CHEMISTRY LETTERS, pp. 121-122, 1987.

Isolation of the Strained Bridgehead Enol Ether of a Bicyclo[3.3.1]nonan-2-one System †

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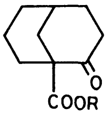
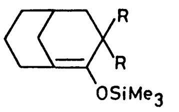
8-Methyl-2-(trimethylsiloxy)tricyclo[5.3.1.0^{3,8}]undec-2-ene (11) was prepared and characterized, which is the first example of the isolable strained bridgehead enol ether of a bicyclo[3.3.1]nonan-2-one system. The reactions of 11 with electrophiles readily occurred at the C-3 bridgehead position.

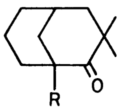
Since the preparation of bicyclo[3.3.1]non-1-ene by Marshall$^{1a)}$ and Wiseman$^{1b)}$ in 1967, intensive studies on the synthesis of strained bridgehead olefins have been made.$^{2)}$ Although the decarboxylation of certain bicyclic β-keto acids such as the acid (1) is believed to proceed through the strained bridgehead enols,$^{1,3)}$ the isolation of such intermediates has never been reported. The transient existence of the bridgehead enol ether of bicyclo-[3.3.1]nonan-2-one (3) in the thermolysis of the ester (2) was suggested by Bloch.$^{4)}$



1 R = H
2 R = SiMe$_3$



3 R = H
4 R = Me



5 R = H
6 R = SiMe$_3$

In connection with the synthesis of sesquiterpenes, we have studied the reactivities of the bridgehead enolates of several bicyclo[3.3.1]nonan-2-one compounds. We describe herein the synthesis, characterization, and reactions of 8-methyl-2-(trimethylsiloxy)tricyclo[5.3.1.0^{3,8}]undec-2-ene (11): this is the first example of the isolable bridgehead enol ether of the bicyclo[3.3.1]nonan-2-one system. Initially, we have attempted to obtain the bridgehead enol ether (4) of 3,3-dimethylbicyclo[3.3.1]nonan-2-one (5).$^{5,6)}$ On treatment of the ketone (5) with LDA (THF, -20 °C) followed by reaction with Me$_3$SiCl (-8 °C → room temp), the expected enol ether (4) was not formed, but there was obtained the α-trimethylsilyl ketone (6),$^{7)}$ mp 62-63 °C (63%). By the stereoelectronic reasons, the bridgehead enolate is expected to be more stable in a bicyclo[3.3.1]nonan-2-one containing the cyclohexanone ring with the locked boat form than in the corresponding bicyclo[3.3.1]nonan-2-one with the conformationally flexible cyclohexanone ring.$^{6,8)}$ Thus, we have attempted to prepare the bridgehead enol

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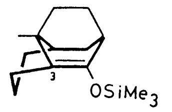
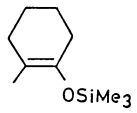
†Dedicated to Professor Teruaki Mukaiyama on the occasion of his 60th birthday.

ether (11) of a tricyclic ketone (7),[6] in which the cyclohexanone ring of the bicyclo[3.3.1]-nonan-2-one skeleton is held in the boat conformation by the two-carbon bridge.[9] The ketone (7) was treated with LDA (DME, -20 °C) and subsequently with Me_3SiCl (0 °C, 10 min, then room temp, 20 min). The mixture, after being diluted with cold $NaHCO_3$ solution, was extracted with pentane. Concentration of the extracts in vacuo gave an oil, which was purified by GLC[10] to give the enol ether (11)[7,11] as a colorless liquid (76%). The structure of 11 was established by the spectral data. The presence of the enol ether group in 11 was revealed by the two olefinic carbon signals [δ 125.4 (s) and 152.7 (s)] in the ^{13}C NMR spectrum, the band due to the double bond (1620 cm^{-1}) in the IR spectrum, and the UV spectrum [220 nm (ε 5500)].[11] Comparison of the IR (1620 cm^{-1}) and UV [220 nm (ε 5500)] spectral data of 11 with those [1685 cm^{-1} and 210 nm (ε 2980)] of the unstrained silyl enol ether (12)[12] reveals that the carbon-carbon double bond character of 11 is significantly reduced in comparison with that of 12. The enol ether (11) is reactive towards electrophiles. Treatment of 11 with 1% AcOD-D_2O (80 °C, 10 min) afforded the monodeuterated ketone (8)[7] (88%). The reaction of 11 with benzaldehyde (CsF, DME, 30 °C, 2 h) afforded the hydroxy ketone (9)[7] (colorless oil, 75%) as a 1.3:1 diastereomeric mixture together with 7 (27%). On reaction of 11 with MeI (CsF, DME, room temp, 2 h) the methylated ketone (10)[7] (colorless oil, 51%) was obtained together with 7 (44%).

7 R = H
8 R = D
9 R = CH(OH)Ph
10 R = Me



11



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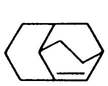

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9) The bridgehead olefin with this tricyclic skeleton, tricyclo[5.3.1.$0^{3,8}$]undec-2-ene (A) was previously prepared and characterized: N. Takaishi, Y. Fujikura, Y. Inamoto, H. Ikeda, and K. Aigami, J. Chem. Soc., Chem. Commun., 1975, 372.
10) A column of 6 mm x 1.5 m packed with 2% XE-60 on Chromosorb W (AW, DMCS), 110 °C, He flow rate 66 ml/min, retention time 4.0 min.
11) IR (CCl_4) 1620, 1370, 1250, 1210 cm^{-1}; UV (95% EtOH) 220 nm (ε 5500); ^1H NMR (90 MHz, C_6D_6) δ 0.20 (9H, s), 1.18 (3H, s); ^{13}C NMR (22.5 MHz, C_6D_6) δ 0.4 (q), 22.1 (q), 24.4 (t), 26.0 (t), 26.1 (t), 28.8 (t), 32.6 (t), 36.7 (t), 40.4 (s), 40.7 (d), 46.4 (d), 125.4 (s), 152.7 (s); MS m/z 250 (M^+), 235, 222.
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(Received September 30, 1986)