Journal of Fluorine Chemistry, *24* (1984) 211–218

Received: March 25, 1983; accepted: May 6, 1983

REACTIONS INVOLVING FLUORIDE ION. PART 28[1]. CYCLISATION AND FORMATION OF DIMERS FROM PERFLUORO-2,5-DIAZAHEXA-2,4-DIENE

R.N. BARNES, R.D. CHAMBERS, M.J. SILVESTER, C.D. HEWITT

Department of Chemistry, University Science Laboratories, South Road,
Durham, DH1 3LE (U.K.)

and E. KLAUKE

Bayer A.G., Zentrale Forschung, 5090 Leverkusen, Bayerwerk, (F.R.G.)

SUMMARY

A variety of dimers is formed by reaction of perfluoro-2,5-diazahexa-2,4-diene (2) with metal fluorides; product composition depends on the reactivity of the fluoride source and the reaction conditions i.e. product may be under kinetic or equilibrium control. Cyclisation of (2) occurs, over hot caesium fluoride, in a flow process. A nitranion, generated by fluoride ion, has been trapped with iodomethane.

INTRODUCTION

So far, in this series of papers, we have concentrated on the chemistry of fluorinated carbanions that are generated by reactions of fluoride ion with fluorinated alkenes and, here, we describe chemistry of some nitranions generated from perfluorinated aza-alkenes. We [2] and others [3] have described some chemistry of nitranions generated from fluorinated azacyclohexene derivatives and some chemistry of the anion derived from perfluoroazapropene has also been reported [4,5].

Generally, fluorinated aza-alkenes are not readily accessible but a good synthesis of perfluoro-2,5-diazahexa-2,4-diene (2), starting from the fluorinated amine (1), has been reported [6] and this followed an earlier, more esoteric synthesis [7]. Here, we describe some reactions of the diazadiene (2) with fluoride ion, to generate corresponding nitranions, both in solution and on the surface of metal fluorides.

0022-1139/83/$3.00

$$(CCl_2\text{-}N{=}CCl_2)_2 \xrightarrow{(i)} \underset{(1)}{(CF_2\text{-}NH\text{-}CF_3)_2} \xrightarrow{(ii)} \underset{(2)}{(CF{=}N\text{-}CF_3)_2}$$

(i) HF; (ii) NaF, 50°C.

Preliminary reports on the formation of dimers from (2) have been published [8] and we have investigated in some detail the effect of temperature and metal fluoride on these systems. We are able to confirm the formation and structures of dimers (5) and (10), reported earlier, together with a small amount of the spiro-dimer (11), not previously detected. However, we find that the products obtained vary dramatically with conditions i.e. the metal fluoride used and the temperature (see Table).

TABLE

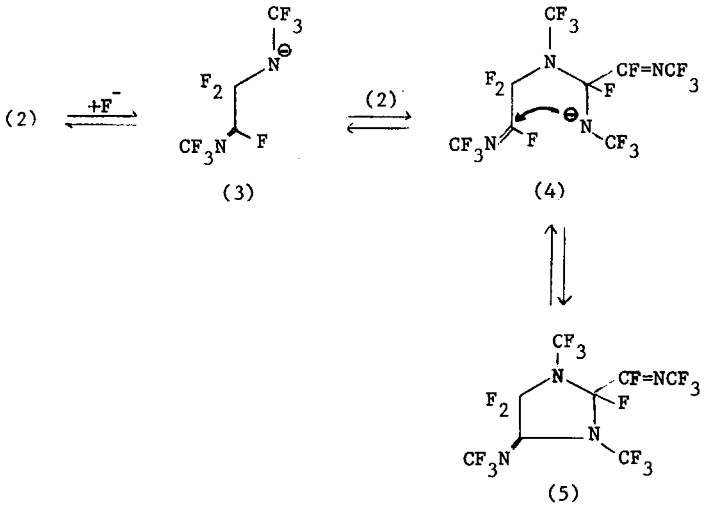
Reaction products (% composition) from (2) plus metal fluoride in sulpholane (room temp.)

MF	5	10	11
NaF	76	24	-
NaF[a]	35	65	-
KF	43	50	7
CsF	37	57	6
CsF[b]	94	6	-

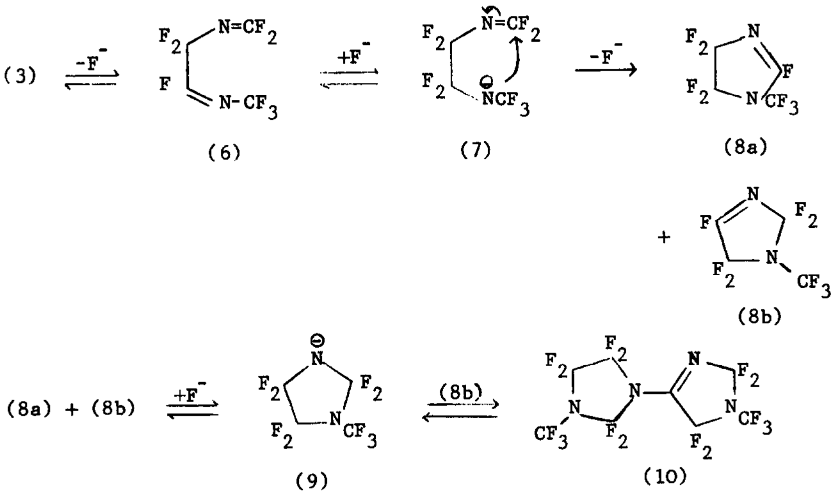
[a] At 120°C

[b] At -23°C

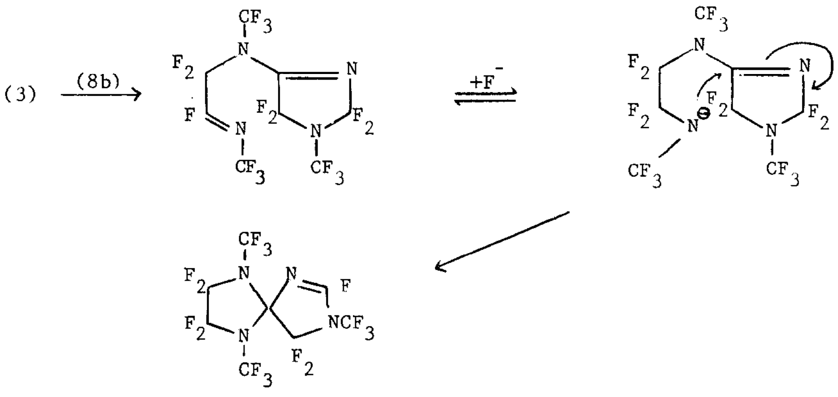
Probable mechanisms for the formation of dimers (5), (10) and (11) are shown in Schemes 1 - 3 . It is important to note that formation of (10) involves an intramolecular step i.e. (7)→(8), at an early stage, and we might anticipate, therefore, that this unimolecular process would be preferred over the competing bimolecular step (3)→(4), involved in Scheme 1 . However, formation of (5), i.e. Scheme 1, is preferred at lower temperatures or using less reactive fluoride sources (see Table) and this implies that the intramolecular cyclisation step (7)→(8) is not easy. This is, in fact, quite consistent with the Baldwin rules for cyclisation because (7)→(8) is an example of a formally disfavoured 5-endo-trigonal



Scheme 1



Scheme 2

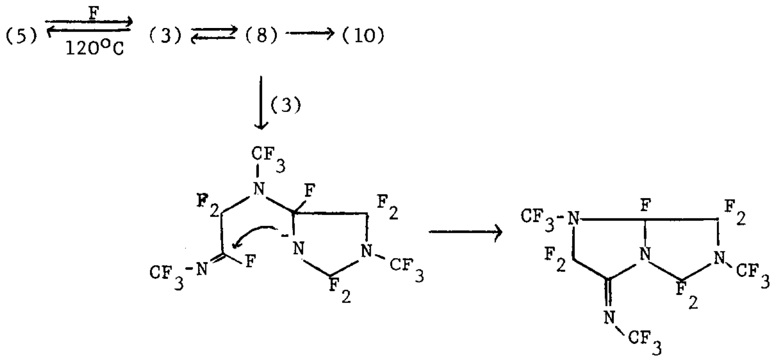


(11)

Scheme 3

cyclisation [9]. Scheme 1 also involves a cyclisation step (4)→(5) but this is an example of a favoured 5-exo-trigonal process [9]. Conversely, at high temperatures or with more reactive fluoride sources, dimer (10) is preferred (see Table) showing that (7)→(8) will occur at higher temperatures and, therefore, this must be a rare example of a formally disfavoured process.

The preferred formation of (10) at 100°C is, at first sight, surprising since a mixture of (10) with (5), the low temperature product, would have been anticipated. We established, however, that further heating of dimer (5) with caesium fluoride at 120°C gave (10), together with a further new dimer of probable structure (12), apparently formed by reaction of nitranion (3) with (8b).



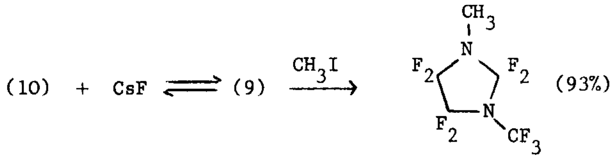
Consequently, formation of significant amounts of (12) can only occur if sufficient time has elapsed to set up an equilibrium mixture at high temperatures.

Only small amounts of cyclic compounds (8a) and (8b) were detected in reactions carried out in solution [8] but these compounds have now been obtained in high yield by the cyclisation (7)→(8) over hot caesium fluoride in a flow system.

$$(3) \xrightarrow{(i)} (8b)\ (16\%) + (8a)\ (65\%)$$

(i), CsF, 220°, N_2 flow

As expected, the cyclic compounds (8a) and (8b) form the dimer (10) rapidly at room temperature, in the presence of fluoride sources, obviously via the nitranion (9). However, the dimer (10) is also in equilibrium with the nitranion (9) in the presence of fluoride, even at room temperature, because reaction of (10) with caesium fluoride, followed by addition of iodomethane, gave a high yield of the corresponding N-methyl derivative (13).



(13)

Further chemistry of these interesting systems is in progress.

EXPERIMENTAL

^{19}F and ^{1}H n.m.r. spectra were recorded at 20°C using a Varian EM360L spectrometer, with trichlorofluoromethane or tetramethylsilane as external reference. Upfield shifts are quoted as positive. Gas chromatography was carried out using columns packed with 20% di-isodecyl phthalate on Chromosorb P (Column A) or 20% 'Krytox' [10] on Chromosorb W (Column K). Percentage yields quoted were measured either by weighing products of by g.l.c. analysis using a gas density balance detector. Mass spectra were recorded using a VG Micromass 12B spectrometer linked with a gas chromatography.

Dimerisation of perfluoro-2,5-diazahexa-2,4-diene (2)

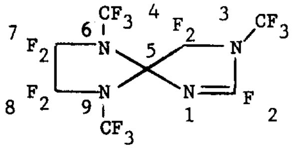
(a) At 120°C

A mixture of perfluoro-2,5-diazahexa-2,4-diene (2) (8.75 g, 38.4 mmol), sodium fluoride (1.12 g, 26.7 mmol), and sulpholane (25 ml) was heated at 120°C for 3 days in a Carius tube. Volatile material was transferred under vacuum into a trap cooled in liquid air. The resultant liquid (7.92 g, 91% recovery) was shown by g.l.c.-m.s. (Column K, 100°C) to consist of (5) (35%) and (10) (65%)[8].

(b) At room temperature

(i) With sodium fluoride A mixture containing perfluoro-2,5-diazahexa-2,4-diene (2) (3.2 g, 14.0 mmol), sodium fluoride (~ 1.0 g), and sulpholane (5 ml) was stirred for 70 hours at room temperature. Volatile material was transferred under vacuum into a trap cooled in liquid air. The resultant liquid (2.9 g) was shown by g.l.c. (Column A, 60°C) to contain two components. Separation by preparative scale g.l.c. gave the known dimers (5) (76%) and (10) (24%), identified by comparison of spectroscopic data with those reported in the literature [8].

(ii) With potassium fluoride A similar experiment using potassium fluoride gave the dimers (5) (43%) and (10) (50%), together with a third component identified as perfluorospiro-1,3,6,9-tetra-aza-3,6,9-trimethylnon-1-ene (11) (nc) (7%); Analysis: C, 21.0; F, 66.7; N, 12.1%; M^{+} 456. $C_8F_{16}N_4$ requires: C, 21.1; F, 66.7; N, 12.3%; M, 456; δ_F 57.8 (6F, broad multiplet, 6, 9-F), 58.5 (3F, broad singlet, 3-F), 71.4 (2F, broad singlet, 4-F), 83.4 (1F, broad singlet, 2-F), 90.7 (2F, multiplet, 7-F), and 91.2 (2F, quartet, J = 8.5 Hz, 8-F).



(11)

(iii) With caesium fluoride A similar experiment using caesium fluoride gave a mixture of dimers (5) (37%), (10) (57%), and (11) (6%).

(c) At -23°C

At mixture of perfluoro-2,5-diazahexa-2,4-diene (2) (8.85 g, 38.8 mmol), caesium fluoride (0.8 g, 5.3 mmol), and acetonitrile (25 ml) was stirred at -23°C for 23 hours. Volatile material was transferred under vacuum into a trap cooled in liquid air and the lower fluorocarbon layer removed. The resultant liquid (6.8 g) was shown by g.l.c.-m.s. (Column K, 95°C) to contain dimers (5) (94%) and (10) (6%).

Isomerisation of compound (5)

A mixture of dimers containing (5) (94%) and (10) (6%) (4.68 g), caesium fluoride (0.82 g, 5.39 mmol), and sulpholane (20 ml) was heated at 100°C for 3 days. Volatile material was transferred under vacuum into a trap cooled in liquid air. The resultant liquid (2.05 g) was shown by g.l.c.-m.s. (Column K, 100°C) to contain (10) (73%) and (12) (27%) [m/e 437 (M-19)]. A sample of (12) separated by preparative scale g.l.c. showed ν_{max} 1760 cm^{-1} (C=N), δ_F 57.7 (3F, C=N-CF_3), 58.3 (6F, -$\overset{|}{N}$-CF_3), 61.4, 76.3 (2F, J_{AX} = 126.8, -CF_2-), 78.5 (2F, -CF_2-), 85.1, 106 (2F, J_{AX} = 166, -CF_2-), 101.9 (1F, -$\overset{|}{C}$F-).

Vapour phase reaction of (2) over caesium fluoride

Perfluoro-2,5-diazahexa-2,4-diene (2) (10.9 g, 47.8 mmol) was passed through a silica tube (30 cm) containing caesium fluoride at 220°C in a flow of nitrogen (contact time ~ 70 secs.) and the product was collected in a trap cooled in liquid air. The resultant liquid (8.8 g, 80% recovery) was shown by g.l.c. (Column A, room temperature) to consist of two components and separation by preparative scale g.l.c. gave compounds (8a) (65%) and (8b) (16%), identified by comparison of spectroscopic data with those reported in the literature [8].

Vapour phase reaction of a mixture of dimers with fluoride ion

A mixture of dimers containing (10) (27%), (5) (67%), and (11) (6%) (5.5 g) was passed through a silica tube (30 cm) containing caesium fluoride at 220°C in a flow of nitrogen (contact time ~ 15 secs) and the product was collected in a trap cooled in liquid air. The resultant liquid (4.5 g) was shown by g.l.c. (Column A, 65°C) to contain four components, identified as compounds (8b) (10%), (8a) (17%), (5) (67%), and (11) (6%) by comparison of g.l.c.-m.s. data.

Reaction of nitranion (9) with iodomethane

Perfluoro-1,3-diaza-1-methylcyclopent-2-ene (8a) (2.1 g, 9.2 mmol) was stirred with dry caesium fluoride (1.35 g, 9.5 mmol) in sulpholane (3 ml) at room temperature. After ~ 30 minutes a lower fluorocarbon layer was observed which was shown by n.m.r. to contain the dimer (10) only. Methyl iodide (1.35 g, 9.5 mmol) was added and the solution stirred for a further 22 hours. Volatile material was transferred under vacuum into a trap cooled in liquid air. The resultant liquid (2.2 g) was shown by g.l.c. (Column A, $80^{o}C$) to consist of one major component. Purification by preparative scale g.l.c. gave 1-methyl-3-trifluoromethyl-2,2,4,4,5,5-hexafluoro-1,3-diazacyclopentane (13) (nc) (93%); Analysis: C, 23.1; H, 1.3; F, 64.8; N, 10.6%; M^+ 262. $C_5H_3F_9N_2$ requires: C, 22.9; H, 1.2; F, 65.3; N, 10.7%; M, 262; δ_F 59.7 (3F, triplet (J = 7 Hz) of triplets (J = 6 Hz), 3-F), 72.3 (2F, quartet, J = 7 Hz, 2-F), 96.6 (2F, quartet (J = 6 Hz) of triplets (J = 8 Hz), 4-F), 100.0 (2F, triplet, J = 8 Hz, 5-F); δ_H 2.43 ($N\text{-}CH_3$, singlet).

REFERENCES

1 Part 27. S. Bartlett, R.D. Chambers, J.R. Kirk, A.A. Lindley, H.C. Fielding, and R.L. Powell, J. Chem. Soc. Perkin Trans. I, submitted for publication.

2 R.N. Barnes, R.D. Chambers, and R.S. Matthews, J. Fluorine Chem., 20 (1982) 307.

3 A.R. Bailey, R.E. Banks, M.G. Barlow, and M. Nickkho-Amiry, J. Fluorine Chem., 15 (1980) 289.

4 A.F. Gontar, E.G. Bykhovskaya, and I.L. Knunyants, Bull. Acad. Sci. USSR, 24 (1975) 2161.

5 A.F. Gontar, E.G. Bykhovskaya, and I.L. Knunyants, Bull. Acad. Sci. USSR, 25 (1976) 205.

6 H.J. Scholl and E. Klauke, B.P. 1,325,619/1973.

7 P.H. Ogden and R.A. Mitsch, J. Amer. Chem. Soc., 89 (1967) 3868.

8 H.J. Scholl, E. Klauke, and D. Lauerer, J. Fluorine Chem., 2 (1972/73) 203; 205.

9 J.E. Baldwin, J. Chem. Soc. Chem. Commun., (1976) 734.

10 E.I. Du Pont de Nemours Ltd. registered trade mark.