FLUOROCARBON DERIVATIVES OF NITROGEN. PART 10. PREPARATION OF HEPTAFLUORO- AND 1-CHLOROHEXAFLUORO-2-NITROSOPROPANE, AND CONVERSION OF THE LATTER TO CHLOROPENTAFLUOROACETONE OXIME

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SUMMARY

Details are given for the preparation of heptafluoro-2-nitrosopropane and 1-chlorohexafluoro-2-nitrosopropane <u>via</u> the routes $CF_3CF=CF_2 \longrightarrow$ [with $CsF-R_FCO_2Ag$ ($R_F = CF_3$, n-C_3F_7)] $(CF_3)_2CFAg \longrightarrow$ (with NOCl) $(CF_3)_2CFNO$ and $CF_3CF=CF_2 \longrightarrow$ (with CsCl-NOCl) $CF_3(CF_2Cl)CFNO$, respectively, and for conversion of the latter nitroso-compound to chloropentafluoroacetone oxime <u>via</u> reduction with aqueous potassium hydrogen sulphite.

INTRODUCTION

Heptafluoro-2-nitrosopropane is said to be obtainable in very good yield by fluoride-initiated addition of the elements of nitrosyl fluoride across the olefinic linkage in hexafluoropropene [1]:

$$CF_3CF=CF_2 + NOF \xrightarrow[\text{30–35 °C}]{\text{KF, Sulpholane}} (CF_3)_2CFNO \quad (88\%)$$

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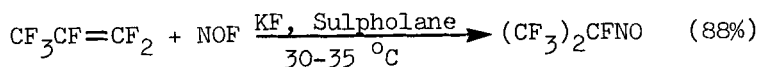
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Wishing to avoid the technical problems associated with the use
of nitrosyl fluoride [2], and knowing that fluorocarbon
derivatives of silver can be generated in aprotic solvents from
perfluorinated olefins, silver trifluoroacetate and caesium or
potassium fluoride [3], we decided to investigate the
following route to the secondary nitrosoalkane:

$$CF_3CF = CF_2 \xrightarrow[\text{MeCN}]{\text{KF, } CF_3CO_2Ag} (CF_3)_2CFAg \xrightarrow{\text{NOCl}} (CF_3)_2CFNO$$
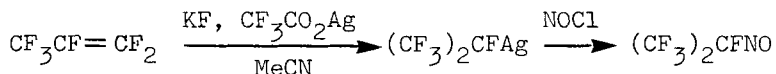
DISCUSSION

In practice, the indirect ('silver-salt') route to hepta-
fluoro-2-nitrosopropane proved highly successful. Using
standard Pyrex apparatus, an excess of commercial hexafluoro-
propene was treated with silver trifluoroacetate and an excess
of dry potassium fluoride in anhydrous acetonitrile at room
temperature; the excess of hexafluoropropene was then removed
from the reaction vessel and nitrosyl chloride was introduced,
causing the formation of the required nitroso-compound in at
least 85% yield. Use of silver heptafluoro-n-butyrate
instead of the trifluoroacetate (both salts are readily
soluble in acetonitrile) did not affect the yield.

Direct fluoride-initiated reaction of hexafluoropropene
with nitrosyl chloride - a procedure recommended for the
conversion of octafluoroisobutene and perfluoro-(2-methylpent-
2-ene) to the tertiary nitrosoalkanes $(CF_3)_3CNO$ [4]* and
$CF_3CF_2CF_2C(CF_3)_2NO$ [5]* respectively - was found to give
mixtures of heptafluoro-2-nitrosopropane and 1-chlorohexafluoro-

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* We have successfully repeated this work (but using aceto-
nitrile as the reaction medium instead of DMF in the case of
nitrosofluorination of octafluoroisobutene). As indicated
previously [6], the 'silver-salt' method works well for the
conversions $(CF_3)_2C=CF_2 \longrightarrow (CF_3)_3CNO$ and $\overline{CF_2CF_2CF=CF}$
$\longrightarrow \overline{CF_2CF_2CF_2CFNO}$.

2-nitrosopropane [eg $CF_3CF=CF_2$ + NOCl + CsF in sulpholane
(4 days at 20 °C) $\longrightarrow (CF_3)_2CFNO$ + $CF_3(CF_2Cl)CFNO$ (ratio ca
6:1; 70% conversion of C_3F_6)]. Clearly the chloride ion derived
from the nitrosyl chloride competes with fluoride ion for
hexafluoropropene - a deduction which prompted us to examine
the reaction of the fluoro-olefin with a 25% excess of a ca
equimolar mixture of caesium chloride and nitrosyl chloride in
dimethylacetamide; formation of the expected blue monomeric
nitroso-compound occurred rapidly and probably quantitatively
(yield of isolated material, 91%) at room temperature:

$$CF_3CF=CF_2 \ + \ Cl^- \ \longrightarrow \ CF_3(CF_2Cl)\bar{C}F \ \xrightarrow{\text{NOCl}} \ CF_3(CF_2Cl)CFNO \ + \ Cl^-$$
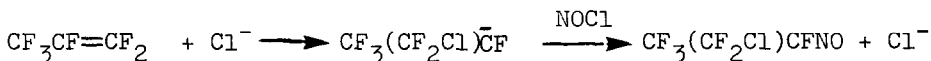
Clearly, this conversion ought to be achievable using a
catalytic amount of caesium chloride; this was not attempted,
nor was the efficacy of potassium chloride as a reagent
determined.

Treatment of 1-chlorohexafluoro-2-nitrosopropane with
aqueous potassium hydrogen sulphite at ambient temperature
converts it to the corresponding oxime $CF_3(CF_2Cl)C=NOH$
(mixture of E and Z isomers){cf $(CF_3)_2CFNO$ + $KHSO_3$ aq $\longrightarrow$
$(CF_3)_2C=NOH$ [6]}.

EXPERIMENTAL

Preparation of Heptafluoro-2-nitrosopropane

Hexafluoropropene (4.57 g, 30.5 mmol) was condensed into
a cold (-196 °C) evacuated Pyrex tube (300 cm^3) equipped with
a Rotaflo (PTFE-glass) valve and containing a dry, degassed
mixture of acetonitrile (25 cm^3), finely powdered silver
trifluoroacetate (4.0 g, 18.1 mmol) and well-ground, anhydrous
potassium fluoride (2.0 g, 34.5 mmol). After the sealed tube
had been shaken mechanically at room temperature for 1 hour,
unreacted hexafluoropropene (15.1 mmol) was removed from it
and nitrosyl chloride (1.05 g, 16.0 mmol) was introduced. The
tube, sealed again, was shaken at 20 °C for 2 h, then the
volatile blue product was washed with water [10 cm^3; after

transference to another Rotaflo tube (300 cm^3)] before being transferred to a vacuum system _via_ a tube containing phosphorus pentoxide and subjected to trap-to-trap fractional condensation at 2 mmHg pressure (trap temperatures: -72, -95, -120, and -196 $^{\circ}$C). Pure (by ir and ^{19}F nmr spectroscopy) hexafluoro-2-nitrosopropane (2.16 g, 13.1 mmol, 85% based on C$_3$F$_6$ consumed) [Found: M (Regnault), 197. Calc for C$_3$F$_7$NO: M, 199] was recovered from the -120 $^{\circ}$C trap.

Preparation of 1-Chlorohexafluoro-2-nitrosopropane

Hexafluoropropene (6.00 g, 40.0 mmol) was condensed into a cold (-196 $^{\circ}$C), evacuated, flame-dried Pyrex tube (300 cm^3) containing nitrosyl chloride (3.38 g, 51.6 mmol), dry dimethylacetamide (50 cm^3) and anhydrous finely-powdered caesium chloride (8.50 g, 50.4 mmol). The tube was sealed (Rotaflo PTFE-glass valve) and shaken mechanically at room temperature, in the dark, for 22 hours.(This was probably an excessive reaction period: even after 1 hour, formation of the deep blue nitroso-compound was quite obvious; in fact, the blue colour appeared while the tube was warming to room temperature and before agitation commenced.) The volatile 1-chlorohexafluoro-2-nitrosopropane was pumped out of the reaction vessel, washed with a saturated aqueous solution (20 cm^3) of sulphamic acid, dried (P$_2$O$_5$) and characterised by elemental analysis (Found: C, 16.7; F, 53.4. Calc for C$_3$ClF$_6$NO: C, 16.7; F, 52.9%) and spectroscopic methods {λ_{max} (vapour) 6.25 μm (N=O str); m/z 187 (C$_3$^{37}ClF$_6$$^+$, 2%), 185 (C$_3^{35}ClF_6$$^+$, 5%), 150 (C$_3F_6$$^+$, 13%), 131 (C$_3F_5$$^+$, 17%), 100 (C$_2F_4$$^+$, 18%), 87 (C^{37}ClF$_2$$^+$, 12%), 85 (C^{35}ClF$_2$$^+$, 39%), 69 (CF$_3$$^+$, 68%), 30 (NO$^+$, 100%), δ_F [soln in CDCl$_3$; 75.26 MHz; ext CF$_3$CO$_2$H (downfield positive)] +16.45 [CF$_2$Cl,centre of an AB-based multiplet (J$_{AB}$ 175 Hz)], +5.93 (CF$_3$, ddd), and -82.65 (CF, ddq) ppm (rel int 2:3:1)}. The yield of purified material was 91% (7.88 g, 36.6 mmol). Inadvertently, the boiling point of the nitroso-compound was not determined; Park _et al._quote a value of 20.5 $^{\circ}$C at 630 mmHg for the

material they believed was 1-chlorohexafluoro-2-nitrosopropane (prepared via photochemical reaction of hexafluoropropene with nitrosyl chloride) [7].

Preparation of Chloropentafluoroacetone Oxime

1-Chloro-2-nitrosohexafluoropropane (10.3 g, 48.0 mmol) was condensed, in vacuo, into a cold (-196 °C) Pyrex tube (300 cm^3) containing potassium metabisulphite (6.64 g $\equiv$ 60.0 mmol of KHSO$_3$) in water (20 cm^3); the tube was sealed (PTFE/glass Rotaflo valve), allowed to warm to room temperature, and shaken mechanically for 7 days in a steel guard. Removal of the two-phase liquid product from the badly etched reaction vessel, followed by distillation of the pale-blue lower organic layer (6.34 g after being dried over 4A molecular sieve) provided chloropentafluoroacetone oxime (3.92 g, 19.8 mmol, 41%) (Found: C, 17.9; H, 0.6; F, 48.2; N, 7.0. C$_3$HClF$_5$NO requires C, 18.2; H, 0.5; F, 48.1; N, 7.1%), bp 105 °C, λ_{max} (film) 2.95 vbr (O-H str) and 6.03 (C=N str) µm, m/z 162 (M‡ -Cl·, 40%) (top mass peak), 161 (M‡ -HCl, 100%), 112(M$^+$ -CF$_2$Cl·, 10%), 87 (CF$_2$^{37}Cl$^+$, 4%), 85 (CF$_2$^{35}Cl$^+$, 14%), and 69 (CF$_3$$^+$, 41%), δ_H (neat liq; 90 MHz; ext Me$_4$Si) +9.61 (br, s) ppm, δ_F(84.6 MHz; ext CF$_3$CO$_2$H) +21.2 (CF$_2$Cl, isomer A; q, J$_{CF_2ClCF_3}$ 6.5 Hz), +20.7 (CF$_2$Cl, isomer B; q, J$_{CF_2ClCF_3}$ 8.5 Hz), +13.1 (CF$_3$, isomer A; t, J 6.5 Hz), +10.3 (CF$_3$, isomer B; t, J 8.5Hz) ppm (rel int 14:19:22:29).

REFERENCES

1   B L Dyatkin, E P Mochalina, R A Bekker, S R Sterlin, and I L Knunyants, Tetrahedron, 23 (1967) 4291.

2   S Andreades, J Org Chem, 27 (1962) 4157.

3   B L Dyatkin, B I Martynov, L G Martynova, N G Kizim, S R Sterlin, Z A Stumbrevichute, and L A Fedorov, J Organometal Chem, 57 (1973) 423.

4   'Sintezy Ftororganicheskikh Soedinenii', ed I L Knunyants and G G Yakobson, Izd Khimiya, Moscow, 1973, p 24.

5   K V Scherer, T F Terranova, and D D Lawson, J Org Chem,
    46 (1981) 2379.

6   R E Banks and N Dickinson, J Chem Soc, Perkin Trans I,
    (1982) 685.

7   J D Park, A P Stefani, G H Crawford, and J R Lacher,
    J Org Chem, 26 (1961) 4017.