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THE REARRANGEMENT OF A TRICYCLIC $C_8H_{11}^+$ ALKYL CARBOCATION INTO A PRIMARY CYCLOPROPYLCARBINYL CATION

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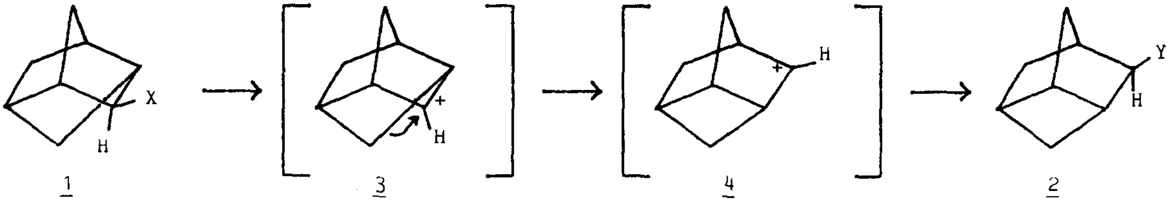
Summary: The first unambiguous observation of a "bisected" primary cyclopropylcarbinyl cation is reported. This cation was formed by ring contraction of a C_8 tricyclic framework. Although totally unexpected from a bond energy-steric strain standpoint, this observation underlines the large resonance stability associated with "bisected" cyclopropylcarbinyl cations.

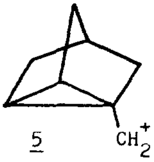
Previously reported solvolysis studies involving the symmetrical tricyclic hydrocarbon, bisnoradamantane (tricyclo[3.3.0.0^{3,7}]octane) 1, C_8H_{12}, have invariably led to the rearranged skeleton 2 (1). As this paper details, this is not the end of cationic rearragements in this system.



The rearranged skeleton 2 is a 2-norbornyl structure with the 3- and 5- carbon atoms held together by a one carbon bridge. We were consequently interested in preparing and characterizing the corresponding secondary cation 4, since it appeared probable that 4 could not be symmetrically bridged (2). Addition of the chloride 2 (Y=Cl) (1a, 3) to Sb_5 - SO_2ClF - SO_2F_2 at the lowest possible temperature of -130°C led to immediate ionization. Both ^1H and ^{13}C NMR spectra of the resulting solution, taken at this same temperature, were extremely clean but neither spectrum could be remotely interpreted in terms of cation 4.

The decoupled ^{13}C NMR spectrum showed only six peaks, δ 191.2, 113.1, 112.6 (2C), 39.8 (2C), 36.5 and 31.0 p.p.m. The ^1H spectrum (200 MHz) showed seven separate peaks, two low field peaks at δ 7.61 and 7.83 (1H each), one peak at 5.95 (2H), 2.62 (1H), an AB quartet with chemical shifts of 1.91 and 1.82, J = 14 Hz (4H), and 1.63 (2H). Perhaps the most unusual observation was the fact that the low field carbon was a triplet in the coupled ^{13}C spectrum, J = 171 Hz, implying a primary cation centre for what was expected to be the formal C^+ carbon. Specific ^1H decoupling of the ^{13}C spectrum confirmed that the two low field protons were joined to the low field carbon.

Based on the required symmetry showing two sets of equivalent carbons (four out of the total eight) and the presence of the $-CH_2^+$ centre, one is led uniquely to the "primary" cyclopropylcarbinyl cation 5, tricyclo[2.2.1.0^{2,6}]heptane-1-methyl cation, which when written in the "bisected" conformation 5a shows a C_s symmetry plane (4). The ^1H and ^{13}C chemical shift and coupling constant assignments are shown in structure 5a and were consistent with specific ^1H decoupling experiments. Finally, cation 5, identical in all respects, was produced in an independent, unambiguous way from the known alcohol 6 (5). Cation 5 solutions are stable to nearly 0°C, whereupon general decomposition sets in. Up to this temperature, from NMR measurements at a series of temperatures, there are no signs of any degenerate rearrangement processes occuring.



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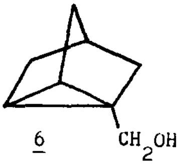

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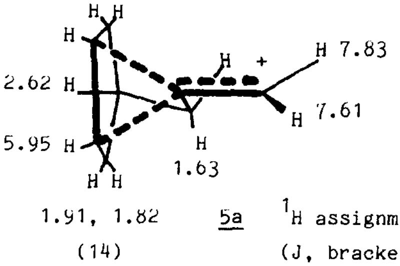
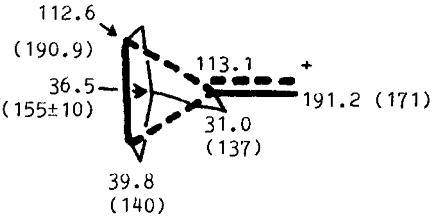


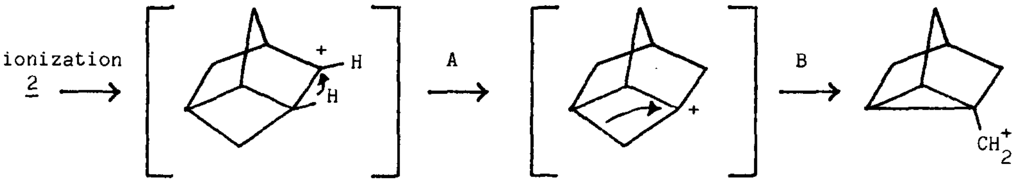
5a ^1H assignment (J, brackets)



5a ^{13}C assignments ($J_{^{13}C-^1H}$ in brackets)

Cation 5 is the first, and thus far only, bisected, primary cyclopropylcarbinyl cation to be unambiguously characterized (6). A reasonable mechanism for 2 → 5 is the following (Equation 1).

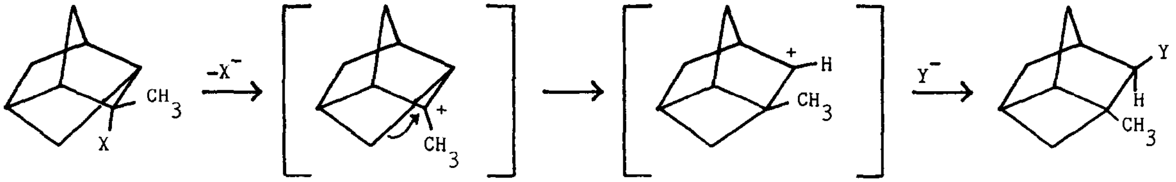
Eq. 1



4 7 5

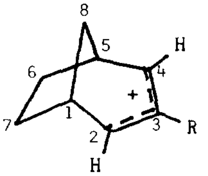
The presumed intermediate 7 appears to be a highly strained bridgehead cation and indeed the C^+ centre would have to be nonplanar. One might therefore question the Eq. 1 sequence. However, fully geometry-optimized MNDO calculations (7) give ΔH_f values of 233.0, 249.4 and 233.0 kcal/mol for 4, 7 and 5 (8). Based on the observation of "immediate" rearrangement of 2 to 5 at -130°C, the overall transition-state barrier (A or B or both in Eq. 1) is experimentally $\lesssim$ 10 kcal/mol (9). While the calculated difference of 16 kcal/mol between 4 and 7 is too high, the number is not too unreasonable given the uncertainty in the calculations, i.e. 7 is not an impossibly strained species.

The radically different behavior of the methyl-substituted system 8 on ionization can also be rationalized from the Eq. 1 mechanism. Solvolysis studies of 8 (10) are also reported to lead to skeletal rearrangement giving 9, i.e.



8 10 11 9

Ionization of 8 (X=OH) in 1:4 SbF_5 - FSO_3H/SO_2ClF (11) gave neither 10 nor 11, nor the ion related to 5, but the 3-methylbicyclo[3.2.1]hept-3-en-2-yl cation 12, uniquely characterized by ^{13}C and ^{1}H NMR spectroscopy (12) as a symmetrical allyl cation and closely related to the known parent system 13 (13). Since 1,2-hydrogen shifts are almost always faster than equivalent 1,2-methyl shifts, cation 11 apparently suffers a competitive β-cleavage which would eventually lead to 12.

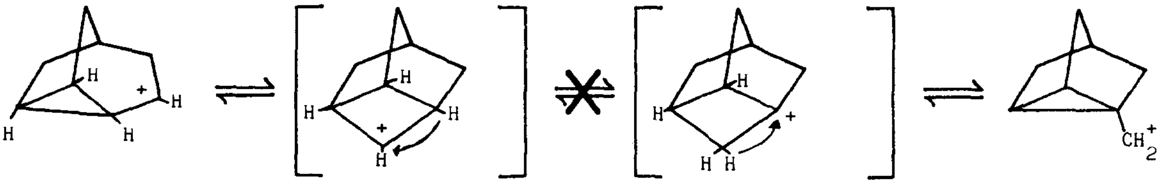


12 R = CH_3

13 R = H

The $C_8H_{11}^+$ Structural Graph

The observation of cation 5 and the implied intermediacy of both 4 and 7 represent one small interconvertible manifold of the complex $C_8H_{11}^+$ structural graph. Interestingly, Olah et. al. (13b) have prepared another closely related series of $C_8H_{11}^+$ cations, the secondary cyclopropylcarbinyl cation 14, for which in addition the cyclobutyl cation 15 is a probable intermediate in explaining the degenerate rearrangement of 14 (13b). Grob et. al. (14) have also carried out extensive solvolysis studies involving 14 and 15. There does not appear to be a low energy connection between 15 and 7 since experimentally 14 and 5 are not interconverted (15).



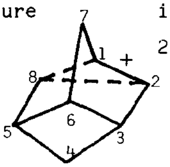
14 15 7 5

This is consistent, however, with recent results of Staral and Roberts (16) showing that a 1,2-hydrogen shift in cyclobutyl cations requires a relatively high energy.

Acknowledgement

We thank the N.S.E.R.C. of Canada for generous support.

References and Notes

1. (a) P.K. Freeman, R.B. Kinnel and T.D. Ziebarth, Tetrahedron Letters, 1059 (1970).
   (b) R.R. Sauers and B.R. Sickles, Tetrahedron Letters, 1067 (1970).
   (c) R.R. Sauers, K.W. Kelly and B.R. Sickles, J. Org. Chem., 37, 537 (1972).
   (d) R.R. Sauers, R.A. Parent and S.B. Damle, J. Am. Chem. Soc., 88, 2257 (1966).
   (e) E.N. Peters, Tetrahedron Letters, 751 (1977).
2. The structure  is beset by serious steric problems if one attempts to bring carbons 2 and 8 to within the same bonding distance as 1 and 8.

3. Alcohol 2 (Y = OH) gives only the protonated alcohol, which does not easily ionize.
4. Cation 5 can also be (probably better) regarded as a vinyl-bridged 2-norbornyl cation.
5. H. Hart and R.A. Martin, J. Org. Chem., 24, 1267 (1959).
   Cation 5 can also be produced from 1 (X = Tosyl) but in this case there are other ions also produced (probably allyl cations from competing β-cleavage).
6. (a) The parent primary cyclopropylcarbinyl cation, as an observable species, has been the subject of several studies. The latest interpretation (6b) is that the cation solution is a mixture of cyclobutyl and cyclopropylcarbinyl cations in very rapid equilibrium, the latter being the minor constituent.
   (b) J.S. Staral, I. Yavari, J.D. Roberts, G.K. Surya Prakash, D.J. Donovan and G.A. Olah, J. Am. Chem. Soc., 100, 8017 (1978).
7. M.J.S. Dewar and W. Thiel, J. Am. Chem. Soc., 99, 4899 (1977).
8. Geometries are available on request. In 7, the C^+ centre is distorted 34.5° from planarity.
9. Assuming $t_{\frac{1}{2}}$ for rearrangement is $< 10^3$s at −130°C, using the absolute rate expression.
10. R.R. Sauers and E.M. O'Hara, J. Am. Chem. Soc., 96, 2510 (1974).
11. Initially at −120°C one seems to get a protonated alcohol, which ionizes at about −55°C to give the allylic ion.
12. ^{13}C NMR peaks, ^1H - ^{13}C coupling constants in brackets, at: δ 49.8 (155), C-1 and C-5; 211.0 (169), C-2 and C-4; 147.9 C-3; 19.7 (135), C-6 and C-7; 39.3 (133), C-8; 18.5 (131), CH_3. ^1H NMR peaks at: δ 4.46 (broad m, 2H), H-1 and H-5; 9.62 (J_{12}=6.3), H-2 and H-4; 3.08 ($J_{exo-endo}$= 7.9), H-6_{exo} and H-7_{exo}; 1.36 ($J_{exo-endo}$= 7.9), H-6_{endo} and H-7_{endo}; 1.63 and 1.93 (ABX_2 system, $J_{syn-anti}$= 13.0, $J_{anti-H-1,5}$=3.6), H-8 anti and syn respectively; 2.52 (3H), CH_3. Numerous other small peaks are also present in both spectra.
13. (a) A.F. Diaz, D.L. Harris, M. Sakai and S. Winstein, Tetrahedron Letters, 303 (1971).
    (b) G.A. Olah and G. Liang, J. Am. Chem. Soc., 98, 7026 (1976).
14. (a) C.A. Grob, M. Geisel, W. Santi and W. Tschudi, Tetrahedron Letters, 4311 (1972).
    (b) C.A. Grob, M. Geisel, W. Santi and W. Tschudi, Helv. Chim. Acta., 56, 1055 (1973).
    (c) M. Geisel, C.A. Grob, R.P. Traber and W. Tschudi, Helv. Chim. Acta., 59, 2808 (1976).
15. Cation 14 should be more stable than 5, but one cannot be too confident in the prediction.
16. J.S. Staral and J.D. Roberts, J. Am. Chem. Soc., 100, 8020 (1978).

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