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SHORT COMMUNICATION

Perfluoroalkyl Derivatives of Nitrogen. Part XLVI [1]. Thermolysis and Photolysis of Heptafluoro-1-nitrosopropane

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The modes of thermal [2] and photochemical [3] decomposition of trifluoronitrosomethane have been studied in some detail. Much less effort [4,5] has been spent on the corresponding chemistry of the equally accessible higher homologue heptafluoro-1-nitrosopropane [6], which was investigated as described below following the chance observation [7] that it gave a mass spectrum compatible with a mixture of the derivatives $n\text{-}C_3F_7N{=}CFC_2F_5$ (I) (mainly), $n\text{-}C_3F_7NO_2$ (II), and $(n\text{-}C_3F_7)_2NOC_3F_7\text{-}n$ (III) when analysed with an instrument inlet temperature of 150 °C.*

Previously [4], heptafluoro-1-nitrosopropane was flow-pyrolysed in platinum at 250 °C and 7-9 mmHg pressure to give mainly the hydroxylamine derivative $(n\text{-}C_3F_7)_2NOC_3F_7\text{-}n$ (III) (88% yield) plus, <u>inter alia</u>, $C_3F_7NO_2$ (II; 7%) and $n\text{-}C_3F_7N{=}CFC_2F_5$ (I ; 1.5%). In order to broaden this knowledge of the thermal decomposition of the nitroso-compound, and to check on the information gained from the result of

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*Preliminary thermal decomposition of trifluoronitrosomethane does not occur under identical conditions.

mass-spectrometric analysis mentioned above, a small sample (1.32 g, 6.63 mmol) of heptafluoro-1-nitrosopropane was stored at 80 °C for 24 h in the absence of air in a Pyrex ampoule (30 cm^3). It underwent complete decomposition, and fractionation of the volatile product afforded pure samples of the aza-alkene (I) (0.80 g, 2.40 mmol, 72%), the nitroalkane (II) (0.15 g, 0.72 mmol, 11%), and the tri-substituted hydroxylamine (III) (0.091 g, 0.17 mmol, 8%), which were identified by i.r. spectroscopy and mass spectrometry (see the Table). Formation of these products concurs with previous observations and mechanistic postulates [2,4] about thermal reactions of perfluoronitrosoalkanes.

No literature report appears to exist of a serious attempt to determine the outcome of photochemical decomposition of heptafluoro-1-nitrosopropane; photo-acceleration of the decomposition of a sample of the nitroso-compound has been observed, but the product was not examined in detail [5]. In the present investigation, heptafluoro-1-nitrosopropane (2.03 g, 10.2 mmol) contained in a silica ampoule (40 cm^3) was exposed to U.V. (mainly 2537 Å) light (Hanovia 500w mercury vapour lamp placed about 15cm distant) for 18 h. Trap-to-trap fractional condensation, in vacuo, of the complex product followed by g.l.c. and spectroscopic analysis of the material collected at -22 and 0 °C revealed the formation of the compounds $(n\text{-}C_3F_7)_2NONO$, $(n\text{-}C_3F_7)_2NNO_2$, $(n\text{-}C_3F_7)_2NOC_3F_7\text{-}n$, $(n\text{-}C_3F_7)_3N$, and $(n\text{-}C_3F_7)_2NN(C_3F_7\text{-}n)_2$. Distillation at atmospheric pressure provided a constant-boiling (81.5 °C) mixture (1.54 mmol, 30% yield) of the nitroso-dimers $(n\text{-}C_3F_7)_2NNO_2$ and $(n\text{-}C_3F_7)_2NONO$, which decomposed when subjected to preparative g.l.c. and was identified by i.r. analysis [$\lambda_{max.}$(vap.) 6.01 μm{asym.NO_2 str; *cf.*[8] $(CF_3)_2NNO_2$, 5.99 μm} and 5.5br μm{N=0 str; *cf.* [9] $(CF_3)_2NONO$, 5.47, 5.55 μm (d)}] and mass spectrometry. Again, existing mechanistic schemes (initial photodissociation of the nitroso-compound *via* homolytic C-N fission followed by a series of addition and combination reactions [3,5]) can be adapted to explain the outcome of this experiment. Thus, isolation of the 'dimer' of heptafluoro-1-nitrosopropane, $(n\text{-}C_3F_7)_2NONO$, remains a challenge.

TABLE Mass Spectral Data [a], [b]

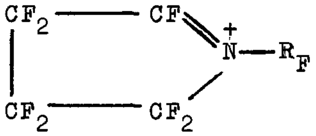
CF_3NO [c]	99,(3.5)CF_3NO, 69(89)CF_3,64(3.9)CF_2N, 50(18)CF_2, 31(7.5)CF, 30(100)NO
$n\text{-}C_3F_7NO$ [c]	199(0.4)C_3F_7NO, 169(21)C_3F_7,150(3.4)C_3F_6, 119(15)C_2F_5,100(25)C_2F_4, 69(55)CF_3, 50(5.3)CF_2,31(13)CF, 30(100)NO
$n\text{-}C_3F_7N{=}CFC_2F_5$ [d] (I)	333(0)$C_6F_{13}N$,314(2.9)$C_6F_{12}N$, 214(11)C_4F_8N,169(55)C_3F_7,119(17)C_2F_5, 100(18)C_2F_4,69(100)CF_3, 31(13)CF
$n\text{-}C_3F_7NO_2$ [e] (II)	215(0.05)$C_3F_7NO_2$,169(81)C_3F_7, 119(31)C_2F_5,100(20)C_2F_4,69(100)CF_3, 50(4.5)CF_2,46(23)NO_2,31(10)CF,30(38)NO
$(n\text{-}C_3F_7)_2NOC_3F_7\text{-}n$ [f] (III)	537(0)$C_9F_{21}NO$,418(1.2)$C_7F_{16}NO$, 368(2.7)$C_6F_{14}NO$, 314(8.7)$C_6F_{12}N$, 214(18)C_4F_8N, 169(100)C_3F_7, 119(42)C_2F_5, 69(87)CF_3

[a] AEI MS2 Spectrometer; source temp. 80 °C, electron beam energy 55eV.

[b] For each compound the molecular ion and up to eight most abundant fragment ions are shown in order of decreasing mass as *m/e* (rel.int.%).

c The low intensity of $\underline{M}^{+\bullet}$, coupled with the identity of the base peak (NO^+), arises from the powerful -I effect of the perfluoroalkyl group.

d The spectrum is noteworthy for the complete absence of a molecular ion and for the presence of the even-electron **series** $C_{\underline{n}}F_{2\underline{n}}N^+$ [$\underline{n}$ = 4,5 (rel.int. 1%),6] which may well be cyclic, as for the hydrocarbon analogue:



(R_F = F, CF_3, C_2F_5)

e The appearance of the fragment NO_2^+, not found in the spectrum of the hydrocarbon analogue, reflects the -I effect of the n-C_3F_7 group. Also of interest is that the molecular ion loses nitric oxide, as does that of nitrobenzene.

f A metastable peak at $\underline{m}/\underline{e}$ 126, previously ascribed [4] to the transition

$$C_4F_8NO^+(230) \longrightarrow C_3F_7^+\ (169) + CFNO\ (61)(\underline{m}/\underline{e}\ \text{calc.}124.2)$$

is now reassigned to the fragmentation

$$C_4F_8N^+(214) \longrightarrow C_3F_6N^+(164) + CF_2(50)\ (\underline{m}/\underline{e}\ \text{calc.}125.7)$$

The expected primary β-cleavage of the molecular ion presumably yields the fragment $CF_2{=}\overset{+}{N}(C_3F_7)OC_3F_7$ rather than $(C_3F_7)_2\overset{+}{N}O{=}CF_2$.

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6 Both nitroso-compounds are best made *via* the route

$(R_FCO)_2O$ (available commercially) $\xrightarrow{N_2O_3}$

$R_FCO_2NO \xrightarrow{\Delta} R_FNO$ [R.E. Banks, M.G. Barlow,

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