Simple Entry into Tricyclo[3.3.0.0^{3,7}]octanes

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1,5-Dimethylbicyclo[3.3.0]octan-3,7-dione (**2**) was converted into 1,5-dihydroxy-3,7-dimethyltricyclo[3.3.0.0^{3,7}]octane (**3**) in the presence of SmI_2 in 76% yield.

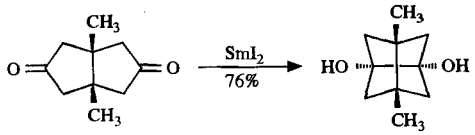
Tricyclo[3.3.0.0^{3,7}]octane (**1**) is a spherical molecule, which is related to the quinane chemistry[1] as is adamantane to the cyclohexane chemistry. Unlike adamantane, the tricyclic hydrocarbon **1** is, of course, quite strained as becomes obvious by viewing **1** as a norbornane skeleton in which the positions C-2 and C-5 are endo-bridged by a methylene group (**1a**).

1a **1b** **1c**

The C_{2v}-symmetric structure of **1** may also be regarded as a constrained cisoid bicyclo[3.3.0]octane (**1b**) or as the symbol of the NATO (**1c**).

The first preparation of a derivative of **1** dates back to 1964[2], and since then, considerable efforts have been made to develop multistep syntheses[3,4].

We wish to report on a simple and efficient one-step route to this carbocyclic system, starting from readily available *cis*-1,5-dimethylbicyclo[3.3.0]octan-3,7-dione (**2**)[5]. SET reduction of **2** with SmI_2 gave a new polar compound in good yield, mp 160°C after chromatography with EtOAc/Et_2O (1:1). The compound (m/z = 168 [M^+]) showed no carbonyl absorption in the IR spectrum, but a broad OH band. Tricyclic structure **3** followed clearly from the simple ^1H- and ^{13}C-NMR spectra.



2 **3**

In general, the bridgehead carbon atoms of a polycyclic compound are the most difficult sites for functionalizations. The skeleton of **3** contains four bridgeheads which are all substituted.

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Experimental

General: Analytical TLC: Aluminium-backed 0.2-mm silica-gel 60-F_{254} plates (E. Merck). – Preparative column chromatography: Silica gel, particle size 30–60 μm (J. T. Baker). – IR: Perkin-Elmer 1710. – ^1H, ^{13}C NMR: Bruker WP 200 SY; TMS as internal standard. – EI-MS: Finnigan MAT 312; room temperature.

1,5-Dihydroxy-3,7-dimethyl[3.3.0.0^{3,7}]octane (**3**): To a solution of SmI_2 (0.04 M in THF, 100 ml, 4 mmol; prepared according to a procedure by Kagan[6]) was added dropwise the dione **2** (166 mg, 1 mmol) in THF (5 ml) under N_2. The mixture was heated to reflux for 1 h, then H_2O (ca. 0.08 ml, 4 mmol) was added. After complete reaction (reflux, 72 h, TLC control), the mixture was cooled, and HCl (0.1 N) was added until the yellow precipitate had dissolved. The solution was extracted with Et_2O (2×), the combined Et_2O extracts were washed (satd. aq. $Na_2S_2O_3$, satd. aq. NaCl) and dried ($MgSO_4$). After evaporation of the solvent, the residue was purified by column chromatography [silica gel; EtOAc/Et_2O (1:1)] to yield 128 mg (76%) of **3**. – IR (KBr): $\tilde{\nu}$ = 3480 cm^{-1}, 3300, 2960, 2880, 1480, 1300, 1062. – ^1H NMR (200 MHz, [D_6]DMSO): δ = 4.88 (s, 2H, OH), 1.57 (d, J = 7 Hz, 4H), 1.47 (d, J = 7 Hz, 4H), 1.01 (s, 6H, CH_3). – ^{13}C NMR (50 MHz, [D_6]DMSO): δ = 78.69 (s, COH), 57.23 (t, CH_2), 41.13 (s, CCH_3), 16.70 (q, CH_3). – EI MS (70 eV): m/z (%) = 168 (1) [M^+], 166 (3.5), 153 (2.6), 110 (100).

CAS Registry Numbers

2: 21170-10-5 / **3**: 134881-45-1 / SmI_2: 32248-43-4

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