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Protonation of *syn*-Bicyclo[4.2.1]nona-2,4,7-trien-9-ol with Fluorosulfuric Acid. Direct Evidence for Protonation Sites

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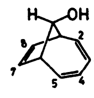
Synopsis. Treatment of *syn*-9-hydroxybicyclo[4.2.1]-nona-2,4,7-triene (**1**) with fluorosulfonic acid in sulfur dioxide-dichloromethane-d_2 cleanly provided protonated dimeric ether and the 7-hydroxytricyclo[4.2.1.0^{2,8}]nona-3-en-5-yl cation. Direct NMR observation as well as quenching experiment of these cations unequivocally established protonation at C-2 (or C-5) and C-7 (or C-8) of **1**.

The bicyclo[4.2.1]nona-2,4,7-triene-9-yl system has been of considerable theoretical interest[1] and practical use.[2] As a part of our investigation on the cationic rearrangement of this system,[3] we have studied the protonation of *syn*-bicyclo[4.2.1]nona-2,4,7-trien-9-ol (**1**) with fluorosulfuric acid. Four possibilities of protonation sites are available—C-2(C-5), C-3(C-4), C-7(C-8), and the oxygen. The last one may lead to the formation of the stabilized, but not bicyclo aromatic cation (**2**).[1] We report herein direct evidence for exclusive protonation at C-2(C-5) and C-7(C-8) in super acid media.



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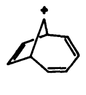

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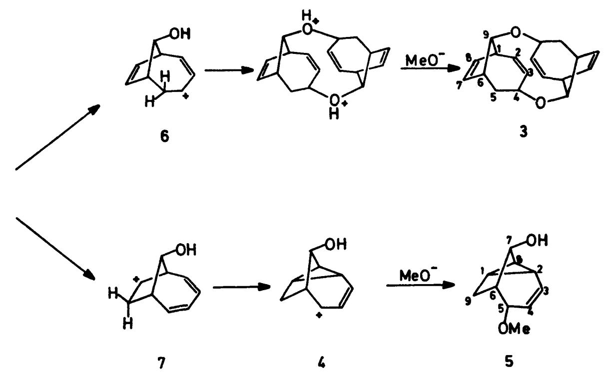
The precursor **1** was prepared by hydride reduction of the corresponding ketone according to the literature method.[3,4] When a solution of **1** in a mixture of sulfur dioxide and dichloromethane-d_2 was mixed with an excess fluorosulfuric acid in an NMR tube at −90 °C, there was obtained a well-defined proton NMR spectrum that could be rationalized as due to a mixture of protonated diether (**3**) and 7-hydroxytricyclo[4.2.1.0^{2,8}]-nona-3-en-5-yl cation (**4**) (see Table 1).

When this solution was quenched, either with sodium acetate in methanol or sodium methoxide in methanol, two products **3** and 5-methoxytricyclo[4.2.1.0^{2,8}]nona-3-en-7-ol (**5**) were isolated. The first of these was assigned the structure **3** on the basis of its spin-decoupled proton NMR spectrum, IR, UV, mass spectrum, and elemental analysis. The proton NMR spectrum of **3** showed that **3** is a symmetric molecule. Moreover since most of the protons exhibited the first order splitting, connectivity pattern of these protons was easily established by complete spin-decoupling experiments. The absence of a conjugated diene moiety was confirmed by its UV spectrum; only end absorption was detected.

The other quenched product, isolated as a single stereoisomer, was assigned the structure **5**. This assignment was consistent with its spin-decoupled proton NMR spectrum, IR, and elemental analysis. In particular, complete spin-decoupling experiment strongly supported structure **5**. Stereochemistry at C-5(OMe) cannot be inferred at present.

When the dimeric ether **3** was redissolved in a super acid solution at −82 °C, it produced peaks in three regions of the proton NMR spectrum that coincided entirely with several peaks present in the original solution from which the ether **3** had been obtained. The structure of cation **4** was therefore tentatively assigned by subtracting the NMR spectrum of **3** in super acid solution from that of the products (*i.e.* **3** and **4**) obtained



Scheme 1. Protonation of **1**.

Table 1. ^{1}H-NMR spectra of protonated **3** and cation **4** in superacid solution[a)]

Mixture of **3** and **4**[b)]	Protonated **3**[c)]	**4**[d)]
10.42(t, J=8.8 Hz)	—	10.42(1H, t, J=8.8 Hz, H-3)
8.74(t, J=8.8 Hz)	—	8.74(1H, t, J=8.8 Hz, H-5)
8.51(t, J=8.8 Hz)	—	8.51(1H, t, J=8.8 Hz, H-4)
6.22(m)	6.22(12H, m)	≈5.98(1H, H-1)[e)]
4.99(m)	—	4.99(4H, m, H-1,2,6, and 8)
3.94(m)	3.94(4H, m)	—
2.34(m)	2.43(4H, m)	≈2.50(1H, H-9)[e)]
1.02(d, J=17.6 H)	—	1.02(1H, d, J=17.6 Hz, H-9)

a) Observed at −90 °C—−82 °C in SO_2-$CDCl_2$-FSO_3H (60 MHz). $CHDCl_2$ as an internal standard (δ=5.30). b) Obtained by treatment of **1** with FSO_3H at −90 °C. c) Dimeric ether **3** in the acid solution at −82 °C. d) Tentative assignments by spectral subtraction. Proton numbering indicated in structure **4** (Scheme 1). e) Obscured by **3**.

from the reaction of **1** with fluorosulfuric acid. The resulting NMR spectrum of **4** is listed in Table 1. The three low-field protons at δ=10.42, 8.74, and 8.51 are characteristic of an allyl cation.[5]

The formation of **3** and **5** upon quenching with methanol could be explained as the products of protonated **3** and cation **4** (Scheme 1). Protonation on C-2(C-5) of **1** would give an allyl cation **6** which would undergo dimerization to give **3**. On the other hand, protonation on C-7(C-8) would initially give cation **7** which rearranges to the 3-cyclopropylallyl cation **4**.

Experimental

Direct NMR Observation of Protonated 3 and Cation 4. Alcohol **1** (17 mg, 0.13 mmol)[4] was dissolved in dichloromethane-d_2 (0.22 ml) in a thin-walled NMR tube. The solution was cooled to −78 °C and sulfur dioxide (0.22 ml) was distilled into the NMR tube. The sample was then cooled to −120 °C (pentane-liquid N_2 slush) to which freshly distilled fluorosulfuric acid (0.10 ml) was added. The tube was stirred in a −90 °C bath using vortex mixer for 30 s and was quickly set in the NMR probe which had been maintained at −90 °C.

Quenching of the Cation Solution with Methanol. The alcohol (**1**, 643 mg, 4.83 mmol) in a mixture of dichloromethane and sulfur dioxide (1 : 1, 10 ml) was treated with fluorosulfuric acid (2 ml) at −78 °C for 1 h. The mixture was quenched with 150 ml methanol saturated with sodium acetate at room temperature. The methanol was removed by rotary evaporator at 0 °C. 100 ml water was added to the residue. The mixture was then extracted with three portions of ether and the combined ether layers washed with water, saturated aqueous sodium hydrogencarbonate and water, and then dried over magnesium sulfate. Concentration provided 534 mg crude oil, which was separated by preparative TLC to afford **3** (146 mg) and **5** (85 mg) as colorless oils.

Spectral Data of 3. MS (70 eV) *m/e* 268 (M^+). IR (CCl_4) 3070, 2960, 1450, 1062, 1040, and 694 cm^{-1}. UV (cyclohexane) 217.5 (ε 2400). ^{1}H-NMR (CCl_4) δ (numbering of protons indicated in structure **3**) 6.13 (1H, dd, *J*=9.6, 5.0 Hz, H-3), 5.86 (2H, d, *J*=1.1 Hz, H-7 and 8), 5.76 (1H, dd, *J*=9.6, 4.1 Hz, H-2), 5.00 (1H, dd, *J*=6.5, 6.6 Hz, H-9), 4.40 (1H, dd, *J*=7.0, 5.0 Hz, H-4), 3.15 (1H, ddd, *J*=6.4, 4.1, 1.8 Hz, H-1), 2.83 (1H, ddd, *J*=3.2, 10.4, 6.6 Hz, H-6), 1.94 (1H, ddd, *J*=11.4, 10.4, 6.8, H-5), 1.44 (1H, ddd, *J*=11.4, 3.2, 0.5 Hz, H-5).

Found: C, 80.19, 80.27; H, 7.57, 7.67%. Calcd for $C_{18}H_{20}O_2$: C, 80.55; H, 7.51%.

Spectral Data of 5. MS (70 eV) *m/e* 134 (M^+ −MeOH). IR (CCl_4) 3500, 3020, 1660, 1390, and 1092 cm^{-1}. ^{1}H-NMR (CCl_4) δ (numbering of protons based on nomenclature) 6.05 (1H, ddd, *J*=12.0, 7.5, 1.5 Hz, H-3), 5.57 (1H, ddd, *J*=12.0, 4.0, 3.0 Hz, H-4), 4.64 (1H, ddd, *J*=6.0, 4.0, 4.0 Hz, H-7), 3.81 (1H, ddd, *J*=1.5, 4.0, 4.0 Hz, H-5), 3.47 (1H, d, *J*=4.0 Hz, OH), 3.40 (3H, s, OMe), 2.65 (1H, dddd, *J*=9.0, 6.0, 4.0, 3.0 Hz, H-6), 2.25 (1H, ddd, *J*=12.0, 9.0, 4.0 Hz, H-9), 1.98 (1H, ddd, *J*=8.0, 6.0, 4.0 Hz, H-8), 1.63 (1H, ddd, *J*=8.0, 7.0, 4.0 Hz, H-1), 1.45 (1H, d, *J*=12 Hz, H-9), 1.35 (1H, ddd, *J*=7.5, 7.0, 4.0 Hz, H-2).

Found: C, 72.11; H, 8.43%. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49%.

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