247. Rearrangements Involving C_8H_8F-Cations of the Cage Type

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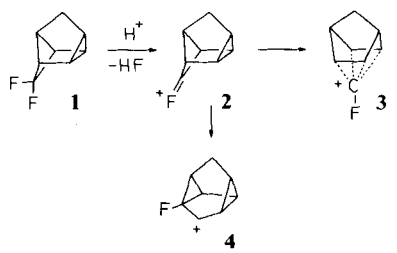
Summary

The homo-1,4 adduct obtained from difluorocarbene and bicyclo[2.2.1]hepta-2,5-diene (**1**) was treated successively with HCl, FSO_3H and SbF_5 in SO_2ClF at low temperature. The protic acids underwent electrophilic addition to the cyclopropane part of **1**, giving the corresponding derivatives. However, in FSO_3H at $-50°$, protonation of the *gem*-difluoro grouping also occurred to give the 2-fluoro-6-fluorosulfonylbicyclo[3.2.1]oct-2-en-3-yl cation. The reaction of **1** with SbF_5 at $-78°$ led initially to the formation of the 2-fluorobicyclo[3.2.1]octa-2,6-dien-4-yl cation, which rearranged to 4-fluorotricyclo[5.1.0.$0^{5,8}$]oct-3-en-2-yl cation at $-40°$. These rearrangements are discussed in the light of those expected for C_8H_8F square pyramidal cations.

We have already demonstrated that the homo-1,4 adduct obtained from dichlorocarbene and bicyclo[2.2.1]hepta-2,5-diene serves as a useful and readily accessible molecule [1] for studying the chemistry of novel C_8H_9-cations and C_8H_8-zwitterions of the cage type [2] [3]. The analogous difluorocarbene adduct **1**, although possessing substituents which are usually regarded as poor leaving groups [4], could by the device of protonation and elimination of hydrogen fluoride engender the fluoronium cation **2**. Once formed, cation **2** could evolve further either by haptotropic rearrangement to the centrosymmetric cation **3** or by *Wagner-Meerwein* rearrangement to the bis(cyclopropyl)methyl cation **4** [5] *(Scheme 1)*. We have examined this question by subjecting **1** to a variety of acidic conditions and herewith report our findings [6].

Scheme 1



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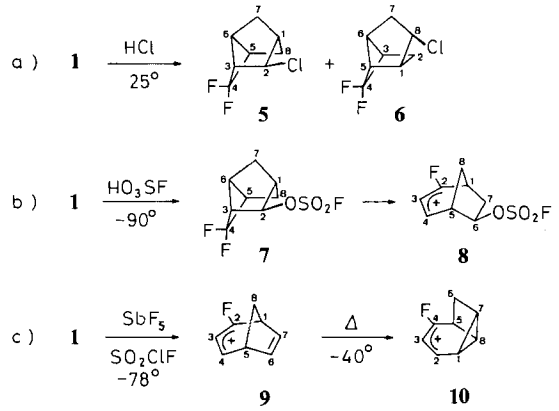
First, **1** was treated with HCl in $CHCl_3$ at 25°. These conditions were previously shown to be suitable for opening the *gem*-difluorocyclopropane ring [7]. To our surprise, the *gem*-difluorocyclobutane grouping stayed intact; protonation occurred instead at the cyclopropane ring to give the pair of *exo*-chloro derivatives **5** and **6** in 25 and 75% yield, respectively. Both **5** and **6** were stable entities and were easily isolated by GC. and identified by NMR. spectroscopy *(Scheme 2a)*.

In a second experiment, **1** was allowed to react with fluorosulfonic acid at −90°. Again the *gem*-difluoro group remained untouched. Only one product of addition to the cyclopropane ring was detected, the *exo*-fluorosulfonate **7**. However, on carefully warming to −50°, ionization with loss of fluoride occurred, generating the 2-fluorobicyclo[3.2.1]octenyl cation **8**, which was unambiguously identified by its ^{1}H-, ^{19}F- and ^{13}C-NMR. spectra *(Scheme 2b)*.

Scheme 2



Lastly, in an attempt to ensure that the cyclopropane unit could play its participatory role, aprotic and superionizing conditions were tried. The *gem*-difluoro adduct **1** was carefully dissolved in excess SbF_5 and SO_2ClF at −78°. After 40 min, ionization was complete and the resulting orange solution was examined by ^{1}H- and ^{19}F-NMR. spectroscopy. A new species, the fluorobicyclo[3.2.1]octadienyl cation **9** had formed, corresponding to at least 95% conversion of **1** into **9**[1]). Cation **9** proved to be quite stable up to −40°. However, at −40° its half-life was already shortened to an hour by irreversible rearrangement; a new cation appeared, the structure for which is best represented by **10** *(Scheme 2c)*.

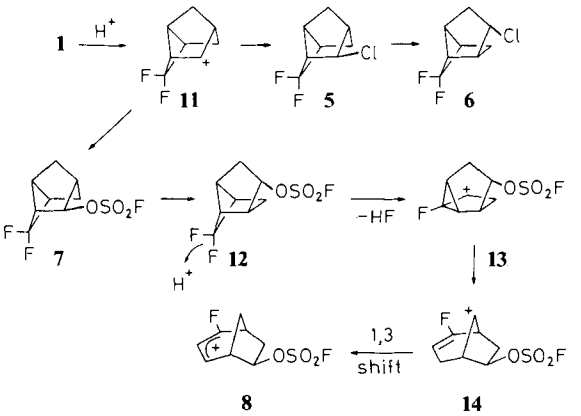
The diversity of the results is undoubtedly due to the different acid conditions employed. The protic species bring about typical electrophilic cleavage of the cyclopropane moiety [8], whereas stronger acids cause ionization of a F-substituent.

The addition of HCl to **1** probably generates as a first, kinetic event, the norbornyl cation **11** which is immediately captured by chloride ion exclusively on the *exo*-side to give **5**. Isomerization to **6** could then occur *via* a concerted dyotropic rearrangement [9], or within the compass of an intimate ion pair.

[1]) About 5% of unidentified by-product was also formed.

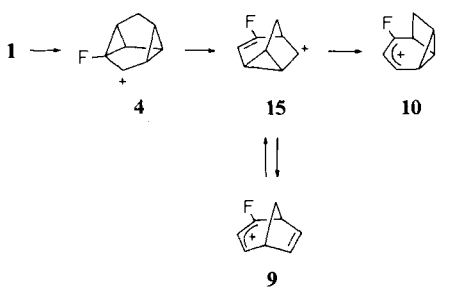
Fluorosulfonic acid undoubtedly behaves the same way, although its addition to cyclopropanes is not well documented [10]. The first-formed adduct **7**, unlike its chloro analogue **5**, does not visibly isomerize; however, the structure of the ensuing rearranged cation **8** requires that prior migration of the sulfonate group must have occurred. Once **7** has isomerized to **12**, protonation of the F-substituent and elimination of HF causes ring contraction to **13**. The subsequent opening of the cyclopropane ring generates the homo-allylic cation **14**, which by 1,3-H-shift furnishes the observed stable allylic cation **8** *(Scheme 3)*.

Scheme 3



Equally complex rearrangements also occur in the superionizing medium. The key step is straightforward and demonstrates that the axial F-substituent is preferentially removed by *Lewis* acid. Departure of fluoride produces the bis(cyclopropyl)methyl cation **4** which by sequential bond migrations leads to **15** and finally the bicyclo[3.2.1]octadienyl cation **9** *(Scheme 4)*.

Scheme 4



Although it has been mechanistically invoked [11], this apparently antiaromatic species **9**, or rather the parent cation, has never been directly observed before. It probably owes its existence to the F-substituent and the spreading apart of the olefinic segments [5], thereby stabilizing the allylic cation part.

Further conversion of **9** to the unusual tricyclic cation **10** is unprecedented although it formally corresponds to a di-π-methane rearrangement. Nonetheless, the thermal process can be accommodated by isomerization to the (cyclopropyl)-methyl cation **15** which achieves further allylic stabilization by rearrangement to **10**.

From these findings we conclude that *gem*-dihalo adducts such as **1** prefer to undergo ring contraction to the stable bis(cyclopropyl)methyl cation **4**, rather than give the square pyramidal structure **5**. Moreover, the resulting bicyclo[3.2.1]-octadienyl cation **9** does not constitute the thermodynamic endpoint in this series, despite its calculated stability [5], but evolves further to the novel tricyclic structure **10**.

Lastly, our results should be compared and contrasted with those obtained for the trimethyl derivatives of **1**, the rearrangement chemistry of which, although similar in that cations like **9** are formed, is dominated by 1,2-bridge shifts and circumambulation [12].

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Experimental Part

General remarks. NMR. samples in HO_3SF and SbF_5/SO_2ClF were prepared in a *Saunders* reactor [13] by adding **1**, dissolved in a minimum of CD_2Cl_2, to an excess of the ionizing mixture. The samples were sealed under Ar. NMR. measurements for ^1H, ^{19}F and ^{13}C were performed at 2.3 Tesla on a *Varian XL-100* FT. spectrometer. All assignements and coupling constants given are in agreement with homo and heteronuclear decoupling experiments. *^1H-NMR.* (100.1 MHz, δ(ppm) relative to external TMS; *m* = multiplet, *s* = singlet, *d* = doublet, *t* = triplet, br. = broad. Apparent coupling constants (*J*) in Hz. *^{19}F-NMR.* (94.1 MHz, δ(ppm) relative to external $FCCl_3$. Negative sign indicates resonance at high field from the reference. *^{13}C-NMR.* (25.2 MHz), δ(ppm) relative to external TMS. Multiplicities for proton off-resonance decoupling: *s* = singlet, *d* = doublet, *t* = triplet, *qa* = quadruplett, *qi* = quintuplett.

Spectral data of **5**. – ^{1}H-NMR. (100.1 MHz, $DCCl_3$): 1.48 ($d\times m$, ^2J = 11.8, 1 H, H_{ax}–C(8)); 1.74 (narrow *m*, 2 H, H_2C(7)); 2.4 ($d\times m$, ^2J = 11.8, 1 H, H_{eq}–C(8)); 2.6–3.1 (complex *m*, 4 H, H–C(1), H–C(3), H–C(5) and H–C(6)); 4.15 (br. *s*, 1 H, H–C(2)). – ^{19}F-NMR. (94.1 MHz, $DCCl_3$): –102.5 (*d*, ^2J(F,F) = 189, F_{ax}–C(4)); –110.4 ($d\times m$, ^2J(F,F) = 189, F_{eq}–C(4)).

Spectral data of **6**. – ^{1}H-NMR. (100.1 MHz, $DCCl_3$): 0.98 ($d\times m$, ^2J = 12.0, 1 H, H_{endo}–C(2)); 1.86 (*m*, 1 H, H_{exo}–C(2)); 2.0 (*m*, 1 H, H_{exo}–C(7)); 2.25 ($d\times d$, ^2J = 15, ^3J(7,8) = 5.8, 1 H, H_{endo}–C(7)); 2.5–2.7 (complex *m*, 3 H, H–C(1), H–C(3) and H–C(5)); 3.16 (*m*, ^4J(H,F_{eq}) = 6.3, 1 H, H–C(6)); 4.27 ($t\times m$, ^5J(H,F_{eq}) = 5.8, 1 H, H–C(8)). – ^{19}F-NMR. (94.1 MHz, $DCCl_3$): –101.9 (*d*, ^2J(F,F) = 176, F_{ax}–C(4)); –135 (*d*, ^2J(F,F) = 176, F_{eq}–C(4)).

Spectral data of **7**. – ^{1}H-NMR. (100.1 MHz, FSO_3H, –80°): 1.9–2.6 (complex *m*, 4 H, H_2C(7) and H_2C(8)); 3.1–3.5 (complex *m*, 4 H, H–C(1), H–C(3), H–C(5) and H–C(6)); 5.7 (br. *s*, 1 H, H–C(2)). – ^{19}F-NMR. (94.1 MHz, FSO_3H, –80°): +38.9 (*s*, F-SO_3C(2)); –100.1 (*d*, ^2J(F,F) = 193, F_{ax}–C(4)); –110.6 (*d*, ^2J(F,F) = 193, F_{eq}–C(4)). – ^{13}C-NMR. (25.2 MHz, FSO_3H, –80°): 27.5 ($d\times t$, C(7) or C(8)); 33.7 ($d\times d$, C(6)); 24.36 ($d\times t$, C(8) or C(7)); 42.1 ($\approx d$, C(1)); 44.3 ($t\times d$, ^2J(C,F_{ax}) = ^2J(C,F_{eq}) = 20.2, C(5) or C(3)); 52.7 ($t\times d$, ^2J(C,F_{ax}) = ^2J(C,F_{eq}) = 20.9, C(3) or C(5)); 94.34 ($\approx d\times d$, ^3J(C,F) = 8.2 (it is unknown which F couples, C(2)); 119.0 ($d\times d\times s$, ^1J(C,F_{ax}) = 266.5 or 295.7, ^1J(C,F_{eq}) = 295.7 or 266.5).

Spectral data of **8**. – ^{1}H-NMR. (100.1 MHz, FSO_3H, –50°): 2.8–3.7 (complex *m*, 4 H, H_2C(7) and H_2C(8)); 4.7 (*m*, ^3J(H,F) = 11.0, 1 H, H–C(1)); 4.8 (*m*, 1 H, H–C(5)); 6.0 (*m*, 1 H, H–C(6)); 7.85 ($t\times m$, ^3J(H,F) = 7.5, ^3J(H,H) = 7.5, 1 H, H–C(3)); 11.4 (*m*, partial overlap with HO_3SF, H–C(4)). –

^{19}F-NMR. (94.1 MHz, FSO_3H, −50°): +38.5 (*s*, F-SO_3C(6)); −133 (*m*, ^3J(F,H−C(1))=11.0, ^3J(F,H−C(3))=7.5, F−C(2)). – ^{13}C-NMR. (25.2 MHz, FSO_3H, −50°): 31.5 (≈*t*, c(7)); 47.3 (≈*t*, C(8)); 47.6 (br. *d*, C(1)); 56.40 (*d*×*d*, ^4J(C,F−C(2))≈8.0, C(5)); 86.5 (*d*, C(6)); 127.3 (br. *d*×*d*, ^2J(C,F)=12.1, C(3)); 220.9 (*d*×*s*, ^1J(C,F)=378.5 (*cf.* equally large values [14], C(2); 228.7 (*d*×*d*, ^3J(C,F)=38.4, C(4)).

Spectral data of **9**. – ^{1}H-NMR. (100.1 MHz, SbF_5/SO_2ClF, −80°): 3.3–3.6 (*m*, ^2J=13.0, 2 H, H_2C(8)); 4.1–4.5 (*m*, 2 H, H−C(1) and H−C(5)); 6.90 (≈*t*, ^3J(H,H)=8.3, ^3J(H,F)=8.0, 1 H, H−C(3)); 7.02 (≈*t*, ^3J(6,7)=4.5, 1 H, H−C(6)); 7.50 (*qa*, ^3J(6,7)=4.5, ^4J(H,F)=3.5, 1 H, H−C(7)); 10.4 (*m*, ^4J(H,F)=6.0, ^3J(3,4)=8.3, ^3J(4,5)=6.0, 1 H, H−C(4)). – ^{19}F-NMR. (94.1 MHz, SbF_5/SO_2ClF, −80°): −140 (*m*, F−C(2)).

Spectral data of **10**. – ^{1}H-NMR. (100.1 MHz, SbF_5/SO_2ClF, −50°): 2.64 (*d*×*d*, ^2J(6,6)=14.5, ^3J(5,8)=8, 1 H, H_{endo}−C(6)); 3.56 (*m*, 1 H, H_{exo}−C(6)); 4.1–4.6 (complex *m*, 4 H, HC(1), H−C(5), H−C(7) and H−C(8)); 7.52 (*d*×*d*×*d*, ^3J(H,F)=6.0, ^3J(2,3)=8.5, 1 H, H−C(3)); 10.20 (*m*, ^3J(1,2)=7.0, ^4J(H,F)=6.0, 1 H, H−C(2)). – ^{19}F-NMR. (94.1 MHz, SbF_5/SO_2ClF, −50°): −139 (*m*, F−C(4)).

REFERENCES

[1] *C. W. Jefford, V. de los Heros & U. Burger,* Tetrahedron Lett. *1976,* 703.

[2] *C. W. Jefford, S. Genevay-Höck, A. Delay, J. Mareda & U. Burger,* Tetrahedron Lett, *1979,* 2549; *C. W. Jefford & V. de los Heros,* ibid. *1980,* 913.

[3] *C. W. Jefford, J. C. Rossier, J. A. Zuber, O. Kennard & W. B. T. Cruse,* Tetrahedron Lett. *1982,* in press.

[4] *A. Streitwieser, Jr.,* 'Solvolytic Displacement Reactions', McGraw-Hill, New York, N.Y. 1962, p. 62.

[5] *C. W. Jefford, J. Mareda, J. C. Perlberger & U. Burger,* J. Am. Chem. Soc. *101,* 1370 (1979).

[6] *J. Mareda,* Doctoral Thesis No 1989, 1981, University of Geneva, Geneva, Switzerland.

[7] *C. W. Jefford, A. N. Kabengele & U. Burger,* Tetrahedron Lett. *1972,* 4799.

[8] *A. Nickon & J. H. Hammons,* J. Am. Chem. Soc. *86,* 3322 (1964); *T. C. Morrill & B. E. Greenwald,* J. Org. Chem. *36,* 2769 (1971); *M. Saunders, P. Vogel, E. L. Hagen & J. Rosenfeld,* Acc. Chem. Res. *6,* 53 (1973); *J. Paasivirta,* Acta Chem. Scand. *27,* 374 (1973).

[9] *M. T. Reetz,* Tetrahedron *29,* 2189 (1973).

[10] *D. Quarroz, J.-M. Sonney & P. Vogel,* Chimia *29,* 306 (1975); *D. Quarroz & P. Vogel,* Helv. Chim. Acta *62,* 335 (1979).

[11] *A. F. Diaz, M. Sakai & S. Winstein,* J. Am. Chem. Soc. *92,* 7477 (1970); *E. Kaufmann, H. Mayr, J. Chandrasekhar & P. v. R. Schleyer,* ibid. *103,* 1375 (1981).

[12] *H. Hart & D. L. Stein,* Tetrahedron Lett. *34,* 3435 (1982).

[13] *M. Saunders, C. Cox & W. Olmstead,* J. Am. Chem. Soc. *95,* 3018 (1973).

[14] *B. Halton, H. M. Hügel, D. P. Kelly, P. Müller & U. Burger,* J. Chem. Soc., Perkin II, *1976,* 258.