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PERFLUOROALKYL DERIVATIVES OF NITROGEN. PART LIII [1]. REACTION OF PERFLUORO(2,5-DIMETHYL-4-OXA-3,5-DIAZAHEX-2-ENE) WITH FLUORO-OLEFINS

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SUMMARY

Thermal decomposition of the title compound at 140 °C gives mainly nitrogen, hexafluoroacetone and tetrakistrifluoromethylhydrazine while reaction with tetrafluoroethylene and chlorotrifluoroethylene affords equimolar mixtures of the 1:1 adducts $(CF_3)_2C{=}NCF_2CFXON(CF_3)_2$ and $(CF_3)_2C{=}NOCFXCF_2N(CF_3)_2$ (X=F and Cl) in high yield via four-centre addition or a radical-cage process.

INTRODUCTION

Few aliphatic compounds containing the N-O-N linkage have been synthesised [2-5] and a study of the chemistry of such compounds has been mainly limited to the diazapentane $(CF_3)_2NON(CF_3)_2$ [2,3], e.g. thermal decomposition [2,6] and reaction with alkenes [6-9], alkynes [10] and allenes [11].

The recent preparation of the unsymmetrical N-O-N compound perfluoro(2,5-dimethyl-4-oxa-3,5-diazahex-2-ene)(I) [12] prompted an initial investigation of its thermal decomposition and reaction with fluoro-olefins.

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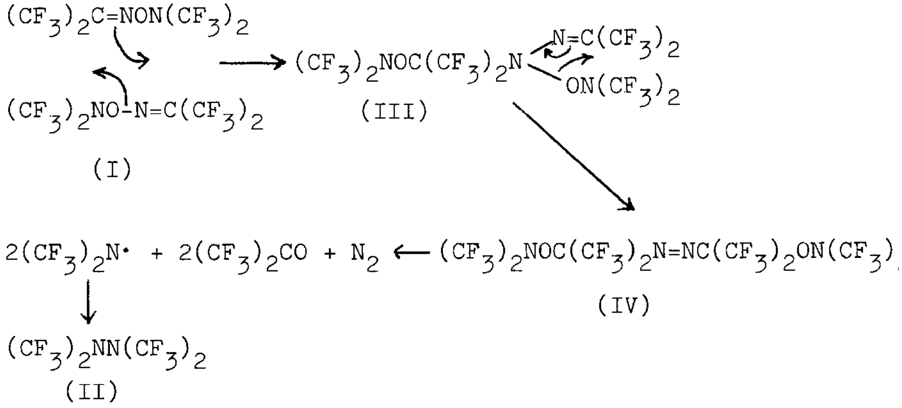
RESULTS AND DISCUSSION

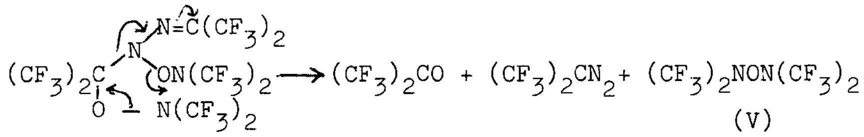
Static pyrolysis at 140 °C of the diazahexene (I) gave nitrogen (44%), hexafluoroacetone, tetrakistrifluoromethylhydrazine (II) (46%) and smaller amounts of the diazoalkane $(CF_3)_2CN_2$, the hydroxylamine $(CF_3)_2NOH$, the amine $(CF_3)_2NH$ and tetrafluorosilane.

The major products are considered to arise *via* interaction between two molecules of (I) followed by homolytic fission involving weak N-O bonds (Scheme 1).



SCHEME 1

The minor product $(CF_3)_2CN_2$ probably arises by an alternative decomposition of compound (III), *i.e.*



while the hydrogen-containing compounds and tetrafluorosilane are formed by reaction of the radicals $(CF_3)_2NO\cdot$ [from decomposition of (V)] and $(CF_3)_2N\cdot$ with the walls of the reaction tube.

Compound (IV) is formed quantitatively from reaction between hexafluoroacetone azine and the oxyl $(CF_3)_2NO\cdot$ [12] and decomposes at temperatures below 140 °C to give the products shown in Scheme 1 [13].

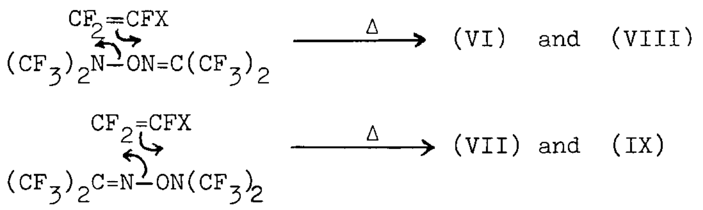
The reaction of compound (I) with tetrafluoroethylene (ca. 1:1 molar ratio) at 100 °C gave nitrogen (trace), hexafluoroacetone (2%), hydrazine (II) (7%) and a 1:1 adduct fraction (89%) which gave one peak on a variety of g.l.c. columns, but which was shown by ^{19}F n.m.r. spectroscopy and mass spectrometry (see later) to be a mixture of perfluoro(2,7-dimethyl-4-oxa-3,7-diazaoct-2-ene) (VI) (44·5%) and perfluoro(2,7-dimethyl-6-oxa-3,7-diazaoct-2-ene) (VII) (44·5%). When a 1:2 molar ratio of reactants was used the products were unchanged tetrafluoroethylene (30% recovered), (VI) (47·5%), (VII) (47·5%), an unidentified higher-boiling compound (5% by weight) and a waxy solid presumed to be polytetrafluoroethylene (4% by weight).

Similarly, reaction of (I) with chlorotrifluoroethylene (ca. 1:1 molar ratio) at 120 °C (5d) gave the 1:1 adducts (VIII) (48·5%) and (IX) (48·5%).

$(CF_3)_2C{=}NOCFXCF_2N(CF_3)_2$		$(CF_3)_2C{=}NCF_2CFXON(CF_3)_2$	
(VI)	X=F	(VII)	X=F
(VIII)	X=Cl	(IX)	X=Cl

There are three mechanisms (a-c) which can account for the products obtained.

(a)



(b)

$$(CF_3)_2C{=}NON(CF_3)_2 \xrightarrow{\Delta} \begin{cases} (CF_3)_2N\cdot \; + \; (CF_3)_2C{=}NO\cdot \\ (CF_3)_2C{=}N\cdot \; + \; (CF_3)_2NO\cdot \end{cases}$$

$$(CF_3)_2N\cdot + CF_2{=}CFX \longrightarrow \underset{(X)}{(CF_3)_2NCF_2\dot{C}FX} \xrightarrow{(CF_3)_2C=NO\cdot} \text{(VI) and (VIII)}$$

$$\underset{}{(CF_3)_2C{=}N\cdot} + CF_2{=}CFX \longrightarrow \underset{\text{(XI)}}{(CF_3)_2C{=}NCF_2\dot{C}FX} \xrightarrow{(CF_3)_2NO\cdot} \text{(VII) and (IX)}$$

$$\text{(c)}\quad \underset{\text{(X)}}{(CF_3)_2NCF_2\dot{C}FX} + \text{(I)} \longrightarrow \text{(VI) and (VIII)} + (CF_3)_2N\cdot \longrightarrow \text{etc.}$$

$$\underset{\text{(XI)}}{(CF_3)_2C{=}NCF_2\dot{C}FX} + \text{(I)} \longrightarrow \text{(VII) and (IX)} + (CF_3)_2C{=}N\cdot \longrightarrow \text{etc.}$$

The corresponding additions of the N-O-N compound (V) across suitable olefins, *e.g.* (*E*) - $CHCl{=}CHSiF_3$, have been shown to give mixtures of *syn*- and *anti*-adducts and therefore do not involve four-centre transition states [8]. It was concluded that such additions take place by a free-radical mechanism involving initial attack on the olefin by the more reactive $(CF_3)_2N\cdot$ radical. The absence of products of type $(CF_3)_2N\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}N(CF_3)_2$ and $(CF_3)_2NO\overset{|}{\underset{|}{C}}\overset{|}{\underset{|}{C}}ON(CF_3)_2$ [14] indicated that a radical chain mechanism analogous to (c) was involved [6-8], although a mechanism analogous to (b), in which coupling occurred between the intermediate radical and oxyl $(CF_3)_2NO\cdot$, could not be ruled out.

The adducts (VIII) and (IX) are consistent with a free-radical mechanism involving initial attack on the olefin $CF_2{=}CFCl$ by $(CF_3)_2N\cdot$ and $(CF_3)_2C{=}N\cdot$ radicals at the CF_2 group where exclusive or near-exclusive radical attack is always observed [15]. However, if chain mechanisms are involved it is difficult to explain why intermediate radicals (X) and (XI) are so specific in their chain-transfer reactions with (I). Both chain transfer at oxygen, but attack by radical (X) results in $(CF_3)_2N{-}O$ bond cleavage while attack by radical (XI) causes $(CF_3)_2C{=}N{-}O$ bond cleavage. The radicals only differ by one group attached to the β-carbon and chain transfer with (I) would have been expected to result in breaking of either N—O bond with the formation of compounds (XII) and (XIII) (X=F and Cl) as additional products. The compounds (XII) have been made previously by reaction of the N—O—N compound (V) with the fluoro-olefins [6] and were not detected in the products of the present reactions.

$(CF_3)_2NCF_2CFXON(CF_3)_2$ (XII) $\qquad$ $(CF_3)_2C{=}NCF_2CFXON{=}C(CF_3)_2$ (XIII)

It is therefore unlikely that the radical-chain mechanism (c) is involved, but the alternative radical mechanism (b) could be operative in which radicals (X) and (XI) couple with the oxyls $(CF_3)_2C{=}NO\cdot$ and $(CF_3)_2NO\cdot$, respectively. If this is correct coupling must be fast and a cage-type mechanism is probably involved, but on the present evidence it is not possible to distinguish between mechanisms (a) and (b).

However, the formation of the two adducts in each reaction in a 1:1 ratio is surprising because it would be expected that the =N-O bond is stronger than the $\rangle$N-O bond and the oxyl $(CF_3)_2C{=}NO\cdot \longleftrightarrow (CF_3)_2\dot{C}{-}N{=}O$ is resonance stabilised.

The reaction of (I) with hexafluoropropene (1:1 molar ratio at 120 °C, 5d) gave nitrogen, unchanged hexafluoropropene (70% recovered), hexafluoroacetone (84%) and a fraction (24% by weight) consisting mainly of hydrazine (II) together with several unidentified compounds. Thus reaction of (I) with hexafluoropropene is much less favourable than reaction with the olefins $CF_2{=}CF_2$ and $CF_2{=}CFCl$, *cf* addition of (V) to hexafluoropropene which requires elevated temperature (85 °C) [6], and decomposition of (I) by the mechanism shown (Scheme 1) is the major process.

The adduct structures were assigned on the basis of their ^{19}F n.m.r. and mass spectra : (VI) and (VII) δ_F +23·0 [6F, $(CF_3)_2NC$ in (VI)], +11·3 [6F, CF_3 (*anti*) in (VI) and (VII)], +8·3 [9F, $(CF_3)_2NO$ in (VII) and CF_3 (*syn*) in (VII) or (VI)], +7·1[3F, CF_3(*syn*) in (VI) or (VII)] and -15·0 to -19·4 [8F, $4CF_2$ in (VI) and (VII)] p.p.m., *m/e* 413 (0·1%, M^+], 268 [3,$(CF_3)_2NOCF_2CF_2^+$ or $(CF_3)_2NCF_2CF_2O^+$], 214 [1, $(CF_3)_2C{=}NCF_2^+$ in (VII)], 202 [3, $(CF_3)_2NCF_2^+$ in (VI)], 180 [5, $(CF_3)_2C{=}NO^+$ in (VI)] and 69 (100, CF_3^+); (VIII) and (IX) δ_F +24·3 [6F, $(CF_3)_2NC$ in (VIII)], +11·9 [3F, CF_3 (*anti*)], +10·2 [3F, CF_3 (*anti*)], +9·0 [9F, $(CF_3)_2NO$ in (IX) and CF_3 (*syn*)], +7·9 [3F, CF_3 (*syn*)], +3·0 to +3·5 (2F, CFCl in both isomers), and -13·0 (4F, CF_2 in both isomers) p.p.m., *m/e* 429 [0·2%, $(M{-}F)^+$], 413 [2, $(\underline{M}\text{-}Cl)^+$], 298 and 296 $\{1, [\underline{M}\text{-}(CF_3)_2N^+\}$, 286 and 284 $\{12, [\underline{M}\text{-}CF_3)_2C{=}N]^+\}$, 236 and 234 [2, $(CF_3)_2NOCFCl^+$ in (IX)], 214 [1, $(CF_3)_2C{=}NCF_2^+$ in (IX)], 202 [11, $(CF_3)_2NCF_2^+$ in (VIII)], 198 and 196 [13, $(CF_3)_2NOCFClCF_2$ or $(CF_3)_2NCF_2CFClO^+$], 180 [8, $(CF_3)_2C{=}NO^+$ in (VIII)] and 69 (100, CF_3^+).

EXPERIMENTAL

Techniques

I.r., n.m.r. and mass spectra were obtained on a Perkin-Elmer 257 spectrophotometer, a Perkin-Elmer R32 or Varian Associates HA-100 spectrometer (at 84·6 and 94·1 MHz, respectively, using external trifluoroacetic acid as reference; positive chemical shifts to low field of reference) and an A.E.I. MS 902 spectrometer with an electron-beam energy of 70 eV, respectively.

Reactions were carried out *in vacuo* in Pyrex tubes (*ca.* 300 cm^3) and volatile products were separated by fractional condensation *in vacuo* .

Preparation of perfluoro(2,5-dimethyl-4-oxa-3,5-diazahex-2-ene) (I)

Compound (I) (*ca.* 80%) was prepared by reaction of bistrifluoromethylamino-oxyl with hexafluoroacetone imine (2:1 molar ratio) at 20 °C [12].

Reactions of perfluoro(2,5-dimethyl-4-oxa-3,5-diazahex-2-ene)

(a) Static pyrolysis

Compound (I) (3·50 g, 10·5 mmol), heated at 140 °C (5d), gave (i) nitrogen (0·13 g, 4·64 mmol, 44%)(Found: $\underline{M}$, 28. Calc for N_2:$\underline{M}$, 28), (ii) hexafluoroacetone (1·59 g, 9·55 mmol, 91%), (iii) a fraction (0·10 g) which was shown by i.r. and n.m.r. spectroscopy to consist of bis(trifluoromethyl)diazomethane (0·06 g, 0·34 mmol, 3%) contaminated with traces of the compounds $(CF_3)_2NH$ and SiF_4, and (iv) a fraction (1·65 g) shown by i.r. and n.m.r. spectroscopy to consist of tetrakis(trifluoromethyl)hydrazine (II) (1·50 g, 4·93 mmol, 46%) (δ_F +16·5 p.p.m.) and NN-bistrifluoromethylhydroxylamine (0·15 g, 0·9 mmol, 8·5%).

(b) With tetrafluoroethylene

A mixture of compound (I) (3·30 g, 9·9 mmol) and tetrafluoroethylene (1·05 g, 10·5 mmol), heated at 100 °C (5d), gave (i) nitrogen (trace), (ii) a mixture (0·15 g) of unchanged tetrafluoroethylene (0·10 g, 1·0 mmol, 9·5% recovered) and hexafluoroacetone (0·05 g, 0·3 mmol, 2%) by ^{19}F n.m.r. (δ_F -58·5 and -0·4 p.p.m., respectively), (iii) hydrazine (II) (0·20 g, 0·7 mmol, 7%), and (iv) a higher-boiling fraction (3·85 g) which was shown by ^{19}F n.m.r. spectroscopy and mass spectrometry to be a mixture of perfluoro(2,7-dimethyl-4-oxa-3,7-diazaoct-2-ene) (VI) (1·90 g, 4·4 mmol, 44·5%) and perfluoro(2,7-dimethyl-6-oxa-3,7-diazaoct-2-ene) (VII) (1·90 g, 4·4 mmol, 44·5%) (Found: C, 19·2; N, 6·4; F, 70·6%; M, 430. Calc. for $C_7F_{16}N_2O$: C, 19·4; N, 6·5; F, 70·4%; M, 432), b.p. 84-88 °C, $\lambda_{max.}$ 5·85 and 6·10 μm (C=N str.); the mixture of 1:1 adducts could not be separated by g.l.c. (OV1, TXP, DNP, Kel-F 10 oil, and APL at 20-100 °C).

A second reaction using compound (I) (3·25 g, 9·8 mmol) and tetrafluoroethylene (2·00 g, 20·0 mmol), heated at 120 °C (5d), gave unchanged tetrafluoroethylene (0·60 g, 6·0 mmol, 30% recovered), a mixture (4·4 g) of compounds (VI) and (VII) (4·02 g, 9·3 mmol, 95%)(1:1 ratio) and a component (ca. 5%) with a longer g.l.c. retention time (6m OV1 at 20 °C), and a waxy solid (0·2 g, 10% on olefin) which was presumed to be polytetrafluoroethylene.

(c) With chlorotrifluoroethylene

A mixture of the olefin (1·30 g, 11·2 mmol) and compound (I) (3·28 g, 9·9 mmol), heated at 120 °C (5d), gave unchanged olefin (0·13 g, 1·1 mmol, 10% recovered) and a mixture (4·3 g) (Found: C, 18·7; Cl, 7·8; N, 6·3; F, 63 8%. Calc. for $C_7ClF_{15}N_2O$: C, 18·7, Cl, 7·7; N, 6·3; F, 63·5%), b.p. 100-103 °C, $\lambda_{max.}$ 5·71 and 6·05 µm (C=N str.), of 5-chloro-1,1,1,5,6,6,8,8,8,-nonafluoro-2,7-bistrifluoromethyl-4-oxa-3,7-diazaoct-2-ene (VIII) (2·15 g, 4·79 mmol, 48·5%) and 5-chloro-1,1,1,4,4,5,8,8,8-nonafluoro-2,7-bistrifluoromethyl-6-oxa-3,7-diazaoct-2-ene (IX) (2·15 g, 4·79 mmol, 48·5%) as shown by ^{19}F n.m.r. spectroscopy and mass spectrometry; the mixture showed only one peak when examined by g.l.c. (SE30, TXP, Kel-F 10 oil and APL at 20-100 °C)

(d) With hexafluoropropene

A mixture of hexafluoropropene (1·60 g, 10·7 mmol) and compound (I) (3·30 g, 9·9 mmol), heated at 120 °C (5d), gave (i) nitrogen (0·08 g, 1·92 mmol, 19·5%), (ii) a mixture (2·50 g) of unchanged hexafluoropropene (1·12 g, 7·47 mmol, 70% recovered) and hexafluoroacetone (1·38 g, 8·3 mmol, 84%) as shown by i.r. and ^{19}F n.m.r. spectroscopy, (iii) a mixture (0·25 g) of bistrifluoromethylamine, tetrafluorosilane and unidentified components as shown by ^{19}F n.m.r. spectroscopy, and (iv) a fraction (1·9 g) which was shown by ^{19}F n.m.r. spectroscopy to be mainly hydrazine (II); ten minor unidentified components were also present as shown by g.l.c. (6m OV1 at 20 °C).

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