Journal of Fluorine Chemistry, 21 (1982) 159–169

Received: February 18, 1982

FLUORINATIONS WITH COMPLEX METAL FLUORIDES. PART 6 [1] FLUORINATION OF PYRIDINE AND RELATED COMPOUNDS WITH CAESIUM TETRAFLUOROCOBALTATE(III) [2]

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SUMMARY

Pyridine has been fluorinated over caesium tetrafluorocobaltate(III) ($CsCo^{III}F_4$) at 300-400°C to give a mixture of undecafluoro-N-methylpyrrolidine, bis(trifluoromethyl)amine, pentafluoropyridine and several polyfluoropyridines; the product composition depended to some extent on the geometry of the reactor. The fluorinations of pentafluoropyridine, piperidine and undecafluoropiperidine were also investigated.

INTRODUCTION

The advent of the reagent, potassium tetrafluorocobaltate(III) [3] widened considerably the scope of the high-valent transition metal fluoride fluorination process. By comparison with cobalt(III) fluoride, products were obtained containing components that retained some of the characteristics of the starting material (e.g. unsaturation [3], functional groups [4] and O and S heteroatoms [5]) but aromaticity was destroyed. It has also been demonstrated that on changing to the caesium analogue ($CsCo^{III}F_4$) the fluorination of arenes (benzene [6], naphthalene [7] benzonitrile [1] and benzo[b]furan[8]) yielded significant quantities of polyfluoroarenes, in some cases the perfluoroarene was produced. We have now extended our studies of this reagent to the fluorination of pyridine.

0022-1139/82/0000-0000/$02.75

Pentafluoropyridine and some polyfluoropyridines are usually prepared by halogen exchange processes [9] since attempts to fluorinate pyridine with cobalt(III) fluoride had been unsuccessful. At 300°C a very small yield of undecafluoropiperidine was isolated [10]. More recently pyridine was fluorinated over $KCo^{III}F_4$ at ca 220°C to give largely a mixture of acyclic products [11] but some polyfluoropyridines, similar to those reported in this paper, were isolated from the high-boiling fractions of the fluorination product [12].

RESULTS

We have found that the small scale (∿ 5 g) fluorination of pyridine over $CsCo^{III}F_4$ at 395-405°C gave pentafluoropyridine and undecafluoro-N-methylpyrrolidine as the major products together with smaller amounts of undecafluoro-2-azahex-2-ene, bis(trifluoromethyl)amineand 2,3,4,5-tetrafluoropyridine (Table 1). Unfortunately, attempts to scale up this process led to a significant decrease in the quantity of pentafluoropyridine produced but several polyfluoropyridines were now present in the product (Table 1). It would appear that changing the reactor geometry must alter

TABLE 1

Fluorination of pyridine with caesium tetrafluorocobaltate (III)

Product		Reactor A Yield %*	Reactor B Yield %*
Undecafluoro-N-methylpyrrolidine	I	32.9 (7.4)+	35.3 (10.6)+
Undecafluoro-2-azahex-2-ene	II	2.9 (0.6)	1.2 (0.4)
Bis(trifluoromethyl)amine	III	8.5 (3.5)	8.2 (4.5)
Pentafluoropyridine	IV	39.9 (14.9)	13.6 (6.8)
2,3,4,5-Tetrafluoropyridine	V	3.9 (1.6)	5.3 (3.0)
2,3,4-Trifluoropyridine	VI nc		2.3 (1.5)
2,3,6-Trifluoropyridine	VII		3.2 (2.0)
2,5-Difluoropyridine	VIII nc		2.1 (1.6)
2,3-Difluoropyridine	IX		2.2 (1.6)
Tetrafluoro-3-(fluoromethyl)pyridine	X nc		2.7 (1.3)
2,6-Difluoropyridine	XI		1.6 (1.2)

* Based on isolated products

\+ Molar % based on pyridine input

the reagent contact time but so far we have been unable to control this to our advantage.

The fluorinations were performed in the traditional way [13]. The crude products were washed thoroughly with water to remove hydrogen fluoride. Although some gaseous material was vented, significant losses of product by reaction with water did not occur. This is consistent with the presence of only small amounts of acyclic fluoroaza-alkenes and -adienes which formed the major part of the product obtained from the similar fluorination over $KCo^{III}F_4$ [11].

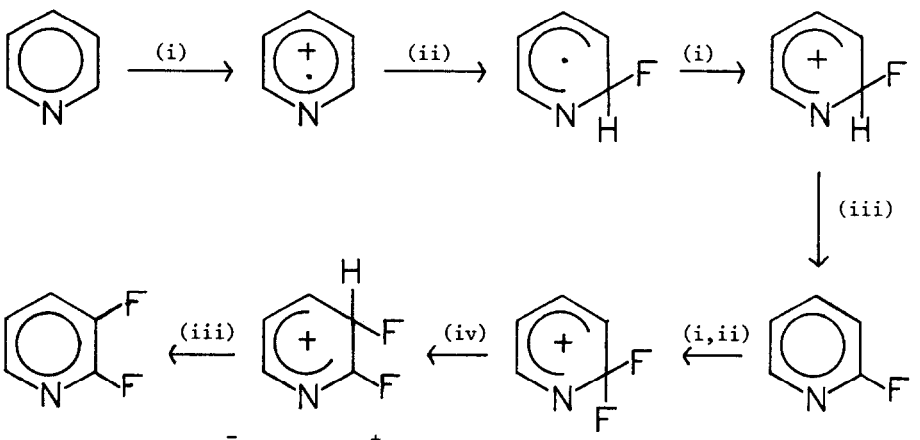
The isolation of the components from the small scale fluorination was achieved efficiently by preparative g.l.c. Undecafluoro-N-methyl-pyrrolidine, undecafluoro-2-azahex-2-ene, bis(trifluoromethyl)amine and pentafluoropyridine were identified by i.r. and n.m.r. spectroscopy and the percentage composition is recorded in Table 1. These components were also separated in a similar way from the product obtained from the larger scale fluorination to leave a complicated mixture of fluoropyridines (composition is recorded in Table 1). Six compounds (VI-XI) were isolated from this mixture with difficulty by g.l.c. The first component VI isolated was new and was identified as 2,3,4-trifluoropyridine. The ^1H n.m.r. spectrum showed the expected broad low field signal (τ 2.08) characteristic of an H substituent on a carbon atom bonded to nitrogen, and a multiplet signal (τ 2.92) of equal intensity.

As described in the following paper [12], for the fluoropyridines made in both studies, ^{19}F n.m.r. chemical shift parameters were calculated from the data for pentafluoropyridine [14] and the tetrafluoropyridine isomers [15]. Our own values were used for these, to minimise errors, but, excepting one case [12], these were very close to published figures. Calculations were done in both studies, but are consolidated in the following paper [12]. The predicted shifts for the 2,3,4-isomer were all within 4.0 ppm of the observed values. The second component isolated was shown by i.r. and n.m.r. spectroscopy to be 2,3,6-trifluoropyridine [15] and the third was the new 2,5-difluoropyridine, also isolated from the pyridine/$KCo^{III}F_4$ fluorination [12]. Unsuccessful attempts had been made to prepare this compound from 5-amino-2-fluoropyridine by the Balz-Schieman reaction [16]. 2,3-Difluoropyridine, originally synthesised from 3-amino-2-fluoropyridine [16] was the fourth component and the fifth was a new picoline, 2,4,5,6-tetrafluoro-3-(fluoromethyl)pyridine. This was

characterised by n.m.r. spectroscopy. The ^{19}F n.m.r. showed signals of equal intensity attributable to four fluorine substituents on the ring, two on C-atoms adjacent to N, also a triplet signal (J_{HF} 48 Hz) characteristic of a $-CH_2F$ group. The ^{1}H n.m.r. spectrum showed a doublet signal (J_{HF} 48 Hz) again indicative of the $-CH_2F$ group. Also the i.r. and n.m.r. spectra were identical to those obtained for the monofluoromethyl compound isolated from the products arising from the $CsCo^{III}F_4$ fluorination of 3-methylpyridine but were different from the isomer isolated from the 2-methylpyridine fluorination and again the n.m.r. parameters agreed with calculated values [17]. The sixth and final component of the mixture to be isolated was 2,6-difluoropyridine [18].

Thus the products from the fluorination of pyridine over cobalt(III) fluoride, potassium and caesium tetrafluorocobaltate(III) at first seem to be different. Cobalt(III) fluoride causes extensive degradation, but gives no fluoropyridines. Potassium tetrafluorocobaltate(III) ruptures the heterocyclic ring to yield as major products a series of acyclic fluoro-azahexenes, whereas caesium tetrafluorocobaltate(III) gives mainly a series of fluoropyridines and perfluoro-N-methylpyrrolidine arising from an unexpected ring contraction reaction.

The reaction pathways which give rise to these products are not yet fully understood. Previously the formation of the products derived from the fluorination of aromatic compounds has been accounted for by an oxidative replacement of hydrogen by fluorine [19].



(i) $-\epsilon$, (ii) $+F^-$, (iii) $-H^+$ and (iv) 1,2, F shift

Assuming that 1,2-fluorine atom migrations [20] are allowed in the cation/radical intermediates this provides an attractive explanation for the production of the series of di-, tri-, tetra- and penta-fluoropyridines isolated from the present fluorination mixture.

We suggest that since the non-aromatic products do not contain hydrogen they are derived from pentafluoropyridine. We have shown that under similar conditions to those used for the pyridine fluorination the major product resulting from the fluorination of pentafluoropyridine is perfluoro-N-methylpyrrolidine and not perfluoropiperidine as might have been expected from the earlier work involving cobalt(III) fluoride [10]. Indeed perfluoropiperidine was recovered unchanged after treatment with caesium tetrafluorocobaltate(III) in the usual way. It was noted that the amount of polyfluoroazahexene accompanying the perfluoro-N-methylpyrrolidine was greater in this reaction than with the pyridine fluorination. The increased proportion of the acyclic product could arise because in the former fluorination the products were not washed with water (the azahexene reacts slowly with water [11]) or the intermediates are generated under conditions where the fluorinating reagent is far less 'exhausted' i.e. depleted of available fluorine (see later).

Any explanation for the formation of perfluoro-N-methylpyrrolidine must be consistent with the formation of acyclic products in the $KCo^{III}F_4$/pyridine fluorination reaction [11]. It is known that further fluorination of pentafluoropyridine with cobalt(III)fluoride under mild conditions affords perfluoro-2-azacyclohex-2-ene [21]. This compound could therefore be produced in our fluorination. Fission of the C_2-C_3 bond in the pyridine ring must be the key step. Under our conditions this does not occur with perfluoropiperidine (cf. pyrolysis at 400-600°C to give perfluoro-N-methylpyrrolidine [22]) and so it is reasonable to suggest that in this fluorination perfluoro-2-azacyclohex-2-ene or dienes produced from pentafluoropyridine affords a 2-azahexenyl radical by rupture of the ring. In the presence of an excess of readily available fluorine atoms this gives an acyclic product. However if quenching of the acyclic radical is hindered by lack of 'available' fluorine cyclisation occurs to the ring contracted product.

This parallels the known behaviour of hexenyl radicals in hydrocarbon chemistry [23]. For even though formation of a five membered ring is thermodynamically less favourable than six there are many examples of

ring closure to cyclopentane derivatives. These reactions are thought to proceed by radical attack in a direction roughly perpendicular to the double bond [24]. Calculations show that this is achieved with less steric hinderance in the transition state leading to five-membered rings. Since substitution of hydrogen by fluorine does not usually alter steric interactions dramatically: similar arguments may be used to explain the formation of the pyrrolidine in the fluorination product.

Further fragmentation of the azahexenyl radical affords perfluoro-2-azapropene [22] which adds hydrogen fluoride to give bis(trifluoromethyl) amine.

The presence of a fluoromethylpyridine is more difficult to explain. A difluoromethylpyridine might have been expected because the orientation of substitution is consistent with a carbene insertion reaction as found in the reaction of pentafluoropyridine with polytetrafluoroethylene at 550°C which gives mainly 3-perfluoromethylpyridine [25]. This compound is also present in trace amounts in the potassium fluoride exchange reaction with pentachloropyridine [26]. However the source of mono-fluorocarbene remains a mystery.

The fluorination of piperidine under comparable conditions gave similar products to those obtained from pyridine but the yields obtained were low. These poor recoveries may be attributable to increased involatile salt formation with hydrogen fluoride by the more basic piperidine leading to retention in the reactor.

In conclusion the different results for the potassium and caesium tetrafluorocobaltates suggest that a structural difference exists which, in the latter case, hinders migration of fluorine species towards the reactive sites at the surface of the reagent.

EXPERIMENTAL

Reactors. Fluorinations were carried out in conventional nickel reactors, as described previously [13], containing caesium tetrafluorocobaltate(III)
Reactor A (250 g) and Reactor B (6.5 Kg).

Gas liquid chromatography. Products were analysed by g.l.c. using two glass columns (1.83 x 4 mm): Unit A, Ucon oil (LB550-X)-chromosorb P

(30-60 mesh) 1:4 and Unit B, dinonylphthalate-chromosorb P (30-60 mesh) 1:3. Preparative g.l.c. utilised several columns (9.14 m x 8 mm): Unit C, Ucon oil (LB550-X)-chromosorb P (30-60 mesh) 1:4; Unit D, Ucon oil (50-HB-2000)-chromosorb P (30-60 mesh) 1:4; Unit E, dinonylphthalate-celite 1:2; Unit F, Kel-F oil-chromosorb P (30-60 mesh) 1:9 and Unit G, di-isodecylphthalate-chromosorb P (30-60 mesh) 1:4 in Pye Series 104 or 105 instruments, also Unit H, column (4.88 m x 75 mm) dinonylphthalate-chromosorb P (30-60 mesh) 1:5.

Spectroscopy. ^{1}H (60 MHz) (τ) and ^{19}F (56.4 MHz) (δ, -ve) n.m.r. spectra were measured with a Perkin Elmer R12B spectrometer. Samples were dissolved in tetrachloromethane with tetramethylsilane and trichlorofluoromethane as internal standards.

Fluorination of Pyridine with Caesium Tetrafluorocobaltate(III).

Reactor A. Aliquots of pyridine (4 g) were added to the reactor at 395-405°C in a stream of nitrogen (2 $\ell\ h^{-1}$) over 25-35 min. Nitrogen was passed for a further 30 min and products were collected in a glass trap cooled in liquid air. The product was washed with ice-cold water to give Product A (3.3 - 4.1 g).

Reactor B. In a typical run, pyridine (98 g) was introduced into the reactor at 310°C in a stream of nitrogen (20 $\ell\ h^{-1}$) over 3.5 hr. The Product B (105 g) was flushed from the reactor with nitrogen (20 $\ell\ h^{-1}$), collected in a nickel trap cooled in solid carbon dioxide and washed with water.

Separation and Identification of the Products.

Product A (31.6 g) from several fluorinations was separated by g.l.c. (Unit H, 82°C, N_2 75 $\ell\ h^{-1}$) to give (i) mainly (> 90%) undecafluoro-N-methylpyrrolidine I (7.1 g) containing some undecafluoro-2-azahex-2-ene II, pure sample of I was obtained by further separation (Unit C, 24°C, N_2 4 $\ell\ h^{-1}$) with ^{19}F n.m.r. spectrum in agreement with published data [22] (ii) a mixture (2.2 g) of I and five unidentified components; (iii) bis(trifluoromethyl)amine III (1.6 g), identified by i.r. [27], ^{1}H and ^{19}F n.m.r. spectroscopy [28], (iv) a mixture (0.5 g), III and IV; (v) pentafluoropyridine IV (7.4 g) identified by i.r. [29], ^{1}H and ^{19}F n.m.r. spectroscopy [14]; (vi) 2,3,4,5-tetrafluoropyridine V (0.7 g) identified by i.r. [30]. ^{1}H and ^{19}F n.m.r. [15] spectroscopy and (vii) a mixture (0.2 g) including V.

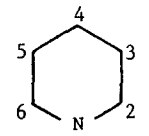
Product B (74.8 g) was separated by g.l.c. (Unit H, 90°C, N_2 75 ℓ h^{-1}) to give I (contaminated with II) (33.1 g), III (5.4 g) IV (8.8 g) V (3.2 g) and a mixture B^1 (15.0 g). An aliquot (9.4 g) of fraction B^1 was further separated (Unit D, 149°C, N_2 5 ℓ h^{-1}) to give (i) a multicomponent mixture (1.0 g) containing some V; (ii) a mixture further purified (Unit C, 111°C, N_2 8 ℓ h^{-1}) to give 2,3,4-trifluoropyridine VI nc b.p. 104.5 - 6°C (Found: C, 44.3; H, 1.6; F, 42.5; N, 10.1. $C_5H_2F_3N$ requires C, 45.1; H, 1.5; F, 42.8; N, 10.5%) ν_{max} 1640 (m), 1611 (s), 1584 (m), 1498 (s) and 1457 (s) cm^{-1}, m/e 133.013 ($C_5H_2F_3N^+$ requires 133.014), ^1H and ^{19}F n.m.r. spectra - see Table 2; (iii) a mixture (4.2 g), an aliquot (1.9 g) was further separated (Unit C, 126°C, N_2 8 ℓ h^{-1}) to give (iiia) 2,3,6-trifluoropyridine VII (0.35 g) identified by i.r. and ^{19}F n.m.r. spectroscopy [15], (iiib) 2,5-difluoropyridine VIII nc (0.11 g) b.p. 115 - 117°C. Found m/e 115.020 ± .005 $C_5H_3F_2N$ requires m/e 115.023, also m/e 115 [M]; 96 [M-F]; 95 [M-HF]; 88 [M-HCN], ν_{max} 1395 (m), 1490 (s), 1600 (s), 3080 (w); λ 265, 203 nm (ethanol) identified by i.r., ^1H and ^{19}F n.m.r. spectroscopy (Table 2) (iiic) a mixture (0.29 g) further separated (Unit G, 135°C, N_2 8 ℓ h^{-1}) to give 2,3-difluoropyridine IX (0.02 g) b.p. 116.5 - 118.5° (lit., [16] 118°C) (Found: C, 53.0; H, 2.7; F, 33.2; N, 12.4. Calc. for $C_5H_3F_2N$. C, 52.2; H, 2.6; F, 33.0; N, 12.2%) ^1H and ^{19}F n.m.r. spectra (Table 2) and tetrafluoro-3-(monofluoromethyl)pyridine X nc (0.03 g) b.p. 141.5 - 143.5°C (Found: C, 39.7; H, 1.2; F, 51.9; N, 7.6. $C_6H_2F_5N$ requires C, 39.4; H, 1.1, F, 51.9; N, 7.6%) ν_{max} 1641 (s), 1610 (m), 1499 (s) and 1475 (s) cm^{-1}, ^1H and ^{19}F n.m.r. (Table 2) [17] and (iiid) 2,6-difluoropyridine XI (0.14 g) identified by i.r., ^1H and ^{19}F n.m.r. spectroscopy [18] and finally (iv) a mixture (1.9 g) of at least five compounds which were not investigated further.

Fluorination of Pentafluoropyridine.

Aliquots of pentafluoropyridine (3 g) were fluorinated (Reactor A) at 400°C to give product (ca. 2 g). This product (2.5 g) was not washed with water but separated by g.l.c. (Unit E, 97°C, N_2 6 ℓ h^{-1}) to give (i) an unresolvable mixture (1.3 g) of undecafluoro-2-azahex-2-ene and undecafluoro-N-methylpyrrolidine (1:4) and (ii) pentafluoropyridine (0.2 g); compounds were identified by i.r. and ^{19}F n.m.r. spectroscopy.

TABLE 2

^{19}F and ^{1}H N.m.r. Data

		CHEMICAL SHIFTS ^{19}F δ (-ve) p.p.m. upfield from CCl_3F (int) ^{1}H τ (10-8) downfield from $Si(CH_3)_4$ (int)					COUPLING CONSTANTS									
							^{3}J				^{4}J			^{5}J		^{6}J
	2 3 4 5 6	2	3	4	5	6	2,3	3,4	4,5	5,6	2,4	3,5	4,6	2,5	3,6	2,6
VI n.c.	F F F H H	83.3 (cdd) {79.7}	165.4 (dddd) {165.4}	123.1 (dddd) {122.8}	[H] 2.92 (dddd)	[H] 2.08 (dddd)	24.5 (F,F)	8.8 (H,H)	6.9 (H,F)	5.5 (H,H)	21 (F,F)	3.4 (H,F)	3.0 (H,E)	0.7 (H,F)	0.6 (H,E)	1.8 (H,F)
VIII n.c.	F H H F H	72.8 (bd) {69.2}	[H] 3.14 (dddd)	[H] 2.52 (dddd)	133.8 (ddd) {135.7}	[H] 2.02 (cdd)	3.4 (H,F)	8.8 (H,H)	6.9 (H,F)	3.4? (H,F)	5.6 (H,F)	3.4 (H,F)	3.0 (H,H)	24.5 (F,F)	0.6 (H,H)	1.8 (H,F)
IX*	F F H H H	87.2 (cd) {84.6}	140.4 (ddd) {144.3}	[H] 2.45 (dddd)	[H] 2.84 (dddd)	[H] 2.09 (ddd)	27 (F,F)	9.0 (H,F)	7.8 (H,H)	4.6 (H,H)	9.0 (H,F)	3.4 (H,F)	1.6 (H,H)	0.9 (H,F)	1.6 (H,F)	1.6 (H,F)
X n.c.	F CH_2F F F F	72.5 (c)	$[CH_2F]$ F213.2 (ct) H4.57 (d, J_{HF}48)	118.0 (ddd)	167.1 (ddd)	81.3 (c)	-	-	19 (F,F)	22 (F,F)	12.4 (F,F)	-	22 (F,F)	25 (F,F)	-	?

* spectral data not published previously

Figures in brackets { } are calculated chemical shifts [12]

Fluorination of Undecafluoropiperidine.

Aliquots of undecafluoropiperidine (3 g) were fluorinated (Reactor A) at 370 - 440°C to give unchanged undecafluoropiperidine (1.4 - 1.7 g); confirmed by i.r. spectroscopy.

Also a mixture of pyridine (3 g) and undecafluoropiperidine (2 g) was fluorinated at 410°C to give a multicomponent product (3.7 g) which was shown to contain undecafluoropiperidine by g.l.c. analysis.

Fluorination of Piperidine.

Piperidine (50 g aliquots) was fluorinated (Reactor B) at 325 - 350°C in the usual way to give a liquid product (3.3 - 13.1 g) whose g.l.c. chromatogram was similar but not identical to that obtained for the pyridine fluorination product.

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