-2-cyanoethyl)-4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**4c**).

A solution of **3a** (407 mg, 1.38 mmoles) and triethylamine (280 mg, 1.66 mmoles) in acetonitrile (30 ml) was refluxed for 2.5 hours. After filtration of the solid, the filtrate was concentrated and the resulting residue was chromatographed using ethyl acetate-hexane 1:5 v/v mixture to afford **4a** (224 mg, 63%), which was recrystallized from a 3:1 v/v mixture of hexane-carbon tetrachloride. A similar treatment of **3a** (500 mg, 1.93 mmoles) and **3c** (796 mg, 3.69 mmoles) with triethylamine gave **4b** (241 mg, 56%) and **4c** (212 mg, 27%), respectively.

Compound **4a** had mp 106-109°; ir (potassium bromide): 3400, 1700, 1620  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.73, 2.25 (each s, 3H, Me), 4.70 (s, 1H, OH);  $^{13}\text{C}$  nmr (deuterio-

chloroform):  $\delta$  13.3, 24.3, 86.0, 124.6, 127.4, 133.2, 171.4, 195.6; ms:  $m/z$  256 (M+).

*Anal.* Calcd. for  $\text{C}_8\text{H}_7\text{O}_3\text{Cl}_3$ : C, 37.32; H, 2.74. Found: C, 37.08; H, 2.77.

Compound **4b** was obtained as a pale yellow oil; ir (neat): 3400, 1700, 1620  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.58, 2.26 (each s, 3H, Me), 5.96 (s, 1H, =CH), 6.60 (s, 1H, OH); ms:  $m/z$  222 (M+).

*Anal.* Calcd. for  $\text{C}_8\text{H}_8\text{O}_3\text{Cl}_2$ : C, 43.03; H, 28.98. Found: C, 43.10; H, 29.12.

Compound **4c** had mp 81-84°; ir (potassium bromide): 3400, 2320, 1710, 1610  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.47, 2.31 (each s, 3H, Me), 2.53 (dd, 1H, CH,  $J_{\text{gem}} = 14.4$  Hz,  $J = 5.6$  Hz), 2.63 (dd, 1H, CH,  $J_{\text{gem}} = 14.4$  Hz,  $J = 8.8$  Hz), 4.34 (dd, 1H, CH,  $J = 8.8$  Hz,  $J = 5.6$  Hz), 6.30 (s, 1H, OH); ms:  $m/z$  215 (M+).

*Anal.* Calcd. for  $\text{C}_9\text{H}_{10}\text{NO}_3\text{Cl}$ : C, 50.13; H, 4.67; N, 6.49. Found: C, 50.29; H, 4.76; N, 6.46.

Dimethyl 5-hydroxy-1,3-dimethyl-4-oxo-2-oxabicyclo[3.2.0]hept-6-ene-6,7-dicarboxylate (**7a**), Dimethyl 2,3-dihydro-4-hydroxy-2,7-dimethyl-3-oxooxepin-5,6-dicarboxylate (**8a**) and Ethyl 2,3-dihydro-4-hydroxy-2,7-dimethyl-3-oxooxepin-5-carboxylate (**8b**).

A solution of **1** (2.00 g, 15.6 mmoles) and dimethyl acetylenedicarboxylate (4.43 g, 31.2 mmoles) in acetonitrile (200 ml) was irradiated for 6 hours. The solvent was then removed *in vacuo* and the residue was chromatographed using ethyl acetate-benzene 1:2 v/v mixture to afford cyclobutene **7a** (1.10 g, 25%). A similar photoreaction of **1** (4.00 g, 31.3 mmoles) with methyl propiolate (4.72 g, 48.2 mmoles) for 17 hours and the same work up gave oxooxepin derivative **8b** (12 mg, 3%). Compound **7a** (471 mg, 1.70 mmoles) was heated in the glass tube oven at 150° for 1 hour. The resulting oil was chromatographed using ethyl acetate-hexane 1:2 v/v mixture to afford **8a** (112 mg, 24%).

Compound **7a** was obtained as pale yellow oil; ir (neat): 3450, 1750, 1720, 1640  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.37 (d, 3H, 2-Me,  $J = 7.2$  Hz), 1.83 (s, 3H, Me), 3.81, 3.88 (each s, 3H, Me), 3.92 (q, 1H, 3-H,  $J = 7.2$  Hz), 4.40 (s, 1H, OH); ms:  $m/z$  272 (M+2).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_7$ : C, 53.33; H, 5.22. Found: C, 53.38; H, 5.44.

Compound **8a** was obtained as pale yellow oil; ir (neat): 3500, 1720, 1690, 1680, 1600  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.50 (d, 3H, 2-Me,  $J = 6.4$  Hz), 2.48 (s, 3H, Me), 3.48 (s, 1H, OH), 3.94, 3.96 (each s, 3H, Me), 4.97 (q, 1H, 2-H,  $J = 6.4$  Hz);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  10.1, 21.0, 52.8, 52.9, 70.3, 126.4, 132.1, 143.6, 146.0, 157.6, 162.5, 193.1; ms:  $m/z$  239 (M-OMe).

*Anal.* Calcd. for  $\text{C}_{12}\text{H}_{14}\text{O}_7$ : C, 53.33; H, 5.22. Found: C, 53.28; H, 5.30.

Compound **8b** was obtained as pale yellow oil; ir (neat): 3450, 1727, 1680, 1590  $\text{cm}^{-1}$ ;  $^1\text{H}$  nmr (deuteriochloroform):  $\delta$  1.39, 4.40 ( $\text{CO}_2\text{CH}_2\text{CH}_3$ ), 1.51 (d, 3H, Me,  $J = 6.8$  Hz), 2.44 (s, 3H, Me), 3.54 (s, 1H, OH), 5.00 (q, 1H, 2-H,  $J = 6.8$  Hz), 7.09 (s, 1H, 6-H);  $^{13}\text{C}$  nmr (deuteriochloroform):  $\delta$  12.0, 14.5, 21.4, 62.0, 70.4, 121.6, 133.5, 145.7, 147.3, 158.3, 193.5; ms:  $m/z$  227 (M+1).

*Anal.* Calcd. for  $\text{C}_{11}\text{H}_{14}\text{O}_5$ : C, 58.40; H, 6.24. Found: C, 58.22; H, 6.20.

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