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ON THE NATURE OF THE TRICYCLO[$5.3.1.0^{4,11}$]UNDECATRIENYL CATION

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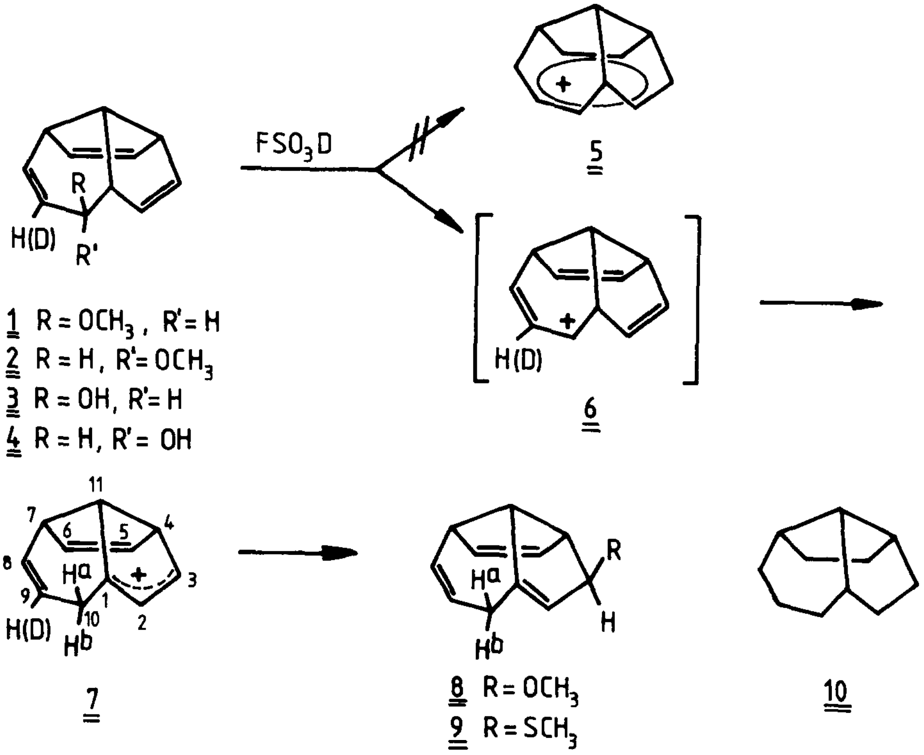
We recently reported the synthesis of the methoxytrienes 1 and 2, potential precursors of the bridged trishomotropylium ion 5[1]. The low temperature ^1H-NMR spectrum of the cation produced by treatment of 1 with $FSO_3H/SO_2ClF/CD_2Cl_2$ (1:3:3) was not, however, consistent with either structure 5 or the simple allylic system 6. Most striking in this spectrum were temperature dependent signals appearing in the region τ -2.50 to 0.25. Due to the lack of additional data, we declined to propose a definite structure for the cation at that time.



Paquette and coworkers have since reported$^{2)}$ the synthesis of the alcohols 3 and 4. The cation produced from 4 by treatment with magic acid gave a ^{1}H-NMR spectrum which was reported to be similar to that which we have described. We have undertaken an extensive reinvestigation of the fate of 1-4 in strongly acidic media, the results of which we report here.

Using a special apparatus with care to exclude air and moisture, the cation solutions were prepared as follows. A cold$^{3)}$ solution of the ether 1 or 2 or alcohol 3 or 4 in CD_2Cl_2 (3 ml/mmol) was added slowly dropwise to a vigorously stirred solution of FSO_3D (1 ml/mmol) in SO_2ClF (3 ml/mmol) maintained at -120°. The resulting clear yellow-orange solutions were transferred under N_2 pressure to NMR tubes and their spectra measured at -70° or below. Except for a peak in each case due to the leaving group, all four compounds gave rise to identical well-resolved ^{1}H-NMR spectra. The temperature-dependent signals which we had previously observed were absent from all of these spectra, and we have been unable to reproduce them using a variety of reaction conditions.

On the basis of the ^{1}H-NMR spectrum (Figure 1 and Table 1), decoupling experiments (Table 2) and its ^{13}C-NMR spectrum (Table 1), we assign the cation structure 7. The presence in the ^{13}C spectrum of a triplet at δ41.4, a singlet at δ269.3, and a doublet at δ231.8 is most consistent with an allylic system which would result from a 1,2-hydride shift (C-1 to C-10) in the initially

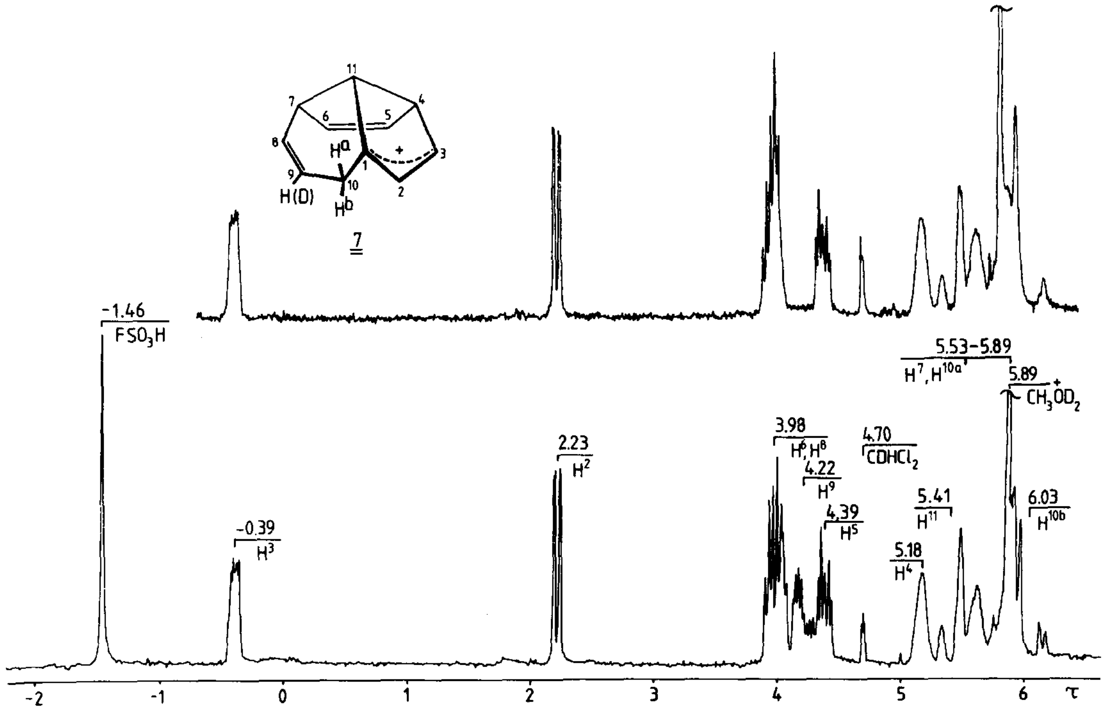


Figure 1: ^{1}H-NMR spectrum of 7 (lower part) and 7-D (upper part) at -70°, 90 MHz, in SO_2ClF/CD_2Cl_2.

formed allylic cation 6. The ^{1}H- and ^{13}C-NMR spectra resemble those of the 1-triquinacenyl cation[4)].

Table 1. ^{1}H-NMR (τ) and ^{13}C-NMR (δ) Data† (J in Hz)

Compd.	
7	^{1}H-NMR: -0.39(m,1H,H-3), 2.23(dd,1H,J=4.3,1.0,H-2), 3.98(m,2H,H-6,H-8), 4.22(m,1H,H-9), 4.39(m,1H,H-5), 5.18(bs,1H,H-4), 5.41(bd,1H,J=13,H-11, part of AB), 5.53-5.89(m,2H,H-7,H-10a), 5.89(s,3H,$C\underline{H}_3\overset{+}{O}D_2$), 6.03(dd,1H, J=18.5,4.3,H-10b, part of ABX). ^{13}C-NMR: 269.3(s,C-1), 231.8(d,C-3), 145.5(d,C-2), 136.6(d,C-5), 130.8(d), 130.2(d), 125.5(d,C-9), 72.3(d, C-4), 65.8(d,C-11), 60.1(q,$\underline{C}H_3\overset{+}{O}D_2$), 54.7(d,C-7), 41.4(t,C-10).
8	^{1}H-NMR: 4.07(bd,1H,J=11.7,H-8,A part of ABX), 4.29(dd,1H,J=11.7,2.5,H-9, B part of ABX), 4.41(s,2H,H-5,H-6), 4.49(m,1H,H-2), 5.89(bs,1H,H-3), 6.49-6.76(m,3H,H-4,H-7,H-11), 6.60(s,3H,$C\underline{H}_3$), 7.16(bs,2H,H-10a,H-10b). ^{13}C-NMR: 148.4(s,C-1), 133.1(d), 130.7(d), 128.4(d), 126.0(d), 119.2(d, C-2), 89.0(d,C-3), 55.64(d or q), 55.56(d or q), 47.2(d), 46.4(d), 27.8 (t,C-10).
9	^{1}H-NMR: 4.13(bd,1H,J=11.4,H-8,A part of ABX), 4.32(dd,1H,J=11.4,2.4, H-9,B part of ABX), 4.46(s,2H,H-5,H-6), 4.73(m,1H,H-2), 6.52(m,1H,H-3), 6.53-6.87(m,3H,H-4,H-7,H-11), 7.21(bs,2H,H-10a,H-10b), 7.93(s,3H,$C\underline{H}_3$). ^{13}C-NMR: 143.5(s,C-1), 132.8(d), 131.4(d), 128.3(d), 126.1(d), 119.6(d, C-2), 57.7(d,C-3), 54.2(d), 47.4(d,2C), 27.4(t,C-10), 12.8(q,$\underline{C}H_3$).

† ^{1}H-NMR: 7-9 (90 MHz), 8,9 in $CDCl_3$. ^{13}C-NMR: 7 (25.2 MHz), 8,9 (22.6 MHz, $CDCl_3$). Assignments are based on all available data.

Additional evidence for structure 7 was obtained from quenching experiments When the cation solution was transferred slowly dropwise into a vigorously stirred suspension of $NaHCO_3$ in CH_3OH at -95° or CH_3SH at -110°, a methyl ether and a methyl thioether, respectively, were formed in 50-60% yield to which we assign structures 8 and 9[5)].

Treatment of the methoxytriene 8 with $FSO_3D/SO_2ClF/CD_2Cl_2$ (1:3:3) regenerated cation 7. Reduction of 9 with Raney nickel followed by 10% Pd/C, H_2, 1 atm gave as the only detectable product tricyclo[5.3.1.0^{4,11}]undecane 10[6)] indicating that the substrates 1-4 had suffered no deep-seated skeletal rearrangements under strongly acidic conditions.

Table 2. Decoupling Experiments† (J in Hz)

Compd.	
7	{H-10a,H-10b}H-9,d,$J_{8,9}$=10. {H-7,H-11}H-9,dd,$J_{8,9}$=10,$J_{9,10b}$=4.3;H-5,dd, $J_{5,6}$=5.8,$J_{4,5}$=2.6. {H-4}H-5,dd,$J_{5,6}$=5.8,$J_{5,7}$=1.5;H-2,d,$J_{2,3}$=4.3,($J_{2,4}$= 1.0);H-3,bd,$J_{2,3}$=4.3. {H-2}H-3,bs,($J_{2,3}$=4.3). {H-3}H-2,d,$J_{2,4}$=1.0,($J_{2,3}$= 4.3).
8	{H-10a,H-10b}H-2,d,$J_{2,3}$=2.8;H-9,d,$J_{8,9}$=11.7,($J_{9,10b}$=2.5). {H-4,H-7,H-11} H-3,d,$J_{2,3}$=2.8,($J_{3,4}\sim$1-2);H-8,shd,$J_{8,9}$=11.7,($J_{7,8}\sim$1). {H-3}H-2,bs,($J_{2,3}$= 2.8). {H-2,H-5,H-6,H-8,H-9}H-10a,H-10b,shs,($J_{9,10b}$=2.5);H-3,bs.

9 {H-10a,H-10b}H-9,d,$J_{8,9}$=11.4,($J_{9,10b}$=2.4). {H-3,H-4,H-7,H-11}H-2,bs;H-8, shd,$J_{8,9}$=11.4,($J_{1,2}$∿1).

† {Proton(s) irradiated}Proton observed, Residual coupling,(Inferred coupling).

We considered[1] the possibility that the allylic system 6 might undergo sequential Wagner-Meerwein shifts of the central bridgehead carbon C-11 (i.e.C-1 →C-10,C-4→C-3, etc.) prior to the 1,2-hydride shift. Such a degenerate process would scramble a peripheral label over all positions except C-11. To test this hypothesis deuterated alcohols 3-D and 4-D were prepared[7]. Following etherification (KH, CH_3I) each of the ethers 1-D and 2-D was treated with $FSO_3D/SO_2ClF/CD_2Cl_2$. The ^{1}H-NMR spectrum in both cases was the same (Figure 1 7-D) and indicated that all deuterium remained at C-9. The Wagner-Meerwein shift clearly does not compete with the 1,2-hydride shift. This is most likely due to the fact that the p orbital at C-10 in 6 is more favorably alligned with the C-10/H-10 bond than with the C-10/C-11 bond.

Further labeling studies are in progress which will enable us to determine whether the cation 6 exists as an unsymmetrical species or as a symmetrical resonance hybrid prior to hydride transfer.

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References and Notes

1. P.Hildenbrand, G.Schröder and J.F.M.Oth, Tetrahedron Lett.,2001 (1976).
2. L.Paquette, P.B.Lavrik and R.H.Summerville, J.Org.Chem., 42, 2659 (1977).
3. Compounds 1-3 were added at -80°. The highly crystalline 4 was considerably less soluble in CD_2Cl_2 at low temperatures and had to be added at -20°.
4. D.Bosse and A.de Meijere, Angew.Chem., 88, 610 (1976); Angew.Chem. Int.Ed. Engl., 15, 557 (1976). P.Bischof, Angew.Chem., 88, 609 (1976); Angew.Chem. Int.Ed.Engl., 15, 556 (1976).
5. The exo-stereochemistry is evident from the small vicinal coupling $J_{3,4}$ and from ^{1}H-NMR measurements in the presence of $Eu(fod)_3$ shift reagent. The structure of 8 and 9 are fully supported by UV,IR, mass spectral, and high-resolution mass spectral data.
6. H.Rapoport and J.Z.Pasky, J.Am.Chem.Soc., 78, 3788 (1956); R.E.Wingard, Jr., R.K.Russell,and L.A.Paquette, J.Am.Chem.Soc., 96, 7474 (1974); Y.Inamoto, K.Aigami, N.Takaishi, Y.Fujikura, K.Tsuchihashi, and H.Ikeda, J.Org.Chem., 42, 3833 (1977).
7. 3-D and 4-D were obtained analogous to the method of Paquette and coworkers for 3 and 4[2]. Treatment of 9-Bromo-10-hydroxytricyclo[5.3.1.0^{4,11}]undeca-2,5,8-triene with D_2O, its subsequent inverse addition to n-BuLi and work-up with D_2O gave 3-D and 4-D with >97% deuterium incorporation at C-9 (mass spectrum and ^{1}H-NMR spectrum in the presence of $Eu(DPM)_3$ shift reagent).

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