

Fluorination of Nitriles over Cobalt Trifluoride and Potassium Tetrafluorocobaltate

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Fluorinations of acetonitrile and propionitrile by cobalt trifluoride and potassium tetrafluorocobaltate leave the nitrile groups mainly intact, as expected from their high ionization potentials. Major products from acetonitrile are $\text{CH}_2\text{F}\cdot\text{CN}$ (main) and $\text{CHF}_2\cdot\text{CN}$, and from propionitrile, $\text{CH}_3\cdot\text{CHF}\cdot\text{CN}$ (main), $\text{CH}_3\cdot\text{CF}_2\cdot\text{CN}$, $\text{CH}_2\text{F}\cdot\text{CHF}\cdot\text{CN}$, and $\text{CH}_2\text{F}\cdot\text{CF}_2\cdot\text{CN}$, with α -fluorination strongly predominating. Succinonitrile and fumaronitrile both give a mixture of difluoro-fumaro- and -maleo-nitriles.

THERE are only a few reports on the fluorination of R_FCN compounds ($\text{R}_F = \text{perfluoroalkyl}$) with cobalt trifluoride¹ or silver difluoride,² and the fluorination of

¹ G. E. Coates, J. Harris, and T. Sutcliffe, *J. Chem. Soc.*, 1951, 2762.

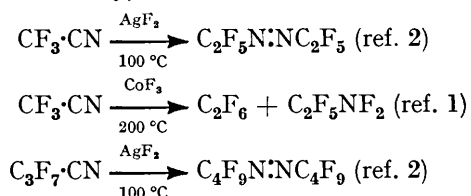
² J. A. Young, W. S. Durrell, and R. S. Dresdner, *J. Amer. Chem. Soc.*, 1960, **82**, 4553.

from the corresponding dichloro-compounds¹⁴ and by pyrolysis¹⁵ of chlorofluoroacetonitrile at 700–900 °C.) This result is surprising for two reasons: first, dimethyl succinate¹⁰ gives only polyfluoropropionyl fluorides as products, with apparently no trace of any dicarboxylic acid fluoride; and secondly, it is unusual, in a fluorination reaction, to obtain products with two fluorine atoms on a double bond; products of the types $\cdot\text{CF}\cdot\text{CH}\cdot$ and $\cdot\text{CH}\cdot\text{CH}\cdot$ are much commoner.^{6,16}

It is possible that fumaro- and perhaps maleo-nitrile are intermediates in the fluorination, since fluorination of the former gave the same products as does succinonitrile.

We have also fluorinated malononitrile and benzonitrile; in both cases complex mixtures were obtained (≥ 35 products in the former case and ≥ 25 in the latter, according to g.l.c.) and so these experiments were abandoned.

There is one further puzzling feature of our fluorinations. The following reactions have been reported (major products only):



However, we have found no trace of any azo- or >N-F compounds in our fluorinations. We conclude that either we have missed such compounds (conceivable in the case of the azo-compounds, because, being partially fluorinated, they could be much higher boiling, or retained longer on g.l.c. than the nitriles actually identified), or that their formation does not begin until replacement of hydrogen by fluorine is virtually complete. If we have missed them, then their amounts must be small, since the yields of the identified products were high. (Note that the azo-compound-producing reactions mentioned above^{1,2} proceed in quite high yields under relatively moderate conditions.)

EXPERIMENTAL

Fluorination of Acetonitrile.—The nitrile (1.5 g) was added dropwise to a stirred reactor containing potassium tetrafluorocobaltate (150 g) and heated to 80–400 °C. Nitrogen (6 dm³ h⁻¹) was then passed through the reactor for a further 1 h. The effluent gases were scrubbed free of hydrogen fluoride by passage over sodium fluoride pellets, and collected in a trap cooled with liquid air. Trap-to-trap distillation yielded fractions (a), b.p. < -15 °C, and (b), b.p. > -15 °C. Fraction (a) contained (i.r.¹⁷) CF₄, CHF₃, C₂F₆, and a trace of C₂HF₅, but no CF₃CN; no liberation of

¹⁴ H. Cenci, Fr.P. 1325307/1963 (*Chem. Abs.*, 1963, **59**, 13830h); B.P. 978241/1964.

¹⁵ S. Proskow, U.S.P. 3121734/1964 (*Chem. Abs.*, 1964, **60**, 10557b).

¹⁶ I. W. Parsons, P. M. Smith, and J. C. Tatlow, *J. Fluorine Chem.*, 1971, **1**, 141; R. G. Plevy, R. W. Rendell, and M. P. Steward, *ibid.*, 1973, **3**, 267.

¹⁷ 'Documentation of Molecular Spectroscopy,' Butterworths, London.

iodine occurred when the fraction was passed through aqueous potassium iodide (absence of >N-F compounds). Fraction (b) was analysed by g.l.c. (Table 1), and a sample (1.0 cm³) from a fluorination at 200 °C was separated [1 : 2 dinonyl phthalate on Celite, column (column A) 9.5 m \times 8 mm, temperature 70 °C, N₂ carrier gas] to give (i) a mixture of six components (ca. 0.05 g); (ii) acetonitrile (0.29 g) (i.r.); and (iii) monofluoroacetonitrile (0.34 g) (i.r.¹⁸), b.p. 81–82 °C (lit.,¹⁹ 81.8–82.0°) [δ_{H} 4.59 (d, *J* 44.4 Hz); δ_{F} 232.3 p.p.m. upfield from CFCI₃ (d, *J* 45.0 Hz)]. Separation of a larger sample (9.0 g) yielded 1,1,1,2-tetrafluoroethane (trace; i.r.²⁰) and difluoroacetonitrile (0.65 g), b.p. 22–23 °C (lit.,¹⁹ 22.8–23.4°) [δ_{H} 5.92 (t, *J* 52.2 Hz); δ_{F} 119.8 p.p.m. upfield from CFCI₃ (d, *J* 52.0 Hz)] as components of the mixture (i).

Similar fluorinations were carried out over cobalt trifluoride; the results are summarised in Table 1.

Fluorination of Propiononitrile.—The nitrile (30.0 g) was fluorinated over potassium tetrafluorocobaltate (2 kg) at 100–335 °C and the products were treated in a similar way to those from acetonitrile. The more volatile fraction (b.p. < -15 °) containing (i.r.¹⁷) CF₄, CHF₃, and C₂F₆. The less volatile products were analysed by g.l.c. and the results are summarised in Table 2. A sample (20.0 g) of these less volatile materials from a fluorination at 220 °C was separated [1 : 5 dinonyl phthalate on Chromosorb P, column (column B) 4.88 m \times 7.5 cm, temp. 96°, N₂ carrier gas] into five fractions [there were eight major peaks].

Analytical g.l.c. of fraction 1 showed three major and at least seven minor components. Separation (column A, 60 °C) gave (i) an unidentified mixture (0.12 g); (ii) a mixture (0.22 g) (analysed by n.m.r.; see Table 4 for parameters) of 2,2,3,3-tetrafluoropropiononitrile (60%) and 2,2-difluoropropiononitrile (40%); (iii) a mixture (0.15 g) (15 : 85) of the components of (ii); (iv) a mixture (0.13 g) (analysed by n.m.r.) of 2,2,3-trifluoropropiononitrile (60%) and 2-fluoroacrylonitrile [the n.m.r. spectra of the latter showed an ABX pattern with δ_{A} 6.51, δ_{B} 6.45 (¹H nuclei), δ_{X} 111.6 p.p.m. upfield from CFCI₃; J_{AB} 5.0, J_{AX} 43.9, J_{BX} 13.2 Hz].

Fraction 2 (3.3 g) was the mixture obtained in Fraction 1 (iv). Fraction 3 (7.2 g) was 2-fluoropropiononitrile, b.p. 83–84 °C (lit.,²¹ 83–83.5°) (Found: C, 49.1; H, 5.4; F, 25.9; N, 19.5. Calc. for C₃H₄FN: C, 49.3; H, 5.5; F, 26.0; N, 19.2%). Fraction 4 (3.3 g) was a mixture of fractions 3 and 5 (i).

Separation of fraction 5 [1 : 9 Ucon fluid 50-HB-2000 on Chromosorb P, column (column C) 9.5 m \times 8 mm, temp. 100 °C, N₂ carrier gas] gave (i) propiononitrile (0.31 g, i.r.) and (ii) 2,3-difluoropropiononitrile (0.29 g), b.p. 135–136 °C (Found: C, 39.4; H, 3.3; F, 41.9; N, 15.3. C₃H₃F₂N requires C, 39.6; H, 3.3; F, 41.7; N, 15.4%).

The product mixture with b.p. ≥ -15 °C (29.9 g) from the 335 °C fluorination was distilled up a column packed with glass helices, and the still residues (1.32 g) were separated (column C, 100 °C) to give (i) bistrifluoromethylamine (0.05 g) (i.r.¹⁷); (ii) 2-fluoropropiononitrile (0.34 g) (i.r.); (iii) propiononitrile (0.40 g) (i.r.); (iv) 2,3,3-trifluoro-

¹⁸ R. G. Jones and W. J. Orville-Thomas, AD-612166 (*Chem. Abs.*, 1965, **63**, 9781c).

¹⁹ F. Swarts, *Bull. Soc. chim. belges*, 1922, **31**, 364.

²⁰ J. R. Nielson and C. J. Halley, *J. Mol. Spectroscopy*, 1965, **17**, 341.

²¹ E. Gryskiewicz-Trochimowski and O. Gryskiewicz-Trochimowski, *Bull. Soc. chim. France*, 1949, 928.

TABLE 1
Fluorination of acetonitrile

Reagent	Temp. (°C)	Total yield (g) ^a	Yield of volatiles (g) (b.p. < -15°C)	Product (fraction b.p. > -15°C) composition ^c (mole %)			
				MeCN	CH ₂ F·CN	CHF ₂ ·CN	CF ₃ ·CH ₂ F ^b
KCoF ₄	80	1.45 ^b	Trace	90	8	Trace	
	140	1.25	0.15	61	34	4	
	400	1.50	0.60	34	45	8	1
CoF ₃	90	1.17	Trace	81	15	1	
	145	1.58	0.67	22	40	9	21

^a From 1.5 g. ^b From 2.0 g. ^c By g.l.c. Difference of total from 100 represents unidentified products.

TABLE 2
Fluorination of propionitrile

Reagent	Temp. (°C)	Total yield (g) ^a	Yield of volatiles (b.p. < -15°C) (g)	Product (b.p. > 15°C) composition ^b (mole %)					
				EtCN	MeCHF·CN	MeCF ₂ ·CN	CH ₂ F·CF ₂ ·CN ^c	CH ₂ F·CHF·CN	CHF ₂ ·CHF·CN (CF ₃) ₂ NH
KCoF ₄	100	28.1	< 1	83	12	1	1		
KCoF ₄	335	72.9	42.9	20	26	16	9	6	3
CoF ₃	125	12.9	1.1	53	45	1			4
CoF ₃	205	15.4	6.1	45	31	11	5	Trace	Trace

^a From 30.0 g. ^b Footnote c, Table 1. ^c Ca. 50 : 50 mixture. ^d Ca. 60 : 40 mixture.

TABLE 3
Fluorination of succino- and fumaro-nitriles over potassium tetrafluorocobaltate

Nitrile	Temp. (°C)	Total yield (g) ^a	Yield of volatiles (b.p. < 0°C) (g)	Product (fraction b.p. > 0°C) composition ^b (mole %)			
				(CH ₂ CN) ₂	CH ₂ F·CN	CHF ₂ ·CN	(CF ₃) ₂ NH
Succinonitrile	160	13.2	Trace	16	41	28	2
	250	23.0	Trace	Trace	45	30	3
	400	37.0	8.9		32	28	10
Fumaronitrile	175	1.6 ^c	0.4		19	24	2

^a From 30.0 g. ^b Footnote c, Table 1. ^c From 2.0 g.

TABLE 4
N.m.r. data for fluorinated propionitriles, CH_m^βF_{3-m}^β·CH_n^αF_{2-n}^α·CN

Compound	Chemical shift ^a				Coupling constants (Hz)					
	F ^α	F ^β	H ^α	H ^β	J _{H^αH^β}	J _{H^αF^α}	J _{H^αF^β}	J _{F^αF^β}	J _{F^αH^β}	J _{H^βF^β}
MeCHF·CN	182.2		5.22	1.72	6.9	46.8			23.4	
CH ₂ F·CHF·CN	196.6	244.7	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>	<i>b</i>
CHF ₂ ·CHF·CN	208.4	131.5	6.10	6.62	2.7 ^c	43.5 ^c	10.8 ^c	7.9 ^c	6.0 ^c	52.5 ^c
MeCF ₂ ·CN	85.4			1.97					18.1	
CH ₂ F·CF ₂ ·CN	102.9	236.5		5.00				18.9	11.7	45.4
CHF ₂ ·CF ₂ ·CN	109.6	135.1		5.89				5.6	1.9	53.6

^a ¹H Shifts in p.p.m. downfield from Me₄Si; ¹⁹F shifts in p.p.m. upfield from CFCl₃. ^b Complex second-order spectrum, coupling not analysed (see text). ^c This spectrum was analysed as the first-order spectrum it appeared to be; this could be misleading as the compound has the same spin system as the one above it in the Table, which did show a second-order pattern.

propionitrile [0.06 g; identified by n.m.r. (see Table 4)]; and (v) 2,3-difluoropropionitrile (0.11 g) (i.r.).

Fluorinations over cobalt trifluoride were carried out in a similar way and the results are summarised in Table 2.

Fluorination of Succinonitrile.—The nitrile (30.0 g) was fluorinated at 160–400 °C over potassium tetrafluorocobaltate (2 kg) as described before; results are summarised in Table 3. The volatile components consisted (i.r.) of CF₄, CHF₃, and C₂F₆. Separation (column A, 70 °C) of a sample (1.00 g) from a 400 °C fluorination gave: (i) a mixture (ca. 0.02 g) of at least 13 components; (ii) bis-trifluoromethylamine (0.09 g) (i.r.); (iii) difluorofumaronitrile [0.21 g; identified by i.r. and ¹⁹F n.m.r.¹⁵ (sharp singlet at 147.9 p.p.m. upfield from CFCl₃; lit.¹⁵ 148.3)], b.p. 80–81.5 °C; and (iv) difluoromaleonitrile [0.18 g;

identified by i.r. and ¹⁹F n.m.r.¹⁵ (s, δ 126.7; lit.¹⁵ 127.1)], b.p. 79–81 °C [lit.¹⁵ 79–81 °C for a mixture of (iii) and (iv)]. Analytical figures for a mixture of (iii) and (iv), isolated in another experiment, were as follows (Found: C, 42.1; F, 33.3; N, 24.5. Calc. for C₄N₂F₂: C, 42.1; F, 33.3; N, 24.6%).

Fluorination over cobalt trifluoride at 200–250° gave products (ca. 8 g from 4 g of succinonitrile) of which 75–95% had b.p. < 0 °C, and experiments were not pursued.

Fluorination of Fumaronitrile.—Results are summarised in Table 3.

J. R. K. thanks the Imperial Smelting Corporation Ltd. for a maintenance award.