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An Efficient Synthesis of Bicyclo[3.1.0]hex-3-en-2-one

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Synopsis. Bicyclo[3.1.0]hex-3-en-2-one is synthesized in fair yield in five steps from 4-cyclopentene-1,3-dione-furan Diels-Alder adduct.

Although a good number of derivatives of bicyclo-[3.1.0]-hex-3-en-2-one (**1**) have been described, there is only one paper dealing with the synthesis of the parent componnd.[1] The preparation starts from 2-cyclopentenone and the total yield is poor. We have recently reported the preparation of 4-cyclopentene-1,3-dione-furan Diels-Alder adduct (*exo*-10-oxatricyclo[5.2.1.$0^{2,6}$]-dec-8-en-3,5-dione) (**2**).[2] In view of ready thermal cycloreversion of furan–Diels-Alder adducts[3] and of high reactivities of 1,3-diones, the adduct (**2**) could be a versatile synthetic intermediate for cyclopentenoids. We here describe an efficient synthesis of the parent compound (**1**) from **2**.

Treatment of **2** with a slight excess of triethyloxonium tetrafluoroborate[4] in the presence of triethylamine in methylene chloride afforded the enol ether (**3**) in quantitative yield. The enol ether (**3**) was then converted into the cyclopentenone derivative (**4**) by reduction with lithium aluminum hydride and following acid hydrolysis of the resulting hydroxy enol ether with aqueous acetic acid in 54% overall yield.

Cyclopropanation of **4** using dimethylsulfoxonium methylide[5] in dimethyl sulfoxide gave the cyclopropyl ketone (**5**) in 84% yield. The configuration of the cyclopropane ring is tentatively assigned to be *anti* to the 2,5-dihydrofuran moiety on the basis of steric hindrance.

As expected, the thermal cycloreversion of **5** to **1** was fairly easy: on heating in a short-path distillating apparatus[6] at 120—140 °C at the pressure of 200 mmHg, **5** gave almost pure material of **1** in 76% yield.

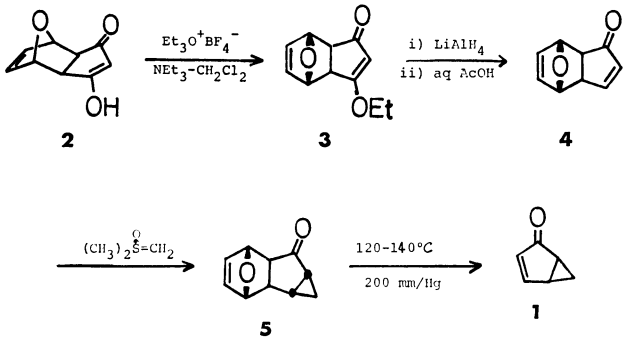

Chart.

Experimental

Melting points were uncorrected. IR spectra were recorded with a Hitachi 215 grating spectrometer and PMR with a Varian A-60A and a JEOL PMX-60 spectrometers. Microanalyses were performed at the Microanalytical Laboratory in this department.

*5-Ethoxy-10-oxatricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (**3**).* To a solution of 10-oxatricyclo[5.2.1.$0^{2,6}$]deca-8-en-3,5-dione (**2**)[2] (10.0 g, 61 mmol) and triethylamine (7.88 g, 78 mmol) in methylene chloride (100 ml) was added rapidly triethyloxonium tetrafluoroborate (14.0 g, 74 mmol) at room temperature. After stirring for one hour, the reaction mixture was washed with water (30 ml×5), dried over $MgSO_4$, and the solvent evaporated off under reduced pressure to give 11.7 g (100%) of **3** as solids. Recrystallization from benzene gave pure materials, mp 137—138 °C. IR (KBr) 1674, 1582 cm^{-1}; PMR ($CDCl_3$) δ 6.53 (2H, s), 5.37 (1H, s), 5.12 (1H, br. s), 5.04 (1H, br. s), 4.14 (2H, q, J 7.0 Hz), 2.88 (1H, d, 5.6), 2.57 (1H, d, 5.6), 1.44 (3H, t, 7.0). Found: C, 68.66; H, 6.54%. Calcd for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29%.

*9-Oxatricyclo[5.2.1.$0^{2,6}$]deca-4,8-dien-3-one (**4**).* To a suspension of lithium aluminum hydride (1.14 g, 30 mmol) in ether (150 ml) was added dropwise a solution of the crude **3** (11.7 g, 61 mol) in tetrahydrofuran (150 ml) under stirring in an ice-bath. The mixture was then stirred at room temperature for two hours. Water (10 ml) was cautiously added to the reaction mixture under ice-cooling and then 20 g of $MgSO_4$. The solids were filtered with suction and washed with tetrahydrofuran (50 ml×3), and the filtrate concentrated to leave 11.2 g of oil which on standing mostly crystallized. The crude product was then dissolved in 60% aqueous acetic acid (50 ml) and the solution was allowed to stand at room temperature for two days. The mixture was added with methylene chloride (250 ml), and the organic layer was washed with water (50 ml×3), saturated aqueous sodium carbonate until no more carbon dioxide evolved, and finally with brine, and the organic layer dried. Removal of the solvent left 8.6 g of pale yellow oil. Chromatography on silica gel (100 g) using benzene–ethyl acetate as eluent afforded 4.9 g (54%) of **4**, mp 69—70 °C. IR (KBr) 1692, 1584 cm^{-1}; PMR ($CDCl_3$) δ 7.65 (1H, ddd, J 5.6, 2.5, 0.5 Hz), 6.5 (2H, m), 6.24 (1H, dd, 5.6, 1.3), 4.99 (1H, m), 4.78 (1H, m), 3.01 (1H, ddd, 5.0, 2.5, 1.3), 2.39 (1H, d, 5.0). Found: C, 72.99; H, 5.44%. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44%.

*11-Oxatetracyclo[6.2.1.$0^{2,7}$.$0^{4,6}$]undec-9-en-3-one (**5**).* To a solution of dimethylsulfoxonium methylide prepared *in situ* from trimethylsulfoxonium iodide (4.0 g, 18 mmol) and sodium hydride (450 mg, 18.8 mmol) in dimethyl sulfoxide (25 ml) was added **4** (2.40 g, 16 mmol) under nitrogen atmosphere at room temperature. After one hour, ice-water (150 ml) was added and the mixture extracted with methylene chloride (50 ml×3), and the organic layer was washed with water (25 ml×2), and dried. After removal of the solvent, the residue was passed through a short silica gel column (30 g) to afford 2.20 g (84%) of **5**, mp 46—48 °C. IR (KBr) 1712 cm^{-1}; PMR (CCl_4) δ 6.4 (2H, m), 4.9 (2H, m), 2.28 (1H, d, J 6.0 Hz), 2.1—1.8 (3H, m), 1.15 (1H, dddd, 8.5, 7.5, 4.5, 1.3), 0.61 (1H, dt, 4.5, 4.0). Found: C, 74.10; H, 6.33%. Calcd for $C_{10}H_{10}O_2$: C, 74.05; H, 6.22%.

*Bicyclo[3.1.0]hex-3-en-2-one (**1**).* The cyclopropyl ketone (**5**) (207 mg) was heated in a short-path distillating apparatus[6] at 120—140 °C under the reduced pressure of

200 mmHg. After about 20 min, 91 mg (76%) of almost pure **1** was distilled. IR (liquid film) 1712, 1692, 1568 cm^{-1}; UV (MeOH) λ 210 (sh, ε 4940), 251 (2060), 325 nm (90). PMR data were identical with the reported ones.[1)]

References

1) G. A. Russel and G. R. Stevenson, *J. Am. Chem. Soc.*, **93**, 2432 (1971).
2) M. Oda, M. Kasai, and Y. Kitahara, *Chem. Lett.*, **1977**, 307.
3) For a recent application of ready cycloreversion of a furan Diels-Alder adduct, see S. Takano and K. Ogasawara, *Synthesis*, **1974**, 42.
4) H. Meerwein, *Org. Synth.*, **46**, 113 (1966).
5) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 867 (1962); **87**, 1353 (1965).
6) The apparatus used here for short-path distillation is a sublimator attached with a small dish at the bottom of the cold finger.