Journal of Fluorine Chemistry, 9 (1977) 15–23

Received: June 23, 1976

REACTIONS INVOLVING FLUORIDE ION
PART XIII.[*] REACTIONS OF PERFLUORO-4-VINYLPYRIDINE

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SUMMARY

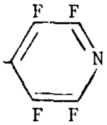
1-Chloro-1-(2',3',5',6'-tetrafluoropyridyl)tetrafluoroethane, obtained by reaction of chlorotrifluoroethylene with pentafluoropyridine in the presence of caesium fluoride, was dehalogenated over iron at 310°, giving perfluoro-4-vinylpyridine (IV). Reactions of (IV) have been surveyed; nucleophilic attack occurs at both the ring and the difluoromethylene group using MeO^- but with PhO^-, selective attack at the difluoromethylene group occurred. A dimer is produced by reaction of (IV) with CsF and the intermediate carbanion was trapped with tetrafluoropyridazine. Thermal cyclodimerisation of (IV) gave a single isomer whose structure was established by n.m.r. and by defluorination to a cyclobutene. Cyclobutanes were formed in thermal cycloaddition reactions with chlorotrifluoroethylene and with hexafluoropropene. Photochemical reaction of (IV) with hexafluoroacetone gave an oxetane.

RESULTS AND DISCUSSION

In principle chlorotrifluoroethylene (I) could be used to introduce the trifluorovinyl group into an aromatic system, as indicated below.

$$\underset{(I)}{CF_2{=}CFCl} + F^- \rightleftharpoons \underset{(II)}{CF_3\bar{C}FCl}$$

$$(II) + Ar{-}F \longrightarrow \underset{(III)}{ArCFClCF_3} \xrightarrow[(-ClF)]{\Delta,\ Fe} \underset{(IV)}{ArCF{=}CF_2} \qquad Ar =$$



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[*] Part XII, see reference 1.

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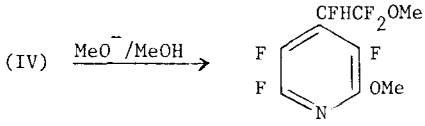
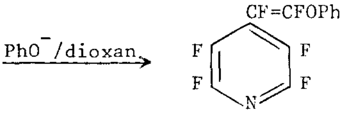
So far, however, we have only been able to introduce the chlorotetrafluoroethyl group efficiently into pentafluoropyridine [2]. We have now established that dehalogenation is readily achieved by passing (III) over iron at 310°, in a stream of nitrogen. Perfluoro-4-vinylpyridine (IV) was obtained in 68% yield. It is important to note that this reaction occurs much more readily than the corresponding defluorination of perfluoro-4-ethylpyridine or the earlier defluorination of perfluoroethylbenzene [3] and this difference is obviously due to the easier initial removal of chlorine. Perfluoro-4-vinylpyridine has been obtained previously [4], by reaction of the synthetically rather inaccessible trifluoroiodoethylene with 2,3,5,6-tetrafluoropyridylcopper. Following in this paper is a survey of the reactions of perfluoro-4-vinylpyridine.

Perfluoro-4-vinylpyridine has two reactive sites towards nucleophiles, a terminal difluoromethylene group and the 2,6-ring sites. Indeed, reaction with methoxide in methanol occurred giving attack at both positions (V), involving substitution at the 2-position together with base catalysed addition of methanol to the trifluorovinyl group. However, sodium phenoxide in dioxan was much more selective and reaction occurred exclusively at the difluoromethylene group, in this case giving substitution. Equal amounts of a mixture of cis- and trans-isomers of (VI) were obtained.



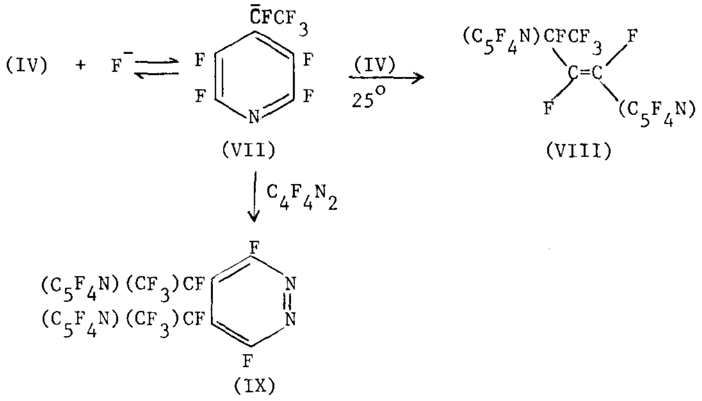
(V)



(cis and trans isomers)

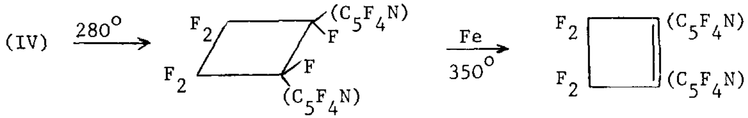
(VI)

Generation of a carbanion from (IV) in the presence of fluoride ion occurs very readily and the further reaction of (VII) with starting material (IV) occurs to give a dimer (VIII) together with a high molecular weight oil. Only the trans-isomer of (VIII) was detected. The carbanion (VII) can be trapped by other species e.g. reaction with tetrafluoropyridazine gave the derivative (IX). Further reactions of carbanion (VII) will be reported at a later date.

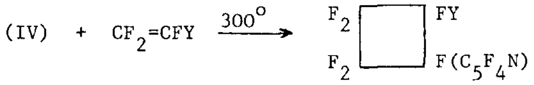


Systems containing trifluorovinyl groups normally undergo cycloaddition reactions giving cyclobutanes [5]. Reaction of (IV) occurred in a sealed tube at 280° giving 75% yield of a dimer. The n.m.r. spectrum showed CF_2 and -CF- groups and clearly a cyclobutane structure had been obtained. It was more difficult, however, to distinguish between head-to-head and head-to-tail isomers. We were unable to carry out a complete analysis of the n.m.r. spectrum of the dimer but a head-to-head structure for (X) was indicated by its defluorination which gave (XI). The assignment (X) is consistent with the findings of Bartlett and co-workers [6] which indicate a non-concerted process for cyclobutane formation and the production of (X) would follow from a reaction proceeding via the most stable intermediate diradical. Bartlett and co-workers [7] have recently shown that α,β,β-trifluorostyrene dimerises in a head-to-head fashion, giving <u>two</u> geometric isomers. This is in some contrast with the dimerisation of (IV) since only one isomer of (X) has been detected. It seems likely that this is the trans isomer (X) the difference arising from greater steric requirements of a fluorinated ring than a phenyl group. Cyclobutanes (XIII) and (XIV) were obtained in thermal reactions of (IV) with chlorotrifluoroethylene (I) and hexafluoropropene (XII), respectively. An oxetane (XV) was obtained by photolysis of a mixture of (IV) with hexafluoroacetone in a sealed silica tube.

We have been unable to polymerize perfluoro-4-vinylpyridine (IV) using γ-rays and this is analogous to the difficulty experienced in (attempted) polymerization of perfluorostyrene [8] which occurs only under very extreme conditions. However, an intractable solid was obtained on photolysis but so far we have been unable to determine the structure of this material.



(X) (XI)



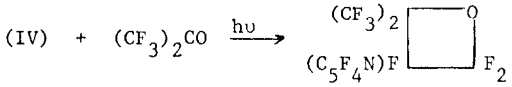
(cis and trans isomers)

(I), $Y = Cl$

(XII), $Y = CF_3$

(XIII), $Y = Cl$

(XIV), $Y = CF_3$



(XV)

EXPERIMENTAL

N.m.r. spectra were measured at 40° on a Varian A56/60D spectrometer using $CFCl_3$ or T.M.S. as external references. Upfield ^{19}F shifts are quoted as positive. Molecular weights were determined by mass spectrometry with an A.E.I. MS9 instrument. G.l.c. was performed on 30% Silicone gum (Column 'O') or 20% di-isodecylphthalate (Column A) on Chromosorb P. Tetrahydrothiophen dioxide (THTD) and 2,5,8,11,14-pentaoxapentadecane (POPD) were redistilled in vacuo and dried over molecular sieve, IVA.

Preparation of 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl)-tetrafluoroethane (III)

Using a procedure which has been described previously [2] a mixture of caesium fluoride (10 g, 66.0 mmol), POPD (120 ml), pentafluoropyridine (16 g, 94.7 mmol), and chlorotrifluoroethylene (23.5 g, 202.5 mmol) was vigorously stirred at room temperature for 24 h, during which time a partial vacuum had formed in the apparatus. Chromatographic analysis (Column 'O', 78°) of the volatile material (19 g) indicated that it consisted of unreacted pentafluoropyridine and one product, identified as 1-chloro-1-(2',3',5',6'-tetrafluoropyridyl)-tetrafluoroethane (83% yield, 45% conversion, based on pentafluoropyridine consumed) by comparison of its infra-red and ^{19}F n.m.r. spectra with those of an authentic sample [2]. The product was further purified by careful fractional distillation.

Dehalogenation of (iii)

The procedure involved passing (III), in a steady stream of dry nitrogen, through a silica tube (ca. 50 x 1 cm.), packed with coarse iron-filings and heated by a cylindrical heater. Products were collected in a cold trap (CO_2) and analysed by g.l.c. (Column 'O', 78°). Starting with (III) (3.2 g, 11.2 mmol) a product (2.0 g) was isolated and g.l.c. indicated a single component. This compound was identified as perfluoro-4-vinylpyridine (IV) [4], b.p. 130°, (Found: C, 36.1; F, 58.0%; M, 231. Calc. for C_7F_7N: C, 36.4; F, 57.6%; M, 231); $\lambda_{max.}$ (cyclohexane) 249 (ε 7430), 282 (ε 6550) mμ; δ_F 89.2, 138.8, (each 2F; 2,6- and 3,5-F respectively); 93.8, 124.1, 175.6 p.p.m. (each 1F) assigned to the vinylic fluorine atoms by comparison with the spectrum of perfluorostyrene [4]. Compound (IV) has previously been synthesised via 2,3,5,6-tetrafluoropyridylcopper [4].

Reactions of Perfluoro-4-vinylpyridine (IV)

(a) With sodium methoxide

A solution of sodium methoxide (1M) in methanol (6.5 ml, 6.5 mmol) was added slowly to a stirred solution of (IV) (1.5 g, 6.5 mmol) in dry methanol (2 ml), maintained at 0°. After pouring the reaction mixture into water (30 ml) the products separated as a lower organic layer, which after drying ($MgSO_4$) yielded a colourless liquid (1.4 g). G.l.c. analysis (Column 'O', 100°) of the product indicated a single component, identified as 2-oxa-4(2'-methoxy-3',5',6'-trifluoropyridyl)-3,3,4-trifluorobutane (V) (79%), b.p. 219°, (Found: C, 39.5; F, 41.0; M, 275. $C_9HF_6NO_2$, requires C, 39.3; F, 41.5; M, 275); δ_F 98.1, 143.4, 154.1 (each int. 1; 6'-, 3'-, 5'-F respectively); 89.5 (int. 2; 3F); 206.8 p.p.m. (int. 1; 4F).

(b) With sodium phenoxide

Compound (IV) (1.5 g, 6.5 mmol) was added to a solution of sodium phenoxide (1M) in dioxan (6.5 ml, 6.5 mmol) at room temperature. On pouring the reaction mixture into water (50 ml) the products separated as a lower organic layer which, after drying ($MgSO_4$), yielded a colourless liquid (1.2 g). G.l.c. analysis (Column 'O', 200^o) indicated two components, in equal amounts, identified as cis- and trans-1-phenoxy-2-(2',3',5',6'-tetrafluoropyridyl)-difluoroethylene (VI) (60%) b.p. 247^o, (Found: C, 50.9; F, 37.2; M, 305. $C_{13}H_5F_6ON$ requires C, 51.1; F, 37.4; M, 305); δ_F 90.9, 137.3 p.p.m. (Each int. 2; 2',6'- and 3',5'-F respectively); two sets of resonances were observed, arising from vinylic fluorine atoms in each of the geometric isomers of (VI); (94.6, 161.4) and (114.4, 166.4) p.p.m.

(c) With caesium fluoride

A mixture of caesium fluoride (1 g, 6.6 mmol), compound (IV) (0.9 g, 3.9 mmol), and THTD (5 ml) was stirred together in a dry flask (50 ml), under an atmosphere of dry nitrogen. On first mixing the reactants the mixture turned red. After 1 hour the reaction was extracted with ether (3 x 20 ml), washed (H_2O, 3 x 20 ml), dried ($MgSO_4$), and the ether removed by vacuum transfer. The recovered product, on sublimation (70^o, 0.005 mm) yielded a white solid (0.3 g) identified as trans-1,3-bis (2',3',5',6'-tetrafluoropyridyl)-hexafluorobut-1-ene (VIII) (33%) m.p. 60.5^o (Found: C, 36.2; F, 57.9; M, 462); ($C_{14}F_{14}N_2$ requires C, 36.4; F, 57.6; M, 462); δ_F 88.0, 139.5 (each int. 4; broad; 2',6'- and 3',5'-F respectively); 78.2 (int. 3; 4-F); 141.8, 148.6 (each int. 1; 1 and 2-F); 167.0 p.p.m. (int. 1; 3-F).

(d) With caesium fluoride and tetrafluoropyridazine

A mixture of caesium fluoride (2 g, 13.1 mmol), THTD (8 ml), and tetrafluoropyridazine (0.5 g, 3.3 mmol) was stirred under an atmosphere of dry nitrogen, and (IV) (1.5 g, 6.5 mmol) was added, over a 15 minute period, via a syringe through a self-sealing cap. On addition of (IV) the reaction turned red, but the colour faded after 5 mins. The product was extracted with ether (3 x 20 ml), but on addition of water a solid (1.3 g) formed at the interface. After filtration and recrystallisation ($CHCl_3$) this yielded a white crystalline solid (0.6 g), identified as 4,5-bis-[1'(2",3",5",6"-tetrafluoropyridyl)-tetrafluoroethyl]-3,6-difluoropyridazine (IX) (30%) m.p. 168^o (Found: F, 55.7; M, 614. $C_{18}F_{18}N_4$ requires F, 55.7; M, 614); δ_F 73.7 (int. 2; 3,6-F); 91.3, 140.9 (each int. 4; 2",6"- and 3",5"-F respectively);

75.8 (int. 6; $-\underset{|}{C}FC\underline{F}_3$); 158.8 p.p.m. (int. 2; $-\underset{|}{C}\underline{F}CF_3$). The ether layer, on drying ($MgSO_4$) and removal of the ether yielded (VIII) (0.2 g).

Cycloaddition Reactions of (IV)

(a) Dimerisation

Compound (IV) (2.7 g, 11.7 mmol) was heated in a small Carius tube, at 280° for 16 h. The recovered material (2.3 g), after sublimation (100°/0.005 mm), yielded a white solid (2.0 g) identified as 1,2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (X) (75%) m.p. 124°, (Found: C, 36.4; F, 57.4; M, 462. $C_{14}F_{14}N_2$ requires C, 36.4; 57.6; M, 462); δ_F 97.5, 138.5 (each int. 4; 2',6'- and 3',5'-F respectively); 121.1, 131.8 (calc. from AB quartet $J_{a,b}$ 220 Hz; each int. 2; 3,4-F); 164.3 p.p.m. (int. 2; 1,2-F).

Defluorination of (X) over iron filings at 350°, using the procedure described above, gave a mixture containing (X) (55%) and (XI) (45%). Compound (XI) was not isolated but the ^{19}F n.m.r. spectrum (XI) showed only ring fluorine atoms, δ_F 91.1 and 138.6 p.p.m. and a single resonance at 113.0 p.p.m. arising from $-CF_2-$.

(b) With chlorotrifluoroethylene

Compound (IV) (1 g, 4.3 mmol) and chlorotrifluoroethylene (1 g, 8.6 mmol) were heated in a small Carius tube (15 ml) at 300° for 38 h. The recovered material consisted of a solid (0.2 g) identified as (X) and a volatile liquid (1.65 g). G.l.c. analysis (Column 'O', 100°) of the volatile material indicated three components, identified as, (IV); dimers of chlorotrifluoroethylene, by comparison of infra-red and ^{19}F n.m.r. spectra with those of an authentic sample [9]; and a mixture of cis- and trans-1-chloro-2-(2',3',5',6'-tetrafluoropyridyl)hexafluorocyclobutane (XIII) (73% yield, 57% conversion). The isomers (XIII) b.p. 173°, gave (Found: F, 54.1; Cl, 10.3; M^{35} 347. $C_9NF_{10}Cl$ requires F, 54.7; Cl, 10.2; M^{35} 347); δ_F 89.8, 137.6 (each int. 4; 2',6' and 3',5'-F respectively); 117-136 (int. 8; 4-overlapping AB quartets; 3,4-F); 141, 144 (each int. 1; $CCl\underline{F}$. two isomers); 154.5, 160.6 (each int. 1; $C\underline{F}$, two isomers).

(c) With hexafluoropropene

Compound (IV) (1 g, 4.3 mmol) and hexafluoropropene (1.3 g, 8.6 mmol) were heated in a Carius tube (15 ml) at 300° for 6 h. A solid product (0.2 g) was recovered and identified as (X) together with a volatile liquid (1.25 g). G.l.c. analysis of the volatile material (Column 'O', 78°) indicated three components, separated by preparative-scale g.l.c. and identified as (IV) plus cis- and trans-1-(2',3',5',6'-tetrafluoropyridyl)-2-trifluoromethylhexafluorocyclobutane (XIV) (80% yield, 67% conversion). Isomer A (shortest retention time), b.p. 161°, gave (Found: C, 31.0; F, 65.4%; M, 381. $C_{10}F_{13}N$ requires C, 31.5; F, 64.8%; M, 381); δ_F 92.6, 135.6 (each int. 2; 2',6'- and 3',5'-F); 76.6 (int. 3, $C\underline{F}_3$); 123.9, 131.6 (calc. from AB quartets, each int. 1, $C\underline{F}_2$); 131.6 (broad, int. 2, $C\underline{F}_2$); 168.4, 193.8 p.p.m. (each int. 1, $C\underline{F}$). Isomer B, b.p. 165°, gave (Found: F, 65.2%, M, 381). δ_F 90.6, 138.8 (each int. 2; 2',6'- and 3',5'-F); 73.1 (int. 3, $C\underline{F}_3$); 126.2, 133.0 (Calc. from AB quartets, each int. 1, $C\underline{F}_2$); 126.5 (broad, int. 2, $C\underline{F}_2$); 170.8, 188.4 p.p.m. (each int. 1, $C\underline{F}$).

(d) With hexafluoroacetone

Compound (IV) (1 g, 4.3 mmol) and hexafluoroacetone (0.5 g, 3.0 mmol) were sealed in a silica tube (200 ml) and irradiated (300 nm) for 590 h. The products recovered consisted of a brown involatile solid (0.1 g) and a volatile white solid (0.9 g), which was purified by vacuum sublimation (40°/0.005 mm) and identified as 2,2-bis-trifluoromethyl-3-(2',3',5',6'-tetrafluoropyridyl)-trifluoro-oxetane (XV), (76%) m.p. 35°,(Found: F, 61.6%; M, 397. $C_{10}F_{13}NO$ requires F, 62.2%; M, 397) δ_F 89.7, 139.7 (each int. 2; 2',6'- and 3',5'-F) 74.0 (int. 6, CF_3); 75.0, 76.2 (calc. from AB quartets, each int. 1, $C\underline{F}_2$); 153.9 p.p.m. (int. 1, CF.).

ACKNOWLEDGEMENTS

We thank the Science Research Council for a C.A.S.E. award (to P.D.P.) and I.C.I. Ltd., Mond Division for co-operation in this award.

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