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HIGHLY FLUORINATED HETEROCYCLES PART XV [1]. THE METAL CATALYSED
DEFLUORINATIVE REARRANGEMENT OF POLYFLUORINATED PYRROLIDINES TO
POLYFLUOROPYRIDINES

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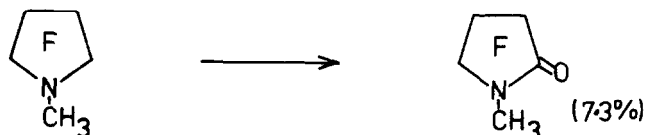
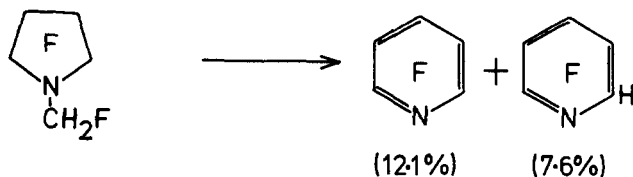
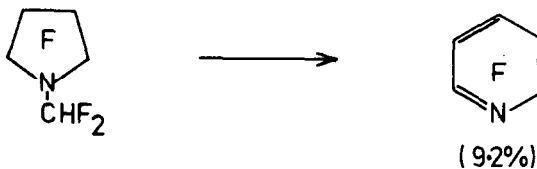
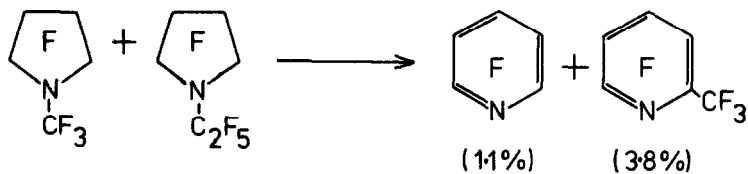
SUMMARY

Pyrolysis of a number of polyfluoro-1-alkyl pyrrolidines over iron gauze at 500-525° affords a small conversion to polyfluoropyridines.

RESULTS AND DISCUSSION

In the search for the elusive perfluoropyrrole and its derivatives we have investigated the defluorination of a series of polyfluoro-1-alkyl pyrrolidines, readily available from our earlier studies [2], over iron gauze. Slightly surprisingly the only products isolated other than a large amount of starting material were polyfluoropyridines. Thus, defluorination of a mixture of 1-trifluoromethyl- and 1-pentafluoroethyl-octafluoropyrrolidine, obtained from the fluorination of 2-methylpyridine [3] and inseparable by any of the techniques available to us, afforded a mixture of unreacted starting material, pentafluoropyridine and 2-trifluoromethyl-3,4,5,6-tetrafluoropyridine. In a similar manner 1-difluoromethyl-octafluoropyrrolidine afforded pentafluoropyridine and 1-fluoro-methyl-octafluoropyrrolidine gave a mixture of pentafluoropyridine and 2,3,4,5-tetrafluoropyridine. Pyrolysis of 1-methyl-octafluoropyrrolidine gave a different result, no pyridines were isolated and apart from starting material a trace of its hydrolysis product 1-methyl-hexafluoropyrrolid-2-one was obtained.

In an attempt to see if unsaturation in the five membered ring assisted the reaction 1-methyl-hexafluoropyrrol-3-ine was pyrolysed. This yielded two products apart from unreacted starting material, namely 1-

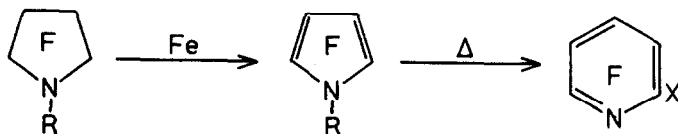


Values shown in parentheses indicate weight % of the product mixture.

methyl-3H-heptafluoropyrrolidine and 1-methyl-tetrafluoropyrrol-3-en-2-one and no pyridines.

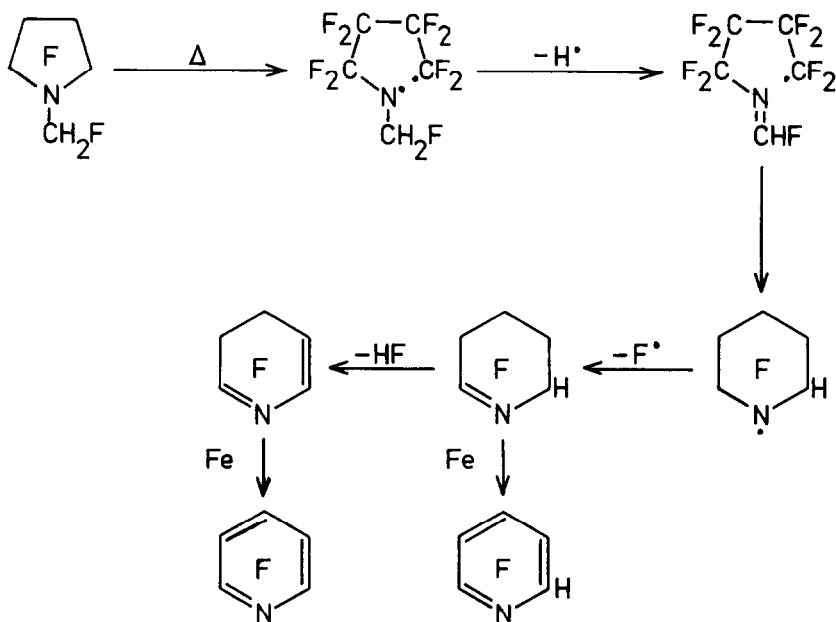
As a point of mechanistic interest to see if the reaction was purely a thermal process, 1-difluoromethyl-octafluoropyrrolidine was pyrolysed over glass beads at 520° to give only starting material in good yield. Thus, it is possible to conclude that the metal surface plays an important part in the process.

There seems to be at least two possible pathways for the rearrangement. Firstly,



i.e., defluorination to a tetrafluoropyrrole derivative which rearranges to the pyridine. Such processes are known in the hydrocarbon field where 1-methylpyrrole on pyrolysis at 650° is reported to give 2-methylpyrrole (85%) and small amounts (2-5%) of pyrrole and pyridine [4].

Alternatively, ring opening of the pyrrolidine and reclosure to the six membered ring followed by defluorination to the pyridines is a possible pathway e.g.



The fact that substituents (H or CF_3) appear in the 2-position in the pyridine would lend support to such a mechanism. There is little doubt that cleavage/recombination reactions of nitrogen containing cyclic fluorocompounds occur, as has been readily demonstrated by ourselves [5] and Haszeldine *et al* [6]. Defluorination of perfluoropiperidines to the corresponding pyridines is also well known [7].

Thus, we have demonstrated that it is possible to prepare polyfluoropyridines, albeit in low yield, from 1-alkyl octafluoropyrrolidines by this pyrolysis procedure. We have not attempted so far to optimise the yield of pyridines.

EXPERIMENTAL

Defluorination of 1-trifluoromethyl- and 1-pentafluoroethyl-octafluoro-pyrrolidine

A mixture of the pyrrolidines (1.5g) (ratio CF_3/C_2F_5 7:24 as determined by ^{19}F NMR) in a stream of nitrogen (1L/h) was passed over iron gauze heated to 525° to yield a colourless liquid (0.6g). The products from several such runs (3.27g) were separated by preparative g.l.c. to give starting material (2.5g), pentafluoropyridine (0.3g) identified by comparison with an authentic sample and 2-trifluoromethyl-3,4,5,6-tetrafluoropyridine (0.1g) [8] identified by comparison of its i.r. spectrum with that of an authentic sample.

Defluorination of 1-difluoromethyl-octafluoropyrrolidine

The pyrrolidine (2g) was passed over iron gauze at 520° as above to yield a clear liquid (1.1g). Separation afforded starting material (0.7g) and pentafluoropyridine (0.07g) identified from its i.r. spectrum.

Defluorination of 1-fluoromethyl-octafluoropyrrolidine

The pyrrolidine (3g) was passed over iron gauze as above at 520° to give a liquid (1.6g). Separation afforded starting material (1.0g), pentafluoropyridine (0.16g) identified by its i.r. spectrum and 2,3,4,5-tetrafluoropyridine (0.1g) [9] identified by its i.r. spectrum.

Pyrolysis of 1-methyl-octafluoropyrrolidine

The pyrrolidine (1.0g) was passed over iron gauze at 520° to yield a liquid (0.5g). Separation yielded starting material (0.4g) and 1-methyl-hexafluoropyrrolide-2-one (0.03g) identified by its i.r. spectrum.

Pyrolysis of 1-methyl-hexafluoropyrrol-3-ine

The olefin (1.5g) was pyrolysed as above at 360° to yield a mixture (0.8g) of three components. Separation afforded starting material (0.4g), 1-methyl-3H-heptafluoropyrrolidine (0.1g) and 1-methyltetrafluoropyrrol-3-en-2-one (0.12g) b.p. $117-118^\circ$ (Found: C, 35.5; H, 1.7; F, 44.7; N, 8.1.

$C_5H_3F_4NO$ requires C, 35.5; H, 1.8; F, 44.9; N, 8.3% the mass spectrum showed strong peaks at 169 (M^+), 150 ($(M-F)^+$), 140 ($(C_4F_4O^+)$) and 112 ($(C_3F_4^+)$). The i.r. spectrum showed a band at 1770cm^{-1} characteristic of a C=O group. The ^{19}F n.m.r. spectrum showed peaks at 105 ppm (rel. CCl_3F) (2F d,d J_{FF} 12 and J_{FF} 6 Hz), 150 (1F t,d J_{FF} 12 and J_{FF} 7 Hz) and 155.9 (1F d,t J_{FF} 7 and J_{FF} 6 Hz) consistent with the proposed structure.

Pyrolysis of 1-difluoromethyl-octafluoropyrrolidine over glass

The pyrrolidine (2g) was pyrolysed in a stream of nitrogen (0.2L/h) over glass beads at 520° . The clear liquid collected (1.92g) was shown by analytical g.l.c. and i.r. spectroscopy to be starting material.

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