Fluorination with Xenon Difluoride. Part 15. Stereochemistry of Fluorine Addition to Acenaphthylene and Dihydronaphthalenes

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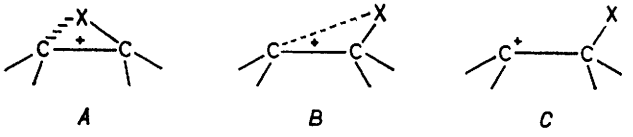
Acid-catalysed liquid-phase addition of fluorine by xenon difluoride to acenaphthylene and 1,2-dihydronaphthalene gives vicinal difluorides in high yield. The addition proceeds predominantly *via* trans-attack. The reaction with 1,4-dihydronaphthalene affords a complex mixture of naphthalene, 1-fluoronaphthalene, 2-fluoronaphthalene, and 2-fluoro-1,2,3,4-tetrahydronaphthalene.

MECHANISMS of electrophilic addition of halogens to alkenes have been widely investigated, from both kinetic and stereochemical points of view.[1] Apart from the relative importance of the various kinetically significant processes, it is now known that the nature of the intermediate depends on the structure of the substrate, the nature of the halogen, and the reaction medium, ranging from a strongly bridged halogenonium ion of type *A* through a weakly bridged species of type *B* to an open ion of type *C* (Scheme 1). If the cation is of the open



SCHEME 1

structure *C*, a mixture of *cis*- and *trans*-adducts is generally expected. However, ion-pairing phenomena can cause preferential formation of the *cis*-adduct and electronic, steric, or conformational effects can cause attack at one or other side of the carbonium *p*-orbital of *C* to be favoured. On the other hand, a bridged structure *A* (X = Br) will presumably be opened stereospecifically to give a *trans*-adduct.

Recently, we have observed that xenon difluoride readily adds fluorine to phenyl-substituted olefins [2] and acetylenes [3] in the presence of hydrogen fluoride as catalyst to give the corresponding 1,2-difluoro- or 1,1,2,2-tetrafluoro-(phenyl)ethanes in high yield and under mild conditions. Fluorine addition to phenyl-substituted olefins, *e.g. cis*- and *trans*-1-phenylpropene, *cis*- and *trans*-stilbene, and *cis*- and *trans*-1-phenyl-2-t-butylethylene, resulted in vicinal difluorides in high yield. The ratios of (±)-*erythro*- and (±)-*threo*-difluorides were nearly independent of the starting olefin, and in the *trans*-series, *anti*-addition of fluorine predominates [(±)-*erythro* : (±)-*threo* 1.5—1.7].[4] We have suggested the formation of an open β-fluorocarbocation intermediate. The intermediate from *trans*-olefin collapses preferentially to an *anti*-adduct, whereas the *cis*-olefin intermediate can rotate freely about the newly formed single bond, thus assuming a sterically more favourable conformation identical with that of the *trans*-intermediate. We have now studied acenaphthylene and dihydronaphthalenes as substrates for acid-catalysed liquid-phase fluorination with xenon difluoride, in the hope of eliminating the complexity which exists in the acyclic systems, in which there is the possibility of rotation about the carbon–carbon single bond in the β-fluorocarbocation.

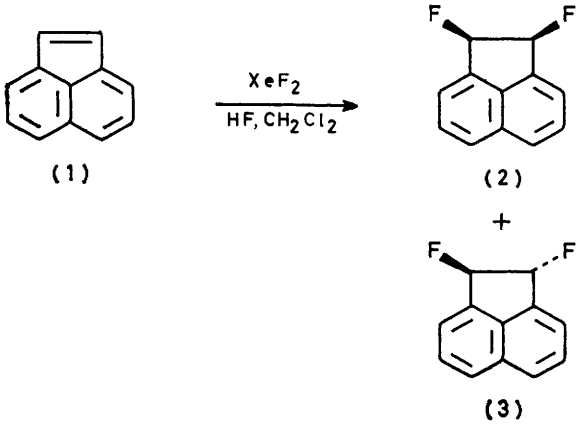
RESULTS AND DISCUSSION

The preparation of fluoroalkanes presents a different problem from that of other halogenoalkanes, and necessitates a specific method of fluorination.[5] Direct addition of fluorine to acenaphthylene at −78 °C has been shown to produce three products, *cis*-1,2-difluoro- (35%), *trans*-1,2-difluoro- (11%), and 1,1,2-trifluoroacenaphthene.[6] The fluorination of acenaphthylene (1) with xenon difluoride under the conditions usually used [2] afforded polymeric materials. The reaction in a ten times more dilute solution in methylene chloride at room temperature, with work-up after 5 min, gave a mixture, which showed in its ^{19}F n.m.r. spectrum two multiplets as a typical AA'XX' system, at δ_F −181.85 and −198.4 p.p.m., with relative intensities 84% and 16%, respectively. The products were separated by preparative t.l.c.; comparison of their physical and spectral data with those reported [6] enabled us to establish that the major product was *trans*-1,2-difluoroacenaphthene (3) and the minor one as *cis*-1,2-difluoroacenaphthene (2) (Scheme 2).

Fluorination of 1,2-dihydronaphthalene with xenon difluoride at room temperature resulted in a mixture whose ^{19}F n.m.r. spectrum showed two pairs of multiplets with relative intensities 74% [compound (5)] and 26% [compound (6)] (Scheme 3). The products were separated by preparative g.l.c. Product (6) underwent rapid elimination of hydrogen fluoride with potassium t-butoxide in t-butyl alcohol at room temperature, whereas the product (5) underwent similar elimination on heating at 60 °C for 4 h. Comparison of the ^{19}F n.m.r. data showed very little differences between the three-bond coupling constants. On the basis of the

[1] R. C. Fahey, *Topics Stereochem.*, 1968, **3**, 280; P. B. D. De La Mare, 'Electrophilic Halogenation,' Cambridge University Press, Cambridge, 1976.
[2] M. Zupan and A. Pollak, *J.C.S. Chem. Comm.*, 1973, 845; *J. Org. Chem.*, 1976, **41**, 4002.
[3] M. Zupan and A. Pollak, *J. Org. Chem.*, 1974, **39**, 2646.
[4] M. Zupan and A. Pollak, *J. Org. Chem.*, 1977, **42**, 1559.
[5] W. A. Sheppard and C. M. Sharts, 'Organic Fluorine Chemistry,' Benjamin, New York, 1969.
[6] R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, 1966, **31**, 1859.

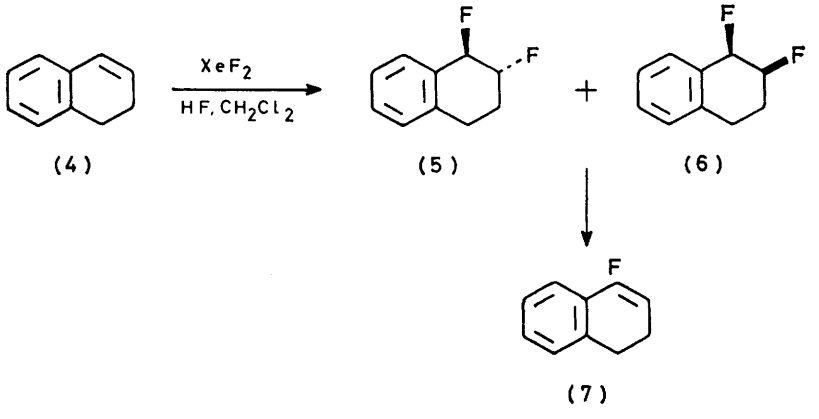
coupling constants, chemical shifts, and rates of elimination of hydrogen fluoride, we consider that the major

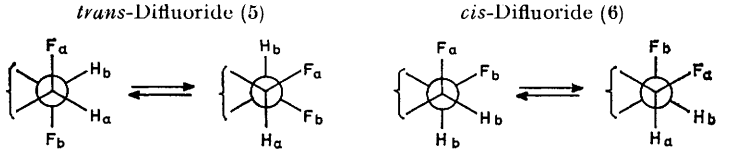


SCHEME 2

product arose *via* *trans*-addition, and the minor one from *cis*-addition. Fluorination in the presence of a naphthalene, 2-fluoronaphthalene, and 2-fluoro-1,2,3,4-tetrahydronaphthalene. The products were identified on the basis of their n.m.r. and mass spectral and physical data (Scheme 4).

On the basis of earlier observations of additions of fluorine by xenon difluoride in liquid-phase acid-catalysed reactions with phenyl-substituted olefins,[4] and the observations already made in this paper, the reaction mechanism in Scheme 5 is suggested. The fluorination must involve catalysis by hydrogen fluoride, since the reaction was very slow without it. It might be expected that in the presence of hydrogen fluoride xenon difluoride behaves as an electrophile, as suggested by Filler *et al.*[7] for the fluorination of aromatic compounds. In the next step a π-complex is probably formed between this electrophilic species and the olefin, which could be transformed by heterolytic Xe–F bond cleavage into an open β-fluorocarbocation intermediate. Preferential *anti*-attack of the fluorine anion would then result in *trans*-difluorides, and *syn*-attack in *cis*-difluorides. Another possibility is the formation of an ion





$J_{(F_aF_b)}$/Hz	15	18
$J_{(H_aH_b)}$/Hz	6	1.5
$J_{(F_aH_b)}$/Hz	15	18
$J_{(F_bH_a)}$/Hz	12	12
$\delta(F_a)$	−180.4	−183
$\delta(F_b)$	−195	−200.3
$\delta(H_a)$	5.46	5.45
$\delta(H_b)$	4.86	4.84

SCHEME 3

free radical inhibitor (oxygen) had no significant effect on the product distribution.

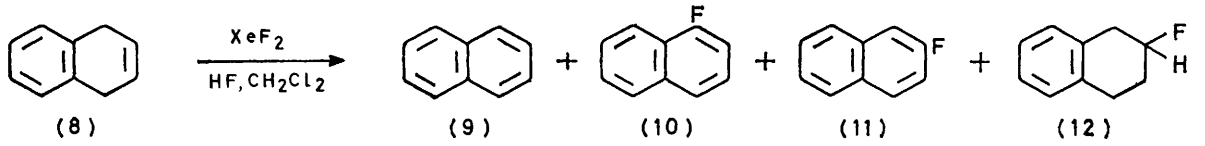
The reaction of xenon difluoride with 1,4-dihydronaphthalene proceeded *via* a different pathway from that of 1,2-dihydronaphthalene. Room temperature fluorination gave four products which could be separated by preparative g.l.c., *viz.* naphthalene, 1-fluoro-

radical, as observed in the fluorinaton of benzene and its derivatives,[7] transformed in the next step by XeF· or XeF_2 into an open carbocation. The lower oxidation

[7] M. J. Shaw, J. A. Weil, H. H. Hyman, and R. Filler, *J. Amer. Chem. Soc.*, 1970, **92**, 5096; M. J. Shaw, H. H. Hyman, and R. Filler, *ibid.*, p. 6498; *J. Org. Chem.*, 1971, **36**, 2917; S. P. Anand, L. A. Quarterman, H. H. Hyman, K. G. Migliorese, and R. Filler, *ibid.*, 1975, **40**, 807.

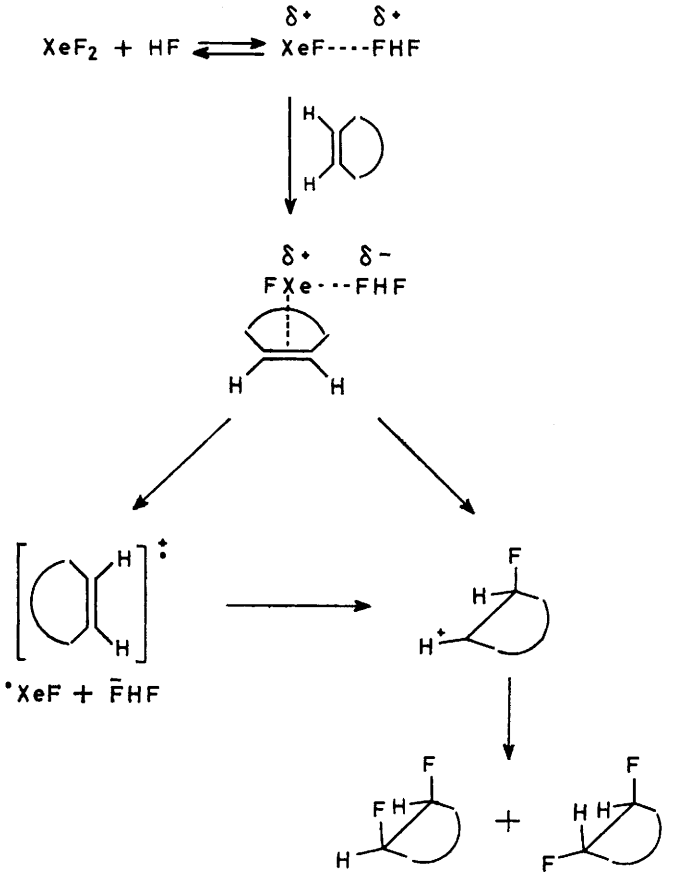
potentials of olefins (in comparison with those of benzo-derivatives) make the suggested path quite reasonable.

An explanation for the formation of four products in the fluorination of 1,4-dihydronaphthalene (8) is presented in Scheme 6. Formation of a β-fluorocarbocation (8a), elimination of a proton to give (8c) followed by



SCHEME 4

elimination of HF, results in naphthalene (9). However, naphthalene could also be formed by elimination of HF from (8b), resulting from fluoride anion attack on (8a). Recently, Filler *et al.*[8] have shown that naphthalene reacts readily with xenon difluoride forming 1-fluoro-



SCHEME 5

and 2-fluoro-naphthalene, which could explain the isolation of the monofluorides (10) and (11). 2-Fluoro-1,2,3,4-tetrahydronaphthalene (12) is presumably formed by addition of HF to 1,4-dihydronaphthalene.

[8] S. P. Anand, L. A. Quaterman, P. A. Christian, H. H. Hyman, and R. Filler, *J. Org. Chem.*, 1975, **40**, 3796.
[9] F. Straus and L. Lemmel, *Ber.*, 1913, **46**, 232, 1051.

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer, and ^1H and ^{19}F n.m.r. spectra with a JEOL JNM-PS-100 instrument for solutions in CCl_4 solution with Me_4Si or CCl_3F as internal reference. Mass spectra (including high resolution measurements) were taken with a CEC-21-110 spectrometer. G.l.c. was carried out with a Varian Aerograph 1800 instrument and t.l.c. with Merck PSC-Fertigplatten silica gel F-254 (activated for 3 h at 120 °C before use).

Materials.—1,2-Dihydronaphthalene [9] and 1,4-dihydronaphthalene [9] were preparated by known methods. Acenaphthylene was commercially available and purified before use. Hydrogen fluoride (Fluka Purum) was used without further purification. Methylene chloride was purified [10] and stored over molecular sieves. Xenon difluoride was prepared by a photosynthetic method; [11] its purity was better than 99.5%.

Addition and Isolation Procedures.—To a solution of olefin (1 mmol) in methylene chloride (5 ml) [in the case of (1) (50 ml)] in a Kel-F vessel, xenon difluoride (1 mmol) was added at 25 °C, followed with stirring by anhydrous hydrogen fluoride (trace). After a few seconds the colourless solution had turned dark blue and xenon gas was evolved. After 30 min xenon evolution ceased [after 5 min in the case of (1)]. The mixture was diluted with methylene chloride (15 ml), washed with aqueous 5% hydrogen carbonate (10 ml) and water, and dried (Na_2SO_4). The crude product was separated by preparative t.l.c. or g.l.c.

cis- *and* trans-1,2-*Difluoroacenaphthene* [(2) *and* (3)].—Products were separated by preparative t.l.c. [SiO_2; light petroleum (b.p. 40—65 °C) to give 8% *cis*- and 60% *trans*-isomer, both as solids. The *cis*-isomer (2) had m.p. 103—105 °C (lit.,[6] 105 °C); the *trans*-isomer (3) had m.p. 41—43 °C (lit.,[6] 40.5—42.5 °C). In agreement with the literature,[6] the *cis*-isomer showed δ_F −198.4 p.p.m. (AA′XX′) and δ_{CFH} 6.1 p.p.m. (AA′XX′) and the *trans*-isomer δ_F −181.75 p.p.m. (AA′XX′) and δ_{CFH} 6.38 p.p.m. (AA′XX′).

trans- *and* cis-1,2-*Difluoro*-1,2,3,4-*tetrahydronaphthalene* [(5) *and* (6)].—Products were separated by preparative g.l.c. [FFAP (10%) on Chrom-AW; 120 °C] to give 60% of trans-*adduct* and 10% of cis-*adduct*, both as liquids, with n.m.r. data as given in Scheme 3; *m/e* 168 (48%, M^+), 122 (100), 119 (58), and 117 (58) (Found: C, 71.1; H, 6.1%; M^+, 168.075 9. $C_{10}H_{10}F_2$ requires C, 71.4; H, 5.9%; *M*, 168.075 7).

Fluorination of 1,4-*Dihydronaphthalene* (8).—Products were separated by preparative g.l.c. [DEGS (10%) on Chrom-AW; 130 °C] to give naphthalene (9) (15 mg), 2-fluoronaphthalene (11), (13 mg), 1-fluoronaphthalene (10) (45 mg), and 2-fluoro-1,2,3-tetrahydronaphthalene (12) (23 mg). Physical and spectral data of the products (9)—(11) agreed

[10] ' Techniques of Organic Chemistry,' vol. VII, ed. A. Weissberger, Interscience, New York, 1955.
[11] S. M. Williamson, *Inorg. Synth.*, 1968, **11**, 147.

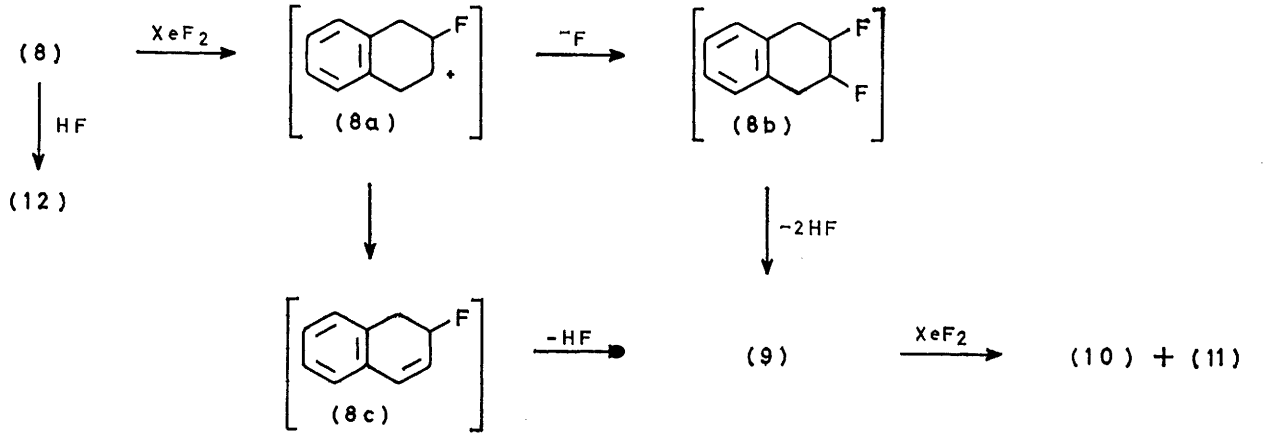
with those reported.[8] *2-Fluoro-1,2,3,4-tetrahydronaphthalene* (12) was a liquid, δ_F −181.1 p.p.m. (m), δ_H 4.95 (1 H, m), 2.9 (4 H, m), and 2 p.p.m. (2 H, m), $J_{F,H}$ 51 Hz; *m/e* 150 (100%, M^+), 130 (90), 129 (65), 128 (65), 115 (45), 105 (86), and 91 (63) [Found: C, 79.75; H, 7.15. $C_{10}H_{11}F$ requires C, 79.95; H, 7.4%).

Stability of the Difluorides.—To test the stability of the difluorides, pure difluoride or a mixture of isomeric difluorides (0.2 g) was dissolved in methylene chloride (2 ml), xenon difluoride (20 mg) and a catalytic amount of hydrogen fluoride were added, and the mixture was stirred for 30 min [in the case of (2) and (3) for 5 min]. After work-up, the n.m.r. spectra showed no significant differences.

Fluorination in the Presence of Oxygen.—1,2-Dihydronaphthalene (4) (1 mmol) was dissolved in methylene chloride (5 ml), xenon difluoride (1 mmol) was added at 25 °C, and with stirring a mixture of anhydrous hydrogen fluoride and oxygen was passed through the mixture for 30 min. After work-up the residue was analysed by n.m.r. spectroscopy, which showed the presence of 72% of (5) and 28% of (6). Thus the free radical inhibitor had no effect on the product distribution.

Elimination of Hydrogen Fluoride from the Difluorides (5) *and* (6).—(*a*) Compound (6) (100 mg) was dissolved in t-butyl alcohol (1 ml) and potassium t-butoxide (300 mg) was added. The mixture was stirred at room temperature for 2 h, then mixed with water and extracted with methylene chloride. The extract was washed with dilute acid and water, dried (Na_2SO_4), and evaporated, and the residue was analysed by g.l.c. and n.m.r. spectroscopy. The product (7) was purified by preparative g.l.c.

(*b*) Compound (5) (100 mg) was dissolved in t-butyl alcohol (1 ml) and potassium t-butoxide (300 mg) was added. After 3 h, 30% of (5) had been converted into (7). After heating for 4 h at 60 °C, elimination appeared to be complete. Work-up gave a 70% yield of *4-fluoro-1,2-dihydronaphthalene* (7), δ_F 123.75 p.p.m., $^3J_{F,H}$ 15 Hz; *m/e* 148 (63%, M^+), 147 (65), 146 (38), 133 (44), and 101 (2) (Found: C, 80.9; H, 6.05%; M^+, 148.086 69. $C_{10}H_9F$ requires, 81.05; H, 6.1%; *M*, 148.085 9).



SCHEME 6

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