

Fluorinations with Complex Metal Fluorides. Part 5.¹ Fluorination of Nitriles over Caesium Tetrafluorocobaltate(III)²

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Benzonitrile and the isomers of benzenedicarbonitrile (phthalo-, isophthalo-, and terephthalo-nitrile) have been fluorinated over caesium tetrafluorocobaltate(III) at elevated temperatures to give mixtures containing undecafluorocyclohexanecarbonitrile. In addition the dinitriles gave decreasing yields (1,4- > 1,3- > 1,2-) of the corresponding cyclohexanedicarbonitriles. Some reactions (addition, defluorination, hydrolysis, and reduction) of undecafluorocyclohexanecarbonitrile are described.

EARLY work suggested that a disadvantage of the high-valency transition-metal fluoride method³ for the fluorination of organic compounds is that functional groups are usually destroyed. However, carbonyl groups were shown to survive although the products were not the perfluoro-analogues of the organic reactants.⁴ The acceptance of the involvement of cation radicals in these fluorinations⁵ suggested that certain groups with high ionisation potentials (*e.g.* nitrile) might be resistant to fluorination. Indeed, mixtures of partially fluorinated nitriles were obtained from fluorinations of aceto- and propiono-nitrile with cobalt trifluoride and potassium tetrafluorocobaltate(III).⁶ These results linked with the preparation of perfluoroaromatic⁷ and heteroaromatic compounds⁸ using caesium tetrafluorocobaltate(III) prompted us to study the fluorination of benzenecarbonitriles.

RESULTS AND DISCUSSION

Caesium tetrafluorocobalt(III) reacted with benzonitrile to give dodecafluorocyclohexane and undecafluorocyclohexanecarbonitrile (1) together with small amounts of perfluoromethylcyclohexane, pentafluorobenzonitrile, 2-fluorobenzonitrile, and minor unidentified compounds (Table 1). The undecafluorocyclohexane-

TABLE 1

Compounds isolated from fluorinations of benzenecarbonitriles; amounts expressed as % total products isolated

	C ₆ F ₁₂	C ₆ F ₁₁ CN	C ₆ F ₁₀ (CN) ₂	Others
C ₆ H ₅ CN	13.2	54.9		28.8 ^a
<i>o</i> -C ₆ H ₄ (CN) ₂	30	42.2	12.2 (1,2-)	15.6 ^b
<i>m</i> -C ₆ H ₄ (CN) ₂	14.2	15.2	50.5 (1,3-)	20.1 ^b
<i>p</i> -C ₆ H ₄ (CN) ₂		16.1	74.8 (1,4-)	9.1 ^c

^a C₆F₅CN, 7.6; *o*-C₆H₄FCN, 2.2; C₆H₅CN, 19.0%. ^b Mixtures aromatic/fluoroaromatic not examined. ^c Mainly *o*-C₆H₄(CN)₂ and *o*-C₆F₄(CN)₂.

carbonitrile (1) is separated easily by fractional distillation of the major and more dense phase of the two-phase liquid fluorination product. This synthesis therefore provides an alternative route to that involving the dehydration of undecafluorocyclohexanecarboxamide (2),^{9,10} prepared from undecafluorocyclohexanecarbonyl fluoride.

The isomeric benzenedicarbonitriles were fluorinated with difficulty because of their low volatility. Each

fluorination product contained dodecafluorocyclohexane and/or undecafluorocyclohexane carbonitrile (1) and the corresponding undecafluorocyclohexanedicarbonitriles. Small amounts of solids were produced in some of the fluorinations and that from the fluorination of the 1,4-isomer was identified as a mixture of hydrocarbon starting material and the perfluoro-analogue. The compositions of typical fluorinations are recorded in Table 1.

The dicarbonitriles were identified by spectroscopic methods. The presence of two geometric isomers in the 1,3-isomer (ratio 1 : 2) and the 1,4-isomer (ratio 1 : 1.3) was indicated by ¹⁹F n.m.r. spectroscopy, although their respective identities were not assigned. The low yield of the 1,2-dicarbonitrile was disappointing since it was hoped to exploit the reactivity of the vicinal nitrile groups in the synthesis of *N*-heterocycles.

These results provide further examples which emphasise the different reactivities of cobalt trifluoride and caesium tetrafluorocobaltate(III) towards aromatic compounds. The absence of hydrogen-containing cyclohexane derivatives from the caesium tetrafluorocobaltate(III) fluorinations suggested that a stepwise replacement of hydrogen by fluorine to form the perfluoroarene becomes the dominant route.¹¹ It is unfortunate that at the high temperatures of these reactions most perfluoroarenes are readily converted to non-aromatic products. 3,3,6,6-Tetrafluorocyclohexa-1,4-diene was one of the major products of the fluorination of benzene⁷ with caesium tetrafluorocobaltate(III) and was resistant to further fluorination under similar reaction conditions. This diene is thought to play a major role in other transition-metal-fluoride reactions with benzene.¹¹ An analogous diene was not found in the caesium tetrafluorocobaltate(III) fluorination of benzonitrile. Whether it was not formed or was very reactive is not known, and so the significance of dienes in caesium tetrafluorocobaltate(III) fluorinations remains unresolved. Similar dienes have been isolated recently from reactions of nitrobenzene and of phenylethanone with lead dioxide in liquid hydrogen fluoride.¹²

Earlier fluorinations of perfluoroalkane nitriles with transition-metal fluorides afforded compounds containing -N=N- or >C=N-F groups¹³ but similar products were not isolated from our fluorinations.

Several reactions of undecafluorocyclohexanecarbonitrile (1) have been reported.^{10,14} Some other derivatives are now described (listed in Table 2). The nitrile is resistant to acidic hydrolysis but is readily converted to the amide (2) with dilute aqueous sodium hydroxide. Under more vigorous conditions ammonia and decafluorocyclohexane are produced, presumably *via* decomposition of the unstable carboxylate anion¹⁵ produced by hydrolysis.

Treatment of the nitrile with sodium dissolved in ethanol or methanol gave the expected imidates (3) and (4), showing characteristic i.r. absorptions in the region 1 670—1 675 cm⁻¹. However, prolonged heating of the former reaction mixture gave a multi-component

ation of the nitrile was not so straightforward. Conditions were chosen to favour the formation of a secondary amine.¹⁷ The reaction stopped after the uptake of approximately three molar proportions of hydrogen and a fuming liquid (HF evolved) was isolated. The characterisation of this material was impossible but boiling it with water afforded a white solid which was tentatively identified by spectroscopy as the cyclohexane-1,3-dione (9). The ¹⁹F n.m.r. spectrum showed three AB systems and a complex signal characteristic of the undecafluorocyclohexyl group and in addition two multiple signals (intensity 1:2) consistent with the presence of three difluoromethylene groups in the planar cyclohexane-1,3-dione ring. Addition of deuterium oxide

TABLE 2

R	1-F	2-F ₂ and 6-F ₂	J _{AB} /Hz	3-F ₂ and 5-F ₂	J _{AB} /Hz	4-F ₂	J _{AB} /Hz
CN (1)	-177.6	-118.1	293	-125.8	292	-126.1	287
CONH ₂ (2) ^a	-178.1	-130.1		-137.4		-140.7	
C(OEt)=NH (3)	-175.0	-118.6	291	-122.3	282	-123.2	282
C(OMe)=NH (4)	-175.0	-131.6		-138.0		-140.4	
C(NH ₂)=NH (5) ^b	-173.3	-118.6	293	-123.5	282	-123.4	288
CH ₂ NH ₂ (6)	-191.8	-132.9		-139.5		-142.1	
CH ₂ NHCOMe (7) ^b	-187.6	-118.6	296	-123.5	279	-122.9	279
CH ₂ NHCOPh (8) ^b	-187.0	-133.0		-139.9		-142.3	
		-116.8	321	-121.9	313	-121.4	290
		-133.1		-138.9		-141.6	
		-120.3	293	-124.0	285	-125.1	284
		-133.5		-140.2		-142.3	
		-118.8	299	-122.7	285	-123.9	291
		-133.8		-139.5		-141.9	
		-118.7	299	-122.5	288	-123.9	289
		-133.9		-139.3		-141.9	
CH ₂ NHCH=C(F ₂) ₂ (F ₂) ₂ (9) ^{b, c}	-186.6	-118.1	294	-122.5	287	-123.8	281
		-131.7		-139.1		-141.6	

^a In [2H₆]DMSO. ^b In [2H₆]acetone. ^c Also ¹⁹F n.m.r. signals at -124.0, -124.7, and -135.2 (ratio 2:2:2).

product comprising the imidate (3) and 1- and 3-ethoxynonafluorocyclohexene as major products. Obviously some of the imidate decomposed to decafluorocyclohexene which reacted with sodium ethoxide in the usual way.¹⁶ The acidic hydrolysis of the imidates gave the amide.

The amidine (5) formed easily when the nitrile was treated with anhydrous or aqueous ammonia. Slow decomposition to the amide (2) occurred which could be accelerated by boiling with dilute hydrochloric acid.

The reduction of the nitrile with lithium aluminium hydride gave a stable primary amine (6) which was characterised by conversion into the acetamido- (7) and benzamido- (8) derivatives. The i.r. spectra of these derivatives suggested a greater degree of hydrogen bonding in the acetamido-compound. Small amounts of neutral product from the reduction could not be positively identified as the aldehyde derived from the hydrolysis of an intermediate imine. The hydrogen-

to a perdeuterioacetone solution of the compound simplified the ¹H n.m.r. spectrum and this was consistent with the presence of a -CH₂-NH-CH= group.

There are many useful examples of the preparation of perfluoroarenes by defluorination of the corresponding perfluoroalicyclic over iron or nickel gauze or iron(III) oxide at elevated temperatures.¹⁸ However, there does not appear to be an example of this reaction involving substituent groups other than perfluoroalkyl. The defluorination of undecafluorocyclohexanecarbonitrile (1) with iron gauze gave a 4:1 mixture of pentafluorobenzonitrile and nonafluorocyclohexanecarbonitrile. The latter compound became the major product when the defluorination was carried out over iron(III) oxide. The u.v. spectrum of this vinylic compound indicated conjugation and the i.r. spectrum showed the presence of the C=C double bond but contained no absorption characteristic of the nitrile group. The presence of the nitrile group was confirmed by mild fluorination over cobalt

trifluoride which gave undecafluorocyclohexanecarbonitrile (1) as the major product. The isolation of the alkene from these defluorination processes is unusual and some reactions of the $\alpha\beta$ -unsaturated nitrile are being studied. These results demonstrate that in certain cases complex transition-metal fluorides can be used effectively for the synthesis of functionalised perfluorocarbons.

EXPERIMENTAL

Fluorinations were carried out as previously described in reactors of conventional design.³

G.l.c. separations were performed using Pye series 104 or 105 chromatographs with five columns (8 mm \times 9.1 m): Unit A, Ucon oil (50-HB-2000)-Chromosorb P (1:4); Unit B, Ucon oil (LB550-X)-Chromosorb P (1:4); Unit C, dinonyl phthalate-Celite (1:2); Unit D, silicone SE30-Universal B (1:9); Unit E, polyethylene glycol adipate-Chromosorb P 30-60 (1:6). I.r. spectra were measured with a Perkin-Elmer 257 grating spectrometer. ^1H (60 MHz) and ^{19}F (56.4 MHz) n.m.r. spectra were measured with Perkin-Elmer R10 or R12B spectrometers. Samples were dissolved in tetrachloromethane, unless stated otherwise, with tetramethylsilane (^1H) and trichlorofluoromethane (^{19}F) as internal standards.

Fluorinations of Benzonitrile, and Benzene-1,2-, -1,3-, and -1,4-dicarbonitriles with Caesium Tetrafluorocobaltate(III).—Benzonitrile (4.5 g portions) was fluorinated over caesium tetrafluorocobaltate(III) (ca. 250 g) at 300 °C in a stream of nitrogen (2 l h⁻¹) during 30 min. The nitrogen flow was increased (10 l h⁻¹) and maintained for a further 1 h. The products (4.8–6.0 g), which comprised two phases (A and B), were collected in glass traps cooled in liquid air, washed with water, and dried (MgSO_4).

In a similar manner to that described above, portions (5 g) of benzene-1,2-dicarbonitrile were fluorinated with difficulty at 375–385 °C to give products (2.1–2.4 g) which were filtered and washed with water. Similarly the 1,3- and 1,4-isomers (5 g) fluorinated at 380–390 °C gave liquid products (2.9–3.9 and 3.1–4.4 g, respectively). In the latter fluorination a solid product (ca. 0.5 g) was also isolated by filtration of the crude product before washing.

Separation and Identification of the Products.—(Unless stated otherwise compounds were identified by comparison of i.r. spectra with those of authentic samples.)

(a) *From benzonitrile.* The product separated into two phases, phase A (67% by weight) and a less dense phase B (33% by weight). A portion (2.03 g) of phase B was separated (Unit A, 167 °C, N_2 4 l h⁻¹) to give (i) undecafluorocyclohexanecarbonitrile (1) (0.11 g), b.p. 73.5 °C (C, 27.6; F, 67.8; N, 4.8%. Calc. for $\text{C}_7\text{F}_{11}\text{N}$: C, 27.4; F, 68.1; N, 4.5%); $\nu(\text{C}\equiv\text{N})$ 2 260 cm^{-1} ; m/e 307 ($\text{C}_7\text{F}_{11}\text{N}^+$); ^{19}F n.m.r., see Table 2; (ii) a mixture (0.04 g); (iii) pentafluorobenzonitrile (0.28 g); (iv) a mixture (0.08 g); (v) benzonitrile (0.38 g); and (vi) a mixture (0.5 g), a portion (0.28 g) of which was separated further (Unit A as above) to give benzonitrile (0.14 g) and 2-fluorobenzonitrile (0.03 g).¹⁹

A portion (1.61 g) of phase A was separated (Unit A, 49 °C, N_2 7.5 l h⁻¹) to give dodecafluorocyclohexane (0.22 g) and undecafluorocyclohexanecarbonitrile (1) (0.88 g, purity >95%).

A large-scale fluorination [Reactor, ca. 6 kg $\text{CsCo}^{\text{III}}\text{F}_4$] of benzonitrile (4 \times 80 g) gave products (523 g; phase A,

90%, and phase B, 10%). Distillation of phase A gave dodecafluorocyclohexane (271 g, >90% pure) and undecafluorocyclohexanecarbonitrile (1) (109 g), b.p. 66.5–74 °C.

(b) *From benzene-1,2-dicarbonitrile.* A portion (3.72 g) of the product was separated (Unit B, 25 °C, N_2 4.5 l h⁻¹) to give (i) mainly dodecafluorocyclohexane (0.68 g); (ii) a multi-component mixture (0.20 g); (iii) undecafluorocyclohexanecarbonitrile (1) (0.56 g); (iv) a multi-component mixture (0.64 g); and (v) a mixture (0.22 g) which was tentatively identified as *cis*- and *trans*-dodecafluorocyclohexane-1,2-dicarbonitriles, $\nu(\text{C}\equiv\text{N})$ 2 263 cm^{-1} .

(c) *From benzene-1,3-dicarbonitrile.* A portion (2.95 g) of the product was separated (Unit B, 25 °C, N_2 4.5 l h⁻¹) to give (i) mainly dodecafluorocyclohexane (0.24 g); (ii) a mixture (0.32 g) containing dodecafluorocyclohexane; (iii) undecafluorocyclohexanecarbonitrile (1) (0.26 g); (iv) a mixture (0.29 g) containing (1); (v) a mixture (0.63 g) of mainly two non-resolvable compounds which were further purified (Unit B, as above) to give *cis*- and *trans*-dodecafluorocyclohexane-1,3-dicarbonitrile (0.22 g), b.p. 97–99 °C (Found: C, 30.4; F, 60.2. $\text{C}_8\text{F}_{10}\text{N}_2$ requires C, 30.6; F, 60.5%); m/e 314 (M^+) and 295 ($M^+ - \text{F}$); $\nu(\text{C}\equiv\text{N})$ 2 270 cm^{-1} ; δ_{F} -108.6 to -135.7 (m), -174.6 (m), and -179.8 (m) (4:0.3:0.7, respectively); and (vi) a mixture (0.24 g) of mainly (v).

(d) *From benzene-1,4-dicarbonitrile.* A portion (4.54 g) of the liquid product was separated (Unit B, 31 °C, N_2 8 l h⁻¹) to give (i) a multi-component mixture (0.24 g); (ii) impure undecafluorocyclohexanecarbonitrile (1) (0.42 g); (iii) a mixture (0.34 g) of (ii) and (iv); and (iv) a mixture (2.10 g) of mainly two non-resolvable compounds, an aliquot (1.16 g) of which was further purified (Unit C, 34 °C, N_2 6 l h⁻¹) to give *cis*- and *trans*-dodecafluorocyclohexane-1,4-dicarbonitrile (0.86 g), b.p. 96.5–98.5 °C (Found: C, 30.4; F, 61.0. $\text{C}_8\text{F}_{10}\text{N}_2$ requires C, 30.6; F, 60.5%); $\nu(\text{C}\equiv\text{N})$ 2 269 cm^{-1} ; δ_{F} -114.3, -127.1 (J_{AB} 294 Hz), -118.1, -126.0 (J_{AB} , 285 Hz), -175.0 (m), and -183.2 (m) (AB: m, 4:1).

Reactions of Undecafluorocyclohexanecarbonitrile (1).—(a) *With sodium hydroxide.* Undecafluorocyclohexanecarbonitrile (1) (1.65 g) and aqueous sodium hydroxide (25 cm³) were shaken together at 25 °C for 40 min, and the mixture was then extracted with ether. The dried (MgSO_4) extract was evaporated and the residue recrystallised (tetrachloromethane) and sublimed (80 °C at 25 mmHg) to give undecafluorocyclohexanecarboxamide (2) (0.7 g), m.p. 103–105 °C (lit.,⁹ 105–106 °C) (Found: C, 25.7; H, 0.6; F, 64.1. Calc. for $\text{C}_7\text{H}_2\text{F}_{11}\text{NO}$: C, 25.9; H, 0.6; F, 64.3%); $\nu(\text{N}-\text{H})$ 3 450; $\nu(\text{C}=\text{O})$ 1 711, and $\nu(\text{N}-\text{H})$ 1 610 cm^{-1} ; τ 1.21 (NH_2); ^{19}F n.m.r., see Table 2.

In a similar experiment the nitrile (5 g) and aqueous 4M sodium hydroxide (50 cm³) were heated under reflux for 20 h. Ammonia was evolved. The organic phase was separated from the reaction mixture, washed, and distilled to give dodecafluorocyclohexene (2.5 g).

(b) *With sodium ethoxide.* A mixture of undecafluorocyclohexanecarbonitrile (1) (5 g), sodium (0.5 g), and ethanol (50 cm³) was kept at 25 °C for 30 min; water was then added and the organic phase separated, washed with water, and dried. Purification by g.l.c. (Unit D, 110 °C, N_2 6.5 l h⁻¹) gave *ethyl undecafluorocyclohexanecarboximidate* (3) (3.8 g), b.p. 144 °C (Found: C, 30.3; H, 1.5; F, 59.5; N, 4.2. $\text{C}_9\text{H}_6\text{F}_{11}\text{NO}$ requires C, 30.6; H, 1.7; F, 59.2; N, 4.0%); $\nu(\text{N}-\text{H})$ 3 330 and 3 300, $\nu(\text{C}=\text{N})$ 1 670 cm^{-1} ;

τ 1.75 (1 H, s, NH), 5.65 (2 H, q, CH₂, J_{HH} 7 Hz), and 8.7 (3 H, t, Me, J_{HH} 7 Hz); ¹⁹F n.m.r., see Table 2.

In a similar experiment the mixture was heated under reflux for 2 h, filtered to remove sodium fluoride (1.15 g), and poured into water. G.l.c. separation (Unit A, 100 °C, N₂ 6.5 l h⁻¹) of an aliquot of the multi-component organic phase (2.7 g) gave 1- and 3-ethoxynonafluorocyclohexene¹⁶ and the imidate (3) (2:1:4, respectively) as the major products, identified by i.r. spectroscopy.

(c) *With sodium methoxide.* In a similar experiment undecafluorocyclohexane carbonitrile (5 g), sodium (0.5 g), and dry methanol (50 cm³) gave *methyl undecafluorocyclohexanecarboximidate* (4) (4.1 g), b.p. 129–130 °C (Found: C, 28.2; H, 1.2; F, 61.3; N, 3.8. C₈H₄F₁₁NO requires C, 28.3; H, 1.2; F, 61.6; N, 4.1%); $\nu(\text{N-H})$ 3 335 and 3 300, $\nu(\text{C=N})$ 1 675 cm⁻¹; τ 1.4 (1 H, s, NH) and 6.1 (3 H, s, Me): ¹⁹F n.m.r., see Table 2.

The ethyl imidate (3) (1.1 g) and 4M hydrochloric acid were refluxed for 12 h. The white solid was filtered off to give undecafluorocyclohexanecarboxamide (2) (0.76 g), m.p. 105 °C, identified by comparison of its i.r. spectrum with that of an authentic sample.

(d) *With ammonia.* Undecafluorocyclohexanecarbonitrile (1) (5 g) and ammonia solution (specific gravity 0.88, 20 cm³) were shaken in a sealed glass tube for 48 h at 25 °C. The white solid was filtered off and washed to give *undecafluorocyclohexanecarboxamidine* (5) (3.5 g), m.p. 97–99 °C (Found: C, 26.5; H, 0.5; F, 64.7. C₇H₃F₁₁N₂ requires C, 25.9; H, 0.9; F, 64.5%); $\nu(\text{NH})$ 3 500 and 3 350 cm⁻¹; τ 3.5 (NH₂); ¹⁹F n.m.r., see Table 2. The amidine (5) (1 g) and 4M hydrochloric acid (15 cm³) were heated under reflux for 12 h. The solid was filtered off to give undecafluorocyclohexanecarboxamide (2) (0.81 g), m.p. 105 °C, identified by i.r. spectroscopy.

(e) *With lithium aluminium hydride.* Undecafluorocyclohexanecarbonitrile (1) (10 g) in dry ether (100 cm³) was added dropwise to a stirred suspension of lithium aluminium hydride (3.8 g) in ether (100 cm³) at 25 °C. After 4 h water (8 cm³) followed by 4M hydrochloric acid (150 cm³) were added carefully. The ether layer was separated and the aqueous layer extracted with ether. The combined ethereal solutions were dried (MgSO₄) and evaporated to leave a brown oil (0.6 g), which was discarded. The aqueous layer was made alkaline with aqueous sodium hydroxide solution and extracted continuously with ether. The dried extract was evaporated and the residue (5.3 g) was distilled to give (undecafluorocyclohexyl)methylamine (6) (2.1 g), b.p. 124–126 °C (lit.,⁹ 127–128 °C). (Found: C, 26.7; H, 1.3; F, 67.3. Calc. for C₇H₄F₁₁N: C, 27.0; H, 1.3; F, 67.2%); $\nu(\text{N-H})$ 3 438, 3 350, and 1 633, $\nu(\text{C-H})$ 2 960 cm⁻¹; τ 8.82 (2 H, s, NH₂) and 6.53 (2 H, d, CH₂, J_{HH} 17.7 Hz); ¹⁹F n.m.r., see Table 2.

Using normal procedures acetylation of the amine (6) (0.8 g) gave the *amide* (7) (0.42 g), m.p. 135.5–136.5 °C (Found: C, 30.6; H, 2.0; F, 58.7; N, 3.8. C₉H₆F₁₁NO requires C, 30.6; H, 1.7; F, 59.2; N, 4.0%); $\nu(\text{N-H})$ 3 272 and $\nu(\text{C=O})$ 1 663 cm⁻¹; τ 8.02 (3 H, s, Me), 5.60 (2 H, dd, CH₂, J_{HF} 19.8 and J_{HH} 6.3 Hz), and 2.36 (1 H, br s, NH); ¹⁹F n.m.r., see Table 2.

Also treatment of the amine (6) with benzoyl chloride gave the *benzamide* (8) (0.51 g), m.p. 130.5–132.5 °C (Found: C, 40.7; H, 1.9; F, 50.9; N, 3.4. C₁₄H₈F₁₁NO requires C, 40.5; H, 1.9; F, 50.4; N, 3.4%); $\nu(\text{N-H})$ 3 333 and $\nu(\text{C=O})$ 1 656 cm⁻¹; τ 5.53 (2 H, d, CH₂, J_{HF} 19.5 Hz) and 2.56, 2.15 (5 H, m, Ph); ¹⁹F n.m.r., see Table 2.

(f) *With hydrogen.* Undecafluorocyclohexanecarbonitrile (1) (5 g) in dry ether (75 cm³) was hydrogenated (H₂, 730 cm³) for 3 h in the presence of 10% palladium-charcoal (0.3 g). The catalyst was removed by filtration and the solvent evaporated to leave a fuming (HF evolved) viscous liquid (3.1 g) which was boiled with water (20 cm³) for 80 min. A pale yellow solid formed which was recrystallised (ethanol) and sublimed (170 °C, 25 mmHg) to give the *cyclohexane-1,3-dione* (9) (0.99 g), m.p. 217–219 °C (Found: C, 31.0; H, 0.7; F, 59.8; N, 2.5. C₁₄H₄F₁₇NO₂ requires C, 31.0; H, 0.8; F, 59.6; N, 2.6%); m/e 541.000 (M^+ requires 540.997); $\nu(\text{C=C})$ 1 709, $\nu(\text{C=O})$ 1 652 and 1 621 cm⁻¹; λ_{max} 307 (ϵ 8 000), 282 (ϵ 11 000), and 264 nm (ϵ 14 600); τ 4.89 (2 H, dd, CH₂, J_{HF} 18.6 and J_{HH} 6.3 Hz), 1.14 (1 H, d, =CH-, J_{HH} 14.4 Hz), and -1.58 (1 H, br s, NH); after D₂O addition, τ 4.87 (2 H, d, CH₂, J_{HF} 18.5 Hz) and 1.10 (1 H, s, =CH-); ¹⁹F n.m.r., see Table 2.

(g) *With iron(III) oxide.* Aliquots (3.1 g) of undecafluorocyclohexanecarbonitrile (containing <5% perfluoromethylcyclohexane impurity) were dripped into a vertical nickel tube (60 × 3.5 cm) packed with iron(III) oxide [pre-treated with perfluoromethylcyclohexane (25–50 g) at 400 °C] at 400–435 °C. The products (1.3–1.8 g) were collected in traps cooled in liquid air. G.l.c. separation (Unit C, 90 °C, N₂ 6.5 l h⁻¹) of a typical product (1.3 g) gave (i) perfluoromethylcyclohexane (0.03 g); (ii) undecafluorocyclohexanecarbonitrile (0.21 g); (iii) nonafluorocyclohexanecarbonitrile (0.68 g), b.p. 100–102 °C (Found: C, 31.0; F, 63.5; N, 5.5. C₇F₉N requires C, 31.2; F, 63.6; N, 5.2%); $\nu(\text{C=C})$ 1 690 cm⁻¹; m/e 269 (C₇F₉N⁺) and 250 (C₇F₈N⁺); λ_{max} 238 (ϵ 54 550) and 276 nm (ϵ 26 150); δ_{F} -103.1 (1 F, m, =CF-), -108.3 (2 F, d, -CF₂-), -120.6 (2 F, d, -CF₂-), and -134.4 (4 F, s, -CF₂-); and (iv) pentafluorobenzonitrile (0.04 g).

(h) *With iron gauze.* Aliquots (0.5 g) of undecafluorocyclohexanecarbonitrile were dripped into a stream of nitrogen flowing through a vertical nickel tube (63 × 2 cm) packed with iron gauze at 260–280 °C. The products (ca. 0.35 g) were flushed from the reactor and collected in a trap cooled in liquid air. G.l.c. separation (Unit C, 90 °C, N₂ 6.5 l h⁻¹) of the mixture (0.95 g) gave (i) a mixture (0.04 g) of perfluoromethylcyclohexane and undecafluorocyclohexanecarbonitrile; (ii) nonafluorocyclohexanecarbonitrile (0.12 g); and (iii) pentafluorobenzonitrile (0.51 g); all compounds were identified by i.r. spectroscopy.

The Fluorination of Nonafluorocyclohexanecarbonitrile.—The nitrile (1.7 g) was fluorinated in nitrogen (2 l h⁻¹) over cobalt trifluoride (150 g) at 97 °C. The product (0.5 g) was washed with iced water and saturated sodium hydrogen carbonate solution, distilled *in vacuo* from phosphorus pentoxide, and separated by g.l.c. (Unit C, 60 °C, N₂ 6.5 l h⁻¹) to give (i) mainly perfluoromethylcyclohexane (0.05 g); (ii) undecafluorocyclohexanecarbonitrile (0.31 g); and (iii) a mixture (0.02 g) of two unidentified compounds.

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