Tetrahedron Letters,Vol.23,No.34,pp 3435-3438,1982
Printed in Great Britain

0040-4039/82/343435-04$03.00/0

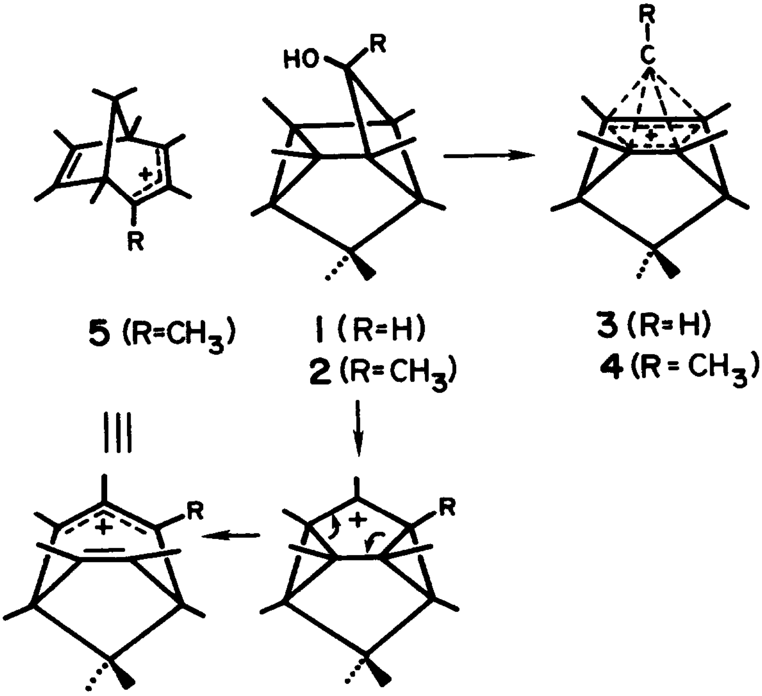
# ATTEMPTS TO PREPARE A PYRAMIDAL CARBOCATION WITH AN APICAL FLUORINE SUBSTITUENT

Harold Hart* and Daryl L. Stein

Department of Chemistry, Michigan State University
East Lansing, Michigan 48824, U.S.A.

Abstract: Gem-difluorides 7 and 8, different only in the location of a methyl substituent and each a potential precursor of the same pyramidal carbocation 9, ionize instead to give allylic carbocation 13 and homotropylium ion 20 respectively.

The theoretical prediction that $(CH)_5$ and its congeners may have a pyramidal structure,[1] has been amply verified experimentally.[2] Our interest in this field originated with the observation that alcohol 1 ionizes to pyramidal carbocation 3.[3] Surprisingly, all attempts to prepare the methyl analog 4 from 2 lead instead to allylic ion 5.[4] Labeling studies showed that 2 rearranges to 5 via a cyclobutane ring contraction and that 4 is not an intermediate in the process.[5]



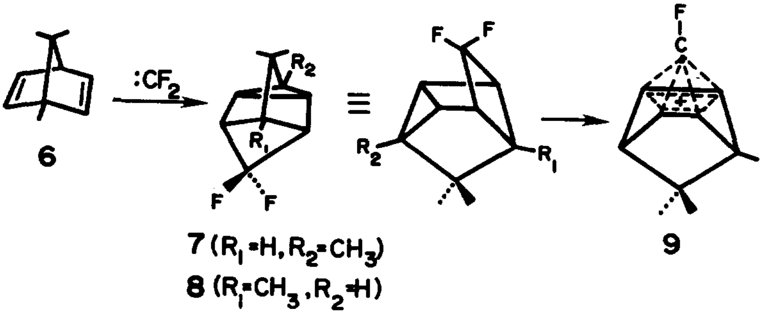
5 ($R=CH_3$)

1 ($R=H$)
2 ($R=CH_3$)

3 ($R=H$)
4 ($R=CH_3$)

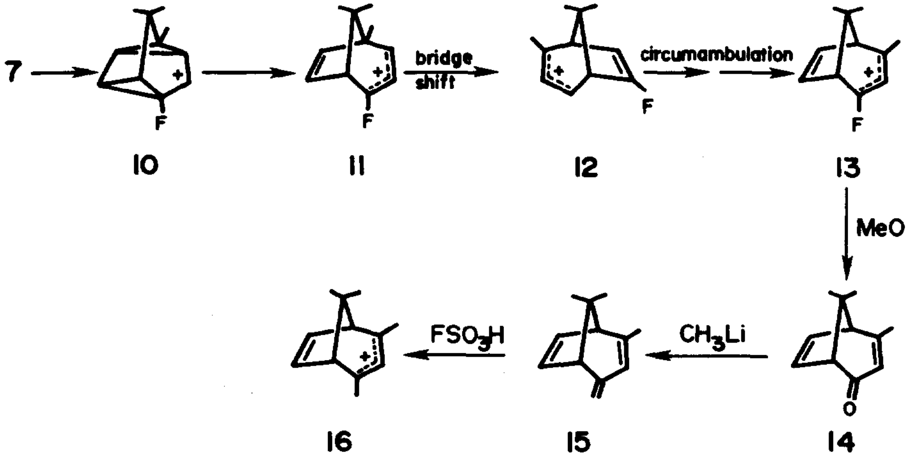
In an attempt to further understand the dramatic effect of apical substitution in the reaction, it was of interest to prepare a pyramidal carbocation with an electron acceptor (in contrast to a donor) at this position. We report here our attempts to prepare an analog of 3 with R=F and fewer methyl substitutents.

Fluorocarbons 7 and 8, which result from homo 1,4-endo carbene addition to 6,[6] are potential precursors of pyramidal ion 9. However, upon ionization with $SbF_5$ in $FSO_2Cl$ at -95°, 7 and



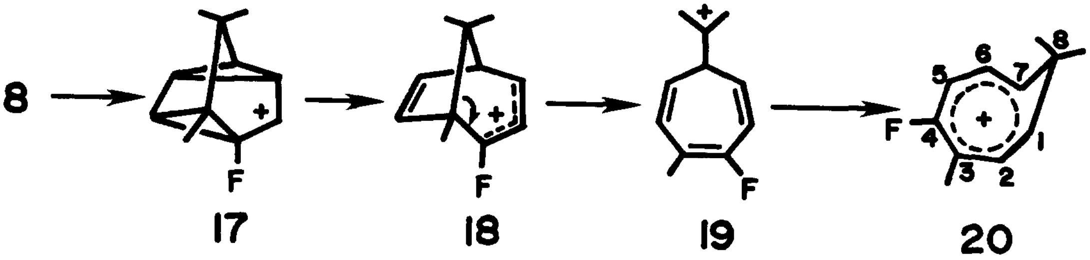
8 formed two different carbocations, neither of which was 9. Symmetric 9 should show only 8 peaks in its $^{13}C$ NMR spectrum, whereas the ions obtained from 7 and 8 each showed peaks for all 11 carbon atoms.

Fluorocarbon 7 ionized to 13. The allylic nature of 13 was evident from its $^{13}C$ NMR spectrum which showed that the positive charge was located primarily on two carbon atoms (δ 218.1, 240.9). The structure was confirmed by quenching in MeOH at -78°C to give ketone 14. This ketone had spectra consistent with expectation, and its structure was verified by conversion with methyllithium to triene 15, which ionized to 16 in $FSO_3H$ at -95°C. The symmetry of 16 was clear from its $^1H$ NMR spectrum, which showed only six signals with the expected chemical shifts.[8]



The mechanism for rearrangement of **7** to **11** involves a cyclobutane ring contraction, as in the rearrangement of **2** to **5**. A 1,2 bridge shift gives **12**, which can then undergo a series of cyclopropylcarbinyl rearrangements (analogous to the circumambulation observed with **5**[9]) to give **13**. Since both stabilizing substitutents are at the termini of the allylic system in **13**, further rearrangement does not occur.

In contrast with **7**, **8** ionizes to a species in which the positive charge is more delocalized, the most deshielded carbon having a chemical shift of $\delta$ 174.6.[10] All of the spectroscopic data are consistent with the homotropylium structure **20**. In particular, the C8 endo and exo methyl protons in **20** appear at $\delta$ -0.10 and 2.43 ppm respectively, in good agreement with the $\delta$ values of -0.48 and 2.36 ppm observed for the methyl groups in 8,8-dimethylhomotropylium ion.[11, 12]



The first steps in the mechanism, rearrangement of **8** to **18**, are analogous to the rearrangement of **7** to **11**. However because of the different relative positions of the F and $CH_3$ in **18** compared with **11**, no energetically favorable path via bridge shifts or circumambulation can lead to **13**, in which both substituents stabilize the positive charge. Consequently bridge cleavage now becomes a competitive possibility, leading to **20**. It is possible that the rearrangement of **18** to **20** is direct, without the intervention of **19**, since only one ion (**20**, and not its isomer in which the methyl and fluorine positions are interchanged) is seen.

The results with **7** and **8** not only demonstrate dramatically how a single methyl substituent can affect the ionization path, but further show that in this ring system, substitution on the potential apical carbon favors other types of rearrangement over pyramidal carbocation formation. The reason is probably because compared with a hydrogen, a methyl group or a fluorine atom (through back bonding) lessen the demand for the cyclopropyl participation which is necessary for pyramidal cation formation.

**Acknowledgement**. We are indebted to the National Science Foundation (Grant 17746) for financial support of this research.

## References and Notes

(1) R. E. Williams, *Inorg. Chem*, **10**, 210 (1971); W-D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 1661 (1972); S. Yoneda and Z. Yoshida, *Chemistry Lett.*, 607 (1972).

(2) For a review, see H. Schwarz, *Angew. Chem. Int. Ed. Engl*. **20**, 991 (1981).

(3) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 6436 (1974).

(4) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **97**, 2459 (1975).

(5) Theoretical calculations on the parent system are permissive of either path; C. W. Jefford, J. Mareda, J-C. Perlberger and U. Burger, *J. Am. Chem. Soc.*, **101**, 1370 (1979).

(6) C. W. Jefford, W. D. Graham and U. Burger, *Tetrahedron Lett.*, 4717 (1975); for a mechanistic study and earlier references, see C. W. Jefford and P. T. Huy, *Tetrahedron Lett.*, **23**, 391 (1982).

(7) For ion **13**: $^{13}$C NMR δ 20.8 (C8, *anti*-Me), 27.9 (C8, *syn*-Me), 34.0 (C4 Me), 64.6 ($J_{C-F}$ = 5.4 Hz, C1), 71.8 (C5), 90.0 ($J_{C-F}$ = 5 Hz, C8), 121.6 ($J_{C-F}$ = 14.8 Hz, C3), 138.8 (C-6), 144.2 ($J_{C-F}$ = 6.0 Hz, C7), 218.1 ($J_{C-F}$ = 372.4 Hz, C2), 240.9 ($J_{C-F}$ = 36.7 Hz, C4). The 180 MHz $^{1}$H NMR spectrum was very complex and could not be interpreted.

(8) For ion **16**: $^{1}$H NMR δ 1.26 (s, 3H, *anti*-Me), 1.49 (s, 3H, *syn*-Me), 2.89 (s, 6H, C2 and C4 methyls), 3.97 (s, 2H, bridgehead), 6.94 (s, 2H vinyl), 7.17 (s, 1H, H3).

(9) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **98**, 1551 (1976).

(10) For ion **20**: $^{13}$C NMR δ 11.7 (C8 *syn*-Me), 19.0 ($J_{C-F}$ = 8.3 Hz, C3 Me), 28.6 (C8 *anti*-Me), 47.1 (C8), 97.2 (C1), 95.7 (C7), 124.5 ($J_{C-F}$ = 36.7 Hz, C5), 138.8 ($J_{C-F}$ = 25.0 Hz, C3), 162.0 ($J_{C-F}$ = 20.7 Hz, C6), 164.7 ($J_{C-F}$ = 14.9 Hz, C2), 174.6 ($J_{C-F}$ = 282.3 Hz, C4); $^{1}$H NMR δ -0.1 (s, 3H, *syn*-Me), 2.43 (s, 3H, *anti*-Me), 2.80 (*d*, 3H, $J_{H-F}$ = 5.0 Hz, C3 Me), 4.80 (dd, 1H, $J_{H-F}$ = 4.3 Hz, $J_{H-H}$ = 7.7 Hz, H1), 5.01 (dd, 1H, $J_{H-F}$ = 4.3 Hz, $J_{H-H}$ = 7.7 Hz, H7), 8.00 (dd, 1H, $J_{H-F}$ = 18.6 Hz, $J_{H-H}$ = 10.1 Hz, H5), 8.45 (m, 2H, H2 and H6).

(11) R. F. Childs and C. V. Rogerson, *J. Am. Chem. Soc.*, **100**, 649 (1978).

(12) A detailed analysis of the spectra, and the results of quenching experiments with methanol, which gave a mixture of labile methyl ethers that rearranged on further workup, will be presented in a full account.

(Received in USA 14 April 1982)