THE ACTION OF ELEMENTAL FLUORINE ON POLYFLUORO-OLEFINS AND AROMATIC COMPOUNDS. PART III* THE FLUORINATION OF PENTAFLUOROPYRIDINE

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SUMMARY

Pentafluoropyridine in the liquid phase at 50-100° and elemental fluorine of low oxygen content gave, in addition to a substantial amount unchanged, nonafluoro-1-azacyclohex-1-ene, heptafluoro-1-azacyclohexa-1,4- and -1,3-diene, a complex mixture suspected to be tetra-enyl dimers $(C_{10}F_{12}N_2)$ and, as the major product, a glassy solid thought to be based on an oligomeric extension of the latter system. No products of fragmentation of the six-membered ring were detected.

INTRODUCTION

Hexafluorobenzene reacts readily with elemental fluorine at 0° to give mainly tetradecafluorobicyclohex-2,2',5,5'-tetra-enyl and a glassy

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* Part II Reference [1].

oligomer based on the same radical intermediate [2]. It was therefore of interest to study the parallel reaction of pentafluoropyridine.

RESULTS AND DISCUSSION

Whereas hexafluorobenzene at 0° reacted vigorously in the liquid phase with a 10:1 mixture of nitrogen and fluorine [2], pentafluoropyridine (I) did not show visible signs of reaction below 40°. In a large-scale experiment, therefore, the reaction temperature was progressively raised to 100° during 6h. The clear yellow liquid product was free of acid fluorides and was separated by distillation and G. L. C. to give nonafluoro-1-azacyclohex-1-ene (II) [3] (5% at 40°, 4% at 100°), heptafluoro-1-azacyclohexa-1,4-diene (III) (20% at 40°, 16% at 100°), heptafluoro-1-azacyclohexa-1,3-diene (IV) [4] (8% at 40°, 6% at 100°), pentafluoro-pyridine (I) (14% at 40°, 39% at 100°), dimeric material (e.g. XIII-XVI) (7% at 40°, 9% at 100°) and a glassy oligomeric material (e.g. XVIII) (46% at 40°, 26% at 100°). No products derived from ring opening were detected at 100°; the elevated temperature merely diminished the production of oligomer by promoting transfer of pentafluoropyridine from the reaction vessel.

The new heptafluoro-1-azacyclohexa-1,4-diene (III) was characterised by elemental analysis, mass spectrometry and I. R.- and ^{19}F N. M. R.- spectroscopy. The known [4] 4-chloro-analogue (XVII) displayed closely similar I. R.- and ^{19}F N. M. R.- spectra.
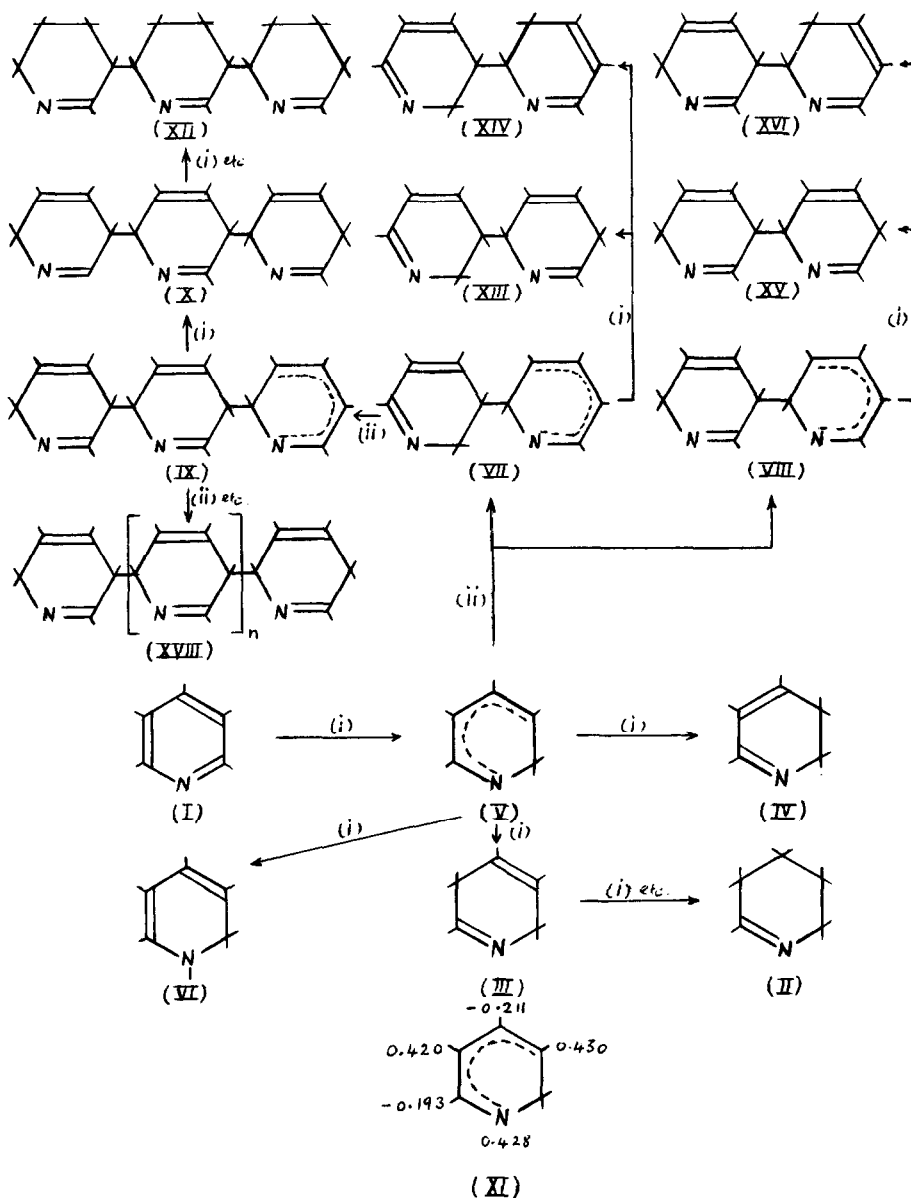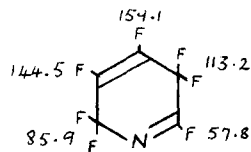
ALL UNMARKED SUBSTITUENTS ARE FLUORINE

Fig. 1 (i) F. or F_2 (ii) C_5F_5N
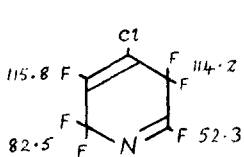
($\overline{XVII}$)   ($\overline{III}$)

The yellow liquid fraction was shown to contain many components

by G. L. C. Its volatility (b. r. 168-170°) was consistent with a dimeric

system; its I. R. spectrum contained vinylic absorption peaks in a broad

band around 1740 cm^{-1}; its ^{19}F N. M. R. spectrum was highly complex

but contained bands at 56. 7 and 86. 9 p. p. m. consistent with the presence

of -N = CF and CF$_2$-N groupings. Vapour phase fluorination over

cobaltic fluoride at 180° gave undecafluoroazacyclohexane as a small

part (6%) of a range of highly volatile fragmentation products. Elemental

analysis of the total dimeric-fraction gave an empirical formula of C$_5$

F$_{6.6}$N indicative of a slightly higher degree of fluorination than the

tetra-ene dimers such as (XIII-XVI) illustrated in Fig. 1; presumably

of distinct species was not achieved, but will be very difficult since the

dimerisation process is theoretically capable of producing unsaturated

compounds derived from di-azacyclohexane in ten different skeletal

arrangements, and from these hundreds of distinct mono-, di-, tri-,

and tetra-ene compounds are possible. Though many are unlikely to be

obtained in this process, the likelier ones are still numerous.

The glass-like oligomer was even more difficult to characterise

than the dimers. Elemental analysis indicated an empirical formula

close to $C_5F_{6.6}N$, analogous to the dimeric material, consistent with some further fluorination of oligomers such as (XVIII). Clearly, the complex situation derived from an extension of the aforementioned $C_{10}F_{12}N_2$ dimer system is even further complicated by the possibility of branching in the oligomeric material. The number average molecular weight of $812 \overset{+}{-} 15$, measured on a Hitachi-Perkin Elmer 115 vapour pressure osmometer at 32° using 1,2,2-trichloro-1,1,2-trifluoroethane as solvent and decafluorobiphenyl as calibration standard, was similar to values obtained for other polyfluoroaromatics oligomerised by elemental fluorine (e.g., $C_6F_{6.2 - 6.6}$ derived from C_6F_6 [2]) where (e.g. XVIII in Fig. 1) n = 1-3 predominantly.

It was not possible to establish whether linkages of all possible types, C-C, C-N, and N-N, occurred between the azacyclohexyl-rings in the extended species. (For simplicity only C-C linkages are depicted in Fig. 1, but the other types may well be present also.)

As in the study of the analogous oligomers of hexafluorobenzene [2], pyrolytic defluorination was interesting and structurally useful. Thus, when the oligomeric material was pyrolysed at 450° over glass helices, it gave nonafluoro-1-azacyclohex-1-ene (II) (4%), heptafluoro-1-azacyclo-hexa-1,4-diene (III) (2%), heptafluoro-1-azacyclohexa-1,3-diene (IV) (24%) and pentafluoropyridine (I) (70%) based on a G.L.C. assessment. A less volatile product was not examined further but may have arisen from oligomeric species containing saturated or partially saturated polyfluoro-azacyclohexyl units.

Fluorinations of pentafluoropyridine with cobalt trifluoride [4], potassium tetrafluorocobaltate [5] and caesium tetrafluorocobaltate [6]

usually give a high degree of fluorination and some ring opening. The proportion of ring opened products has been minimised [4] by using a mixture of calcium fluoride, cobalt difluoride and cobalt trifluoride at 120-125° when nonafluoro-1-azacyclohex-1-ene (II) (77%), heptafluoro-1-azacyclohexa-1,3-diene (IV) (3%) and pentafluoropyridine (I) (20%) were obtained; the heptafluoro-1-azacyclohexa-1,4-diene (III) was not detected. The products were claimed [4] to arise from fluoride ion quenching of radical-cations at C2 to give hexafluoroazacyclohexadienyl radicals which in turn are quenched at C3 by fluorine atoms to produce heptafluoro-1-azacyclohexa-1,3-diene. Calculations of charge densities in the radical cations and radical spin densities in the hexadienyl radicals were in accord with the observed orientational influences. The mechanism may well have something in common with that occurring in our study.

The fluorination of pentafluoropyridine with elemental fluorine appears to be markedly slower than that of hexafluorobenzene [2] and this may be a function of the deactivating influence of the ring nitrogen, the higher aromaticity of the heterocycle and possible complex formation arising from association of the ring nitrogen with fluorine. The process is presumably free radical in nature, the rate determining step being addition of a fluorine atom to pentafluoropyridine.

Although directional effects are not strong, all free radical reactions of pyridine so far reported favour substitution at C2; in particular free-radical chlorination gives 2-chloropyridine almost exclusively. The phenylation of pentafluoropyridine with benzoyl peroxide gives 2-, 3-, and 4-phenyltetrafluoro-pyridine in the ratio of 45:22:30, respectively [7]. Thus, it is likely that attack by F. or F_2 at C2 is the predominant initial

step, but, in considering the scheme set out in Fig. 1, it is important

to keep in mind the very many simultaneous processes that can follow

from alternative points of attack available both in pentafluoropyridine

and in its derived hexadienyl radicals.

Considering the sequence based on attack by F. at C2, the spin

densities for the derived hexadienyl radical (V) have been calculated [8]

to be as shown in (XI). These are in general accord with the isolation of

the dienes (III) and (IV) though more of the former was obtained. The

extension of this sequence to the attack of the radical (V) on pentafluoro-

pyridine at C2 suggests the predominant formation of the four tetra-enyls

(XIII - XVI). However, the phenylation results [7] might imply the

formation of many other species also. The complexity of the appropriate

fraction was too great to allow any compounds to be identified.

The central similarity of the above sequence to that found in the

mechanism proposed for the cobaltic fluoride fluorination of pentafluoro-

pyridine [4] is worthy of comment. It is there postulated that the hexa-

dienyl radical (V) is quenched by F. from cobaltic fluoride so it appears

that the derived heptafluoro-1-azacyclohexa-1,4-diene (III) must be

rapidly isomerised to the more stable 1,3-isomer (IV) in accord with the

arguments forwarded in the latter study. It is probably significant that

the pyrolysis of the glassy oligomer produces substantially more of the

1,3-diene (IV) (24%) than the 1,4-isomer (III) (2%).

It is of further interest and significance that heptafluoro-1-azacyclo-

hexa-1,5-diene, one of the products to be expected from attack at either

C3 or C4 in pentafluoropyridine, is not isolated in this study or in that

involving cobaltic fluoride [4]. Also undetected here are any products

with an $>$ N-F bond, and in particular heptafluoro-1-azacyclohexa-2, 4-diene (VI), which, from spin density considerations alone (XI), might be a possible product. However, compounds with $>$ N-F are formed with difficulty in reactions of this type, and the absence of VI is another example of a fairly general effect.

EXPERIMENTAL

Apparatus

Gas chromatography

Analytical and preparative work was carried out using 1.5 m and 9.1 m glass columns (6 mm diam.), respectively, packed with dinonyl phthalate-celite (1:3) (Pye 104 instrument).

N.M.R. spectroscopy

Spectra were measured with a Perkin-Elmer R 12B instrument at 56.4 M Hz with trichlorofluoromethane as internal reference and chemical shifts are quoted in ppm.

Mass spectra

These were measured on an AEI MS9 instrument.

Fluorination apparatus

Methods for producing fluorine containing a low content of oxygen species, and the mode of fluorination were as described previously [2].

Fluorination of pentafluoropyridine at 100°

Purified fluorine (generated by 2.00 A) and nitrogen (4 dm^3 h^{-1}) were

bubbled for 2 h through pentafluoropyridine (13.07 g) at 50°, for 2 h at 90°,

and finally for 2 h at 100°, in a glass reaction vessel (25 cm^3) fitted with

a thermometer pocket and a reflux condenser. The condenser was fitted

with traps in series held at -78° and -180°. The product (13.18 g)

collected in the first trap, a clear yellow liquid, was shown by I.R.

spectroscopy to be free from any acid fluoride; a portion (12.40 g) was

distilled to give a volatile fraction (9.03 g) and a residual glass (3.33 g).

A portion (1.89 g) of the volatile fraction was separated by G.L.C.

(95°; N$_2$, 6 dm^3 h^{-1}) to give: (i) nonafluoro-1-azacyclohex-1-ene (II)

(0.10 g) with a correct I.R. spectrum [4]; (ii) heptafluoro-1-azacyclohexa-

1,4-diene (III) nc (0.42 g) b.p. 64-66° (one peak on G.L.C. at 50° and N$_2$

3 dm^3 h^{-1}) (Found: C, 29.1; F, 64.1; N, 6.8. C$_5$F$_7$N requires C, 29.0;

F, 64.2; N, 6.8%), ν_{max} 1750 cm^{-1} (broad band; CF = CF and CF =

N), m/e 207 (C$_5$F$_7$N$^+$), its ^{19}F N.M.R. spectrum consisted of five bands

at 57.8 (tc) (C$_2$), 85.9 (ddc) (C$_6$), 113.2 (tddd) (C$_3$), 144.5 (ddtt) (C$_5$) and

159.1 (ddtt) (C$_4$), in the relative intensity ratio of 1:2:2:1:1, respectively;

(iii) heptafluoro-1-azacyclohexa-1,3-diene (IV) (0.16 g) with a correct

I.R. spectrum and ^{19}F N.M.R. spectrum [4]. (iv) pentafluoropyridine (I)

(1.00 g) with a correct I.R. spectrum; (v) a yellow liquid (0.20 g) b.p.

168-170° shown by G.L.C. (95°, N$_2$, 6 dm^3 h^{-1}) to contain at least seven

components (Found: C, 30.4, 30.7, 30.5; F, 63.4, 63.0; N, 7.0, 7.0,

6.2. C$_5$F$_{6.6}$N requires C, 30.1; F, 62.9; N, 7.0%), ν_{max} 1740-1760

cm^{-1} (CF = CF), its ^{19}F N.M.R. spectrum was complex but contained

broad bands at 56.7 (N = CF) and 86.9 (CF_2-N). Further separation of fraction (v) was not attempted.

The residual glass was not fully characterised (Found: C, 29.7, 28.9; F, 62.3, 62.4; N, 6.8, 6.8. $C_5F_{6.6}N$ requires C, 30.1; F, 62.9; N, 7.0%), ν_{max} 1740-1760 cm^{-1} (S) (CF = CF).

Pyrolysis of the oligomer derived from pentafluoropyridine

The molten oligomer (2.60 g) was carried in a stream of nitrogen (1 dm^3 h^{-1}) into a vertical glass tube (30 cm x 30 mm diam.) at 450°. A portion (1.20 g) of the yellow liquid product (1.80 g) was distilled to give a volatile fraction (0.75 g) and a residual yellow oil (0.42 g). The volatile fraction was shown by G.L.C. (95°; N_2, 2 dm^{3}h^{-1}) to contain the following components by a comparison of their retention times with those of authentic specimens: (i) nonafluoro-1-azacyclohex-1-ene (II) (4%), (ii) heptafluoro-1-azacyclohexa-1,4-diene (III) (2%), (iii) heptafluoro-1-azacyclohexa-1,3-diene (IV) (24%) and (iv) pentafluoropyridine (I) (70%). The residual oil was not examined in detail.

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