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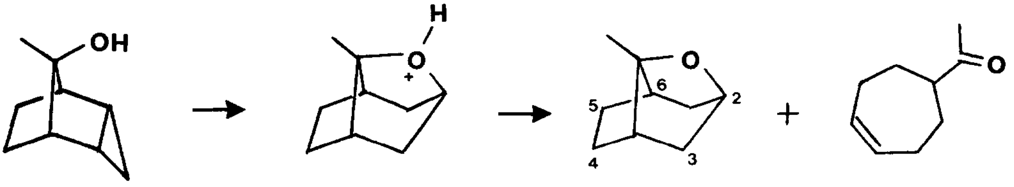
6a-METHYLHEXAHYDRO-2,6-METHANO-2H-CYCLOPENTA[b]FURAN; A NOVEL TRICYCLIC ETHER

David P. Kelly*, Joseph J. Giansiracusa, D. Ralph Leslie and Ian D. McKern
Department of Organic Chemistry, The University of Melbourne, Parkville, Victoria, 3052, Australia

Abstract: The title compound 3 was isolated as the major product from methoxide quenching of a solution of 8-methyl-endo-tricyclo[3.2.1.0^{2,4}]octan-syn-8-ol 1 in fluorosulfonic acid.

In connection with our n.m.r. studies of carbocations[1], we have investigated methyl-substituted tricyclic alcohols as possible precursors to trishomocyclopropenium cations. We wish to report that dissolution of 8-methyl-endo-tricyclo[3.2.1.0^{2,4}]octan-syn- 8-ol 1 in FSO_3H/SO_2ClF at -78°C yields no such cation, but a protonated ether 2, which upon quenching in NaOMe/MeOH produces a 9:1 mixture of the novel tricyclic ether 3, and 1-(4-cycloheptenyl)-ethanone 4.



1 2 3 4

Previous work by others indicates that the alcohol 1 and/or its anti epimer may serve as suitable precursors to a substituted ethano-bridged trishomocyclopropenium cation.[2-5] Accordingly the syn alcohol 1 was prepared by addition of methyl lithium to tricyclo[3.2.1.0^{2,4}]-octan-8-one.[5-7] Addition of 100 mg of 1 in small portions to FSO_3H (0.5 ml) in SO_2ClF (1.5 ml) at -78°C with rapid vortex mixing gave a clear orange solution, the ^{13}C NMR spectrum of which showed six resonances for nine carbons attached to fourteen protons.[8] A deshielded singlet at δ 116, a doublet at 94.1 (J = 173 Hz) and the absence of any one bond ^{13}C-^{1}H coupling constants larger than 173 Hz, were inconsistent with a nonclassical cation.[9]

Careful addition of the acid solution to sodium methoxide in dry methanol at -78°, followed by work-up with water, sodium bicarbonate, and extraction with pentane, gave 90 mg of a pale yellow oil shown by g.l.c. to be 9:1 mixture of two compounds. Neither compound exhibited methoxy signals in their ^{1}H n.m.r. spectra. After separation by preparative g.l.c., the major compound was identified unequivocally by mass spectrometry, infrared, ^{1}H and ^{13}C n.m.r. spectroscopy and elemental analysis as the novel tricyclic ether 3, the first example of this ring system.[10] Comparison of literature data (i.r., m.s., ^{1}H n.m.r.) with the spectroscopic data of the minor component indicated that this compound was the cycloheptenyl ketone 4.[11,12]

The isolation of 3 and the similarity of its ^{13}C spectrum to that of the FSO_3H solution, allows identification of the ionic intermediate as the protonated ether 2.[8,13] Thus in the case of this syn alcohol 1, protonation of the cyclopropyl ring is favoured over that of the hydroxyl group. A 1,2-hydride shift followed by a chair-boat interconversion places the vacant orbital at C_3 adjacent to the syn hydroxyl lone pair of electrons. Internal capture of the cation then occurs to yield 2.[14] As might be expected 2 is relatively stable, no change occurring upon warming of the solution to ca. -30°C, and is simply deprotonated by base to give 3.[15,16]

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References and Notes

1. For example see Kelly, D.P., Leslie, D.R., and Smith, B.D. J. Am. Chem. Soc., 1984, 106, 687 and references therein.
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8. δ ^{13}C (25 MHz, -90°C) 16.2 (q, J 133 Hz), 27.4 (t, J 134), 39.9 (t, J 138), 43.3 (d, J 149), 94.1 (d, J 173), 116.0 (s).
9. The bridging carbons of trishomocyclopropenium cations have small chemical shifts and large one-bond ^{13}C-^{1}H coupling constants; e.g., δ 4.7, J_{CH} 196 Hz[3]; δ 0.0, 19.6[4], J_{CH} 208, 199 Hz.
10. I.r. ν_{max} 1131 cm^{-1}. M.s. (e.i. 70 eV) m/z; 138 ($M^{+\cdot}$ 12%), 95 (23), 94 (46), 88 (10), 86 (63), 84 (100), 71 (39), 43 (30); found 138.1058, $C_9H_{14}O$ requires 138.1044. δ ^{1}H (400 MHz, $CDCl_3$), 1.22 (d, J 10.5 Hz $2H_{3\ endo}$), 1.45 (s, 3H), 1.68 (m, $2H_{4\ endo}$), 1.89 (m, $2H_{3a}$, $2H_{4\ exo}$), 2.15 (m, J 10.5, 4.9 $2H_{3\ exo}$), 4.31 (t, J 4.9 H_2). δ ^{13}C (100 MHz, $CDCl_3$), 17.52 (q, J 125 Hz), 28.10 (t, J 130 $C_{4,5}$), 42.65 (t, J 131 $C_{3,7}$), 44.03 (d, J 137 $C_{3a,6}$), 74.91 (d, J 155 C_2), 93.80 (s, C_{6a}). Satisfactory elemental analysis was obtained (C,H ± 0.3%).
11. Marshall, H., Vogel, F. and Weyerstahl, P. Liebigs Ann. Chem., 1977, 1557.
12. δ ^{13}C (25 MHz, $CDCl_3$); 26.9 (t), 28.0 (q), 28.4 (t), 56.6 (d), 131.6 (d), 211.8 (s).
13. Similar treatment of the anti-alcohol[5] with FSO_3H/SO_2ClF at -78°C gives a solution whose ^{13}C spectrum is consistent with a trishomocyclopropenium cation; δ ^{13}C (-80°C) 8.8 (t), 15.7 (q, J 132 Hz), 20.9 (d, J 194), 25.4 (t, J 132), 29.1 (s), 33.5 (d, J 164).
14. Internal capture of a carbocation was observed by Olah and coworkers when they treated syn-6-carboxy-6-methyl-cis-bicyclo[3.1.0]hex-2-ene with FSO_3H/SO_2ClF, which resulted in the formation of a protonated tricyclic lactone.[2]
15. The absence of signals attributable to protonated 4 in the spectra of the acid solutions indicates that 4 is generated during the quenching reaction.
16. Preliminary experiments (g.l.c.) show that 3 can also be generated by stirring 1 in $MeOH/H_2SO_4$ at room temperature.