FLUOROCARBON DERIVATIVES OF NITROGEN.   PART IV   [1].
PERFLUORO-1-AZACYCLOHEX-1-YLCAESIUM

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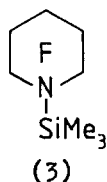of Science and Technology, Manchester M60 1QD (Great Britain)

SUMMARY

Caesium fluoride combined with perfluoro-1-azacyclohexene
in acetonitrile to yield perfluoro-1-azacyclohex-1-ylcaesium
(1), which was characterised by ^{19}F n.m.r. spectroscopy and by
treatment with iodomethane to give 2,2,3,3,4,4,5,5,6,6-
decafluoro-1-methyl-1-azacyclohexane (2). Attempts to
derivatize the caesium salt with chlorotrimethylsilane provided
fluorotrimethylsilane, perfluoro-[1-(1-azacyclohex-1-en-2-yl)-
1-azacyclohexane] (4), and 2-chloro-3,3,4,4,5,5,6,6-octafluoro-
1-azacyclohexene (5); information on the course of this reaction
was obtained through experiments in which perfluoro-1-azacyclo-
hexene was shown to undergo conversion into its chloro-analogue
(5) and its dimer (4) __via__ treatment with chlorotrimethylsilane
and fluoride ion, respectively. Aluminium chloride also converts
perfluoro-1-azacyclohexene into its chloro-analogue (5).

INTRODUCTION

Nitranion generation __via__ addition of fluoride ion to a
C=N bond is well established in aliphatic fluorocarbon chemistry
[2]. Nearly all the examples reported so far fall into the
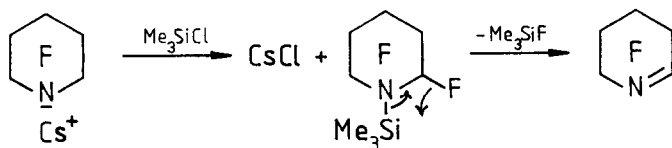acyclic category, the best known system being $CF_3N=CF_2$ + MF

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(M = alkali metal); this can be used to convert electrophilic substrates into bistrifluoromethylamino-derivatives, and initial formation of the salts $(CF_3)_2N^-M^+$ (M = K or Cs; solvent = acetonitrile or diglyme) is easily detected by ^{19}F n.m.r. spectroscopy [3]. The results of an investigation of the system $\overline{CF_2CF_2CF_2CF_2N=CF}$ + CsF are now reported.

DISCUSSION

Chromatographic (g.l.c.) work-up of the product obtained by adding iodomethane to a mixture obtained by stirring anhydrous caesium fluoride with perfluoro-1-azacyclohexene in dry aceto-nitrile at ambient temperature provided sound chemical evidence for the generation of perfluoro-1-azacyclohex-1-ylcaesium (1):

This result encouraged us to seek spectroscopic data for the perfluoro-1-azacyclohex-1-yl nitranion.

The product obtained by stirring anhydrous caesium fluoride (8.4 mmol) with perfluoro-1-azacyclohexene (8.0 mmol) in dry acetonitrile (5 cm^3) at 20 °C in the absence of air for 1 day separated into two layers when agitation was discontinued: an amber solvent-rich phase and a much denser 'milky' liquid containing suspended particles. ^{19}F N.m.r. examination of the lower layer indicated that essentially complete conversion of the azacyclohexene into the salt (1) had occurred [δ_F (ext. CF_3CO_2H) +11.9 (vbr. s; 2-,6-F), -51.4 (br. t; 3-,5-F), and -55.3 (br. q; 4-F) p.p.m.], although the broadness of the absorptions (particularly the band at lowest field) suggested that the product was in rapid equilibrium with its precursors.
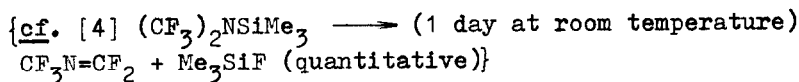
(3)

An attempt to prepare decafluoro-1-trimethylsilyl-1-aza-
cyclohexane (3) _via_ treatment of preformed perfluoro-1-aza-
cyclohex-1-ylcaesium with chlorotrimethylsilane at ambient
temperature under anaerobic conditions for 5 days gave
perfluoro-[1-(1-azacyclohex-1-en-2-yl)-1-azacyclohexane] (4)
(isolated by g.l.c. in 36% yield) and a _ca._ 1:1 mixture of
2-chloro-octafluoro-1-azacyclohexene (5) and an unidentified
component which could not be separated by g.l.c. The
unidentified product, formation of which was not detected when
a duplicate reaction was allowed to proceed for a much longer
period (17 days), appeared from n.m.r. data to contain the
perfluoro-1-azacyclohex-1-yl group [δ_F (ext. CF_3CO_2H) -13.8
(2-,6-F), -56.4 (3-,5-F) and -57.6 (4-F) p.p.m. and δ_H (ext.
$SiMe_4$) 2.0 p.p.m.];the second experiment also revealed the
production of much fluorotrimethylsilane, a product which could
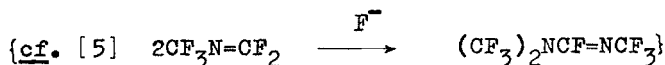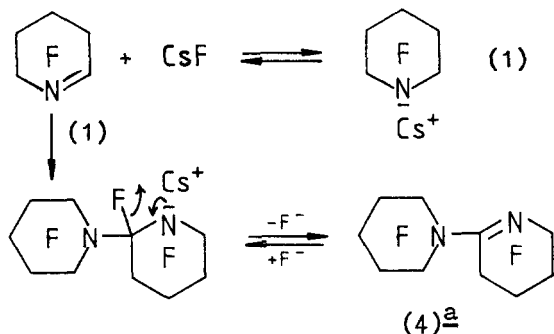have arisen _via_ simple halogen exchange:

$$Me_3SiCl + CsF \longrightarrow Me_3SiF + CsCl$$
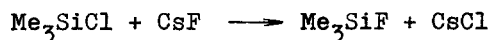
(a reaction shown by separate experiment to occur rapidly in
MeCN at -20 °C) or through decomposition of the unknown
silylamine (3) (Scheme 1).

(3)

{_cf._ [4] $(CF_3)_2NSiMe_3 \longrightarrow$ (1 day at room temperature)
$CF_3N=CF_2 + Me_3SiF$ (quantitative)}

Scheme 1

Scheme 2

$\underline{a}$ δ_F (neat liq.) -17.1 ($CF_2N=$), -17.3 [$(CF_2)_2N$], -41.1 ($CF_2C=$), -55.8 ($3 \times CCF_2C$), -56.3 (CCF_2C), and -58.5 (CCF_2C) p.p.m., of relative intensities $1:2:1:3:1:1$.

Initially, these processes, coupled with fluoride-initiated dimerization of perfluoro-1-azacyclohexene (Scheme 2) and the chlorine-for-fluorine exchange $\overline{CF_2CF_2CF_2CF_2N=CF}$ + $CsCl \longrightarrow$ $\overline{CF_2CF_2CF_2CF_2N=CCl}$ (5), seemed to constitute a plausible mechanistic scenario. However, although perfluoro-1-aza-cyclohexene did dimerize [$\longrightarrow$ (4), albeit slowly] when treated with caesium fluoride in acetonitrile at 20 °C, it was not converted into its chloro-analogue (5) by caesium chloride under similar conditions.[*] Halogen-exchange did occur however, with concomitant and quantitative formation of fluorotrimethyl-silane, when perfluoro-1-azacyclohexene was treated with an equimolar proportion of chlorotrimethylsilane in acetonitrile at room temperature. This reaction was monitored using [19]F n.m.r. spectroscopy and found to occur even at −30 °C, though

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[*] This experiment was monitored by [19]F n.m.r. spectroscopy. During 5 days at 20 °C, the only change in the spectrum involved the slow appearance of several low-intensity absorptions which could not be assigned.

slowly; a spectrum run at -10 °C on a reaction mixture prepared
at -196 °C then kept at ca. -16 °C for 3 days revealed that
formation of the chloro-compound (5) and the fluorosilane was
complete. Several analytical experiments of this type were
performed in an effort to detect the formation of the presump-
tive intermediate (6) (Scheme 3), but to no avail. Note that
2-chloro-octafluoro-1-azacyclohexene (5) is not a new compound:
it was synthesised previously by chlorination of perfluoro-1-
azacyclohexene with aluminium chloride [6] and identified by
conversion into the known [7] 2-diethylamino-octafluoro-1-
azacyclohexene via treatment with diethylamine.
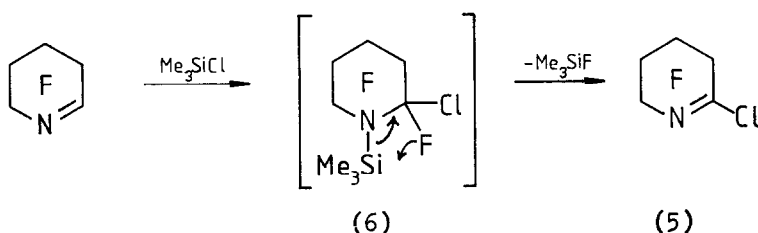
Scheme 3

Thus, the main pathways considered to contribute to the
reaction between preformed perfluoro-1-azacyclohex-1-ylcaesium
and chlorotrimethylsilane are those indicated in Scheme 4.
Conversion of 2-chloro-octafluoro-1-azacyclohexene into
perfluoro-1-azacyclohexene or its dimer (4) through the agency
of fluoride ion is not suspected to play a significant rôle
since formation of the perfluorinated azahexene was not
detected (by [19]F n.m.r. spectroscopy) when its chloro-analogue
in acetonitrile was shaken with caesium fluoride for 2½ days
at room temperature; some new unassignable low-intensity
absorptions did appear in the [19]F n.m.r. spectrum of the mixture,
but their origin was not pursued.

Currently, attention is being devoted exclusively to
determination of the scope of the reaction $\overline{CF_2(CF_2)_3N=CF}$ +
Me_3SiX (X ≠ F) ⟶ $\overline{CF_2(CF_2)_3N=CX}$ + Me_3SiF.
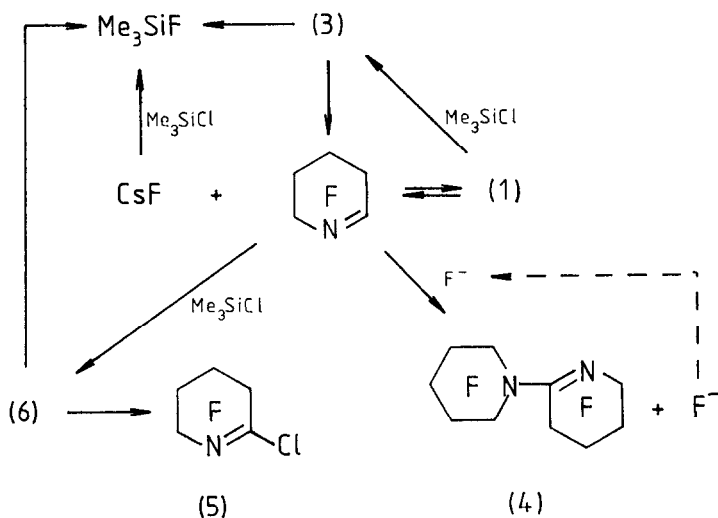
Scheme 4

EXPERIMENTAL

^{19}F N.m.r. spectra were recorded at 84.6 MHz with a Perkin-Elmer R32 spectrometer (ext. CF_3CO_2H ref., chemical shifts to high field designated negative). Perfluoro-1-azacyclohexene was prepared by defluorination (with Ph_3P [8]) of perfluoro-N-fluoropiperidine obtained by electrochemical fluorination of pyridine [9]; it contained < 5% of perfluoro-(1-methyl-pyrrolidine), an inert impurity produced in the fluorination step. Prior to use, commercial finely-powdered caesium fluoride was dried at 150-200 °C under dynamic vacuum for 3-6 h in the Pyrex ampoules subsequently used as reaction vessels.

Reactions of Perfluoro-1-azacyclohex-1-ylcaesium

(a) With iodomethane
A mixture of perfluoro-1-azacyclohexene (1.80 g, 7.35 mmol), anhydrous caesium fluoride (1.82 g, 12 mmol), and thoroughly dried acetonitrile (5 cm^3) was stirred magnetically in the absence of air in a Pyrex ampoule (300 cm^3) for 2 days

(probably excessive) at 20 °C; dry iodomethane (1.10 g, 7.74 mmol) was then added to the mixture and stirring was continued under the same conditions for 4 more days. Work-up of the product by a combination of distillation and g.l.c. (4 m Kel-F oil No. 10/Celite, 50 °C) provided 2,2,3,3,4,4,5,5,6,6-decafluoro-1-methyl-1-azacyclohexane (nc) (1.42 g, 5.09 mmol, 69%) (Found: C, 25.6; H, 0.8; F, 67.8; N, 5.3%; M, mass spec., 279. $C_6H_3F_{10}N$ requires C, 25.8; H. 1.1; F, 68.1; N, 5.0%; M, 279), b.p. (Siwoloboff) 85–86 °C at 743 mmHg, δ_F (neat liq.) −21.6 (2-,6-F), −55.3 (3-,5-F), and −57.2 (4-F) p.p.m., and δ_H (60 MHz; ext. Me$_4$Si ref.) 2.86 p.p.m. {cf. $\overline{CF_2(CF_2)_3NCH_3}$, 2.89 p.p.m. [10]}.

(b) With chlorotrimethylsilane

A mixture of anhydrous caesium fluoride (1.93 g, 12.7 mmol) and perfluoro-1-azacyclohexene (3.06 g, 12.5 mmol) was stirred magnetically for 2 days at room temperature in the absence of air in a Pyrex ampoule (300 cm^3) equipped with a PTFE needle valve (Rotaflo). The ampoule was cooled to −196 °C, charged with chlorotrimethylsilane (1.36 g, 12.5 mmol), re-sealed and left at room temperature (stirring was continued) for 5 days. Work-up of the volatile product by a combination of distillation and g.l.c. (2 m Kel-F No. 10 oil/ Celite, 90 °C) provided perfluoro-[1-(1-azacyclohex-1-en-2-yl) -1-azacyclohexane] (nc) (1.12 g, 2.29 mmol, 36%) (Found: C, 24.6; F, 69.8; N, 6.1%; M, mass spec., 490. $C_{10}F_{18}N_2$ requires C. 24.5; F, 69.8; N, 5.7%; M, 490), $\lambda_{max.}$ (film) 5.92 (C=N str.) μm, and 2-chloro-3,3,4,4,5,5,6,6-octafluoro-1-aza-cyclohexene (ca. 0.5 g) shown by [19]F n.m.r. to be contaminated with unidentified material giving absorptions at −13.8, −56.4, and −58.6 (rel. int. 2:2:1) (δ_F) and 2.0 (δ_H at 100 MHz; Me$_4$Si ref.) p.p.m.

The reaction was repeated using 6.27 g (41.3 mmol) of caesium fluoride, 10.11 g (41.3 mmol) of perfluoro-1-aza-cyclohexene, and 4.48 g (41.3 mmol) of chlorotrimethylsilane, and a reaction period of 17 days. The volatile product was

examined by a combination of distillation, g.l.c., and
coupled g.l.c.-mass spectrometry and shown to contain
perfluoro-(1-methylpyrrolidine) (impurity present in the
starting material), perfluoro-1-azacyclohexene, fluoro-
trimethylsilane, 2-chloro-octafluoro-1-azacyclohexene, and
perfluoro-[1-(1-azacyclohex-1-en-2-yl)-1-azacyclohexane]
(ratio of g.l.c. peak areas = ca. 1:6:5.5:12:30), and traces
of chlorotrimethylsilane. A sample of each of these products
(except Me$_3$SiCl which was identified by i.r. spectroscopy)
was isolated by g.l.c. and characterized by ^{19}F n.m.r.
spectroscopy.

Reaction of Perfluoro-1-azacyclohexene with Chlorotrimethyl-silane

Perfluoro-1-azacyclohexene (3.15 g, 12.9 mmol), chloro-
trimethylsilane (1.40 g, 12.9 mmol), and dry acetonitrile (10
cm^3) were condensed separately into a cold (-196 °C) evacuated
Pyrex ampoule (300 cm^3). The sealed tube was shaken mechanic-
ally for 3 days at room temperature. Examination of the product
by a combination of g.l.c.-i.r. and ^{19}F n.m.r. techniques
showed it to comprise 2-chloro-3,3,4,4,5,5,6,6-octafluoro-1-
azacyclohexene (ca. 100%), fluorotrimethylsilane, and aceto-
nitrile.

Dimerization of Perfluoro-1-azacyclohexene

G.l.c. analysis (with a calibrated 2 m SE30 column at
70 °C) of the volatile product obtained by stirring a mixture
of perfluoro-1-azacyclohexene (5.00 g, 20.4 mmol), anhydrous
caesium fluoride (0.207 g, 1.36 mmol), and dry acetonitrile
(11 cm^3) at room temperature for 20 days in the absence of
air showed it to contain perfluoro-1-azacyclohexene (87%
recovery) and perfluoro-[1-(1-azacyclohex-1-en-2-yl)-1-aza-
cyclohexane] (13%). A sample of the latter was isolated by
preparative g.l.c. and shown to possess the correct
spectroscopic properties (n.m.r. and mass).

Preparation and Characterization of 2-Choro-3,3,4,4,5,5,6,6-octafluoro-1-azacyclohexene (with C. OPPENHEIM)

Perfluoro-1-azacyclohexene (2.97 g, 12.1 mmol) was condensed, in vacuo, onto aluminium chloride (11.3 g) in a cold (-196 $^{\circ}$C) ampoule (60 cm^3). The ampoule was sealed and stored at room temperature overnight. Distillation of the volatile product in a semi-micro Vigreux unit gave perfluoro-1-azacyclohexene (1.00 g, 34% recovery) and 2-chloro-octa-fluoro-1-azacyclohexene (nc) (1.00 g, 3.82 mmol, 48% based on C_5F_9N consumed) [Found: C, 23.0%; $\underline{M}$, 261 (^{35}Cl). C_5ClF_8N requires C, 22.9%; $\underline{M}$, 261.5], b.p. 60 $^{\circ}$C (Siwoloboff), $\lambda_{max.}$ 5.99 μm (N=C str.), δ_F (at 56.46 MHz; neat liq.) -15.4 (CF_2N), -37.5 (CF_2CCl), and -57.7 ($NCF_2C\underline{F}_2C\underline{F}_2$) p.p.m. (rel. int. 1:1:2).

Using the method employed previously [7] with perfluoro-1-azacyclohexene, 2-chloro-octafluoro-1-azacyclohexene (1.72 g, 6.58 mmol) was converted into 2-diethylamino-3,3,4,4,5,5,6,6-octafluoro-1-azacyclohexene (1.43 g, 4.80 mmol, 73%) with the correct spectroscopic properties (i.r. and n.m.r.).

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Et_3N], see A.F. Gontar, E.G. Bykhovskaya, and I.L. Knunyants, Bull. Acad. Sci. U.S.S.R., <u>25</u> (1976) 205.

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