

Reactions of Polyfluorocyclohexane- and Polyfluorocyclohexene-carbonitriles

Gurjeet S. Phull, Raymond G. Plevey,* and John Colin Tatlow

The Department of Chemistry, The University of Birmingham, P.O. Box 363, Birmingham B15 2TT

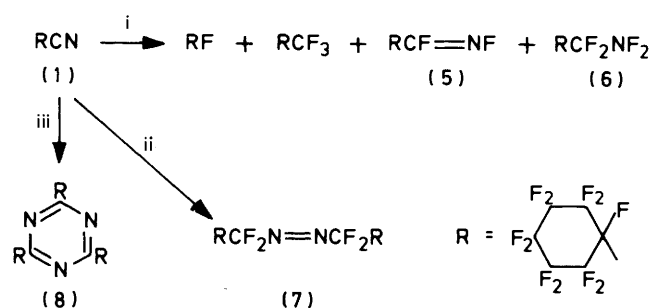
The vapour phase reaction of undecafluorocyclohexanecarbonitrile (1) with cobalt(III) or silver(II) fluoride caused stepwise saturation of the C≡N triple bond to give C₆F₁₁CF=NF and C₆F₁₁CF₂NF₂, whereas reaction in a sealed tube with silver(II) fluoride gave the azomethane C₆F₁₁CF₂N=NCF₂C₆F₁₁ and with silver(I) fluoride gave tris(undecafluorocyclohexyl)-*s*-triazine. Methylamine, isopropylamine, and dimethylamine with the nitrile (1) gave the corresponding amidines. Vapour phase fluorination of pentafluorobenzonitrile by cobalt(III) fluoride or potassium tetrafluorocobaltate(III) afforded the nitrile (1), together with nonafluorocyclohex-3-enecarbonitrile (4). The latter was oxidised by potassium permanganate to 3-cyanoheptafluorohexane-1,6-dioic acid. Nonafluorocyclohex-1-enecarbonitrile (2) underwent classical nucleophilic addition-elimination sequences with methanol and with sodium methoxide to give progressively octafluoro-2-methoxy-, heptafluoro-6,6-dimethoxy-, and hexafluoro-2,6,6-trimethoxy-cyclohex-1-enecarbonitrile, whilst with ammonia, 2-aminoheptafluoro-6-iminocyclohex-1-enecarbonitrile was formed, again by stepwise addition-elimination.

The cation-radical theory of fluorination¹ by high-valency metal fluorides suggests that the C≡N group, with its relatively high ionisation potential, should survive intact in the major products of fluorinations of nitriles. This was shown² for simple aliphatic nitriles, whilst benzonitrile and the three isomeric benzenedicarbonitriles afforded,³ respectively, undecafluorocyclohexanecarbonitrile (1), and the corresponding decafluorocyclohexanedicarbonitriles. This paper now records some further reactions of the nitrile (1), and some nucleophilic addition reactions of nonafluorocyclohex-1-enecarbonitrile (2), obtained,³ together with pentafluorobenzonitrile (3), by defluorination of (1) with iron(III) oxide. Fluorination of pentafluorobenzonitrile (3) by potassium tetrafluorocobaltate(III) afforded compound (1) and an isomer of (2), the 3-ene (4).

Results and Discussion

Undecafluorocyclohexane carbonitrile (1) was made, as before,³ by passing benzonitrile over caesium tetrafluorocobaltate(III) in a standard vapour phase reactor at 300 °C. To determine whether more reactive fluorinating agents would attack the nitrile group, compound (1) was passed over cobalt(III) fluoride in a similar vapour phase reactor at 230–245 °C to give a mixture with two major and three minor constituents. The major components were undecafluoro(trifluoromethyl)cyclohexane, and unchanged (1), and a little dodecafluorocyclohexane was also present. The other two minor constituents were new products, arising by saturation of the C≡N bond: in reverse order of isolation by g.l.c., they were [fluoroimino(fluoro)methyl]undecafluorocyclohexane (5) and the difluoroamino analogue (6). The structures of both were clear from analysis, mass spectrometry, and ¹⁹F n.m.r. spectroscopy, and compound (5) had an i.r. band at 1 680 cm⁻¹ (C=N). The fluorination was very sensitive to reaction conditions, and it was difficult to get good recoveries of (5) and (6). Once the reaction started, significant nitrogen loss to give fluorocarbons also occurred. A similar vapour phase reaction using silver(II) fluoride gave the same products, but showed that the silver fluoride was a more powerful reagent; results at 85–90 °C paralleled those from cobalt(III) fluoride at 230–240 °C.

When the reaction with silver(II) fluoride was carried out in a sealed glass tube at 130 °C, the product obtained was the bis(undecafluorocyclohexyl)azomethane (7). Under these



Reagents: i, CoF₃ or AgF₂; ii, AgF₂ (sealed tube); iii, AgF

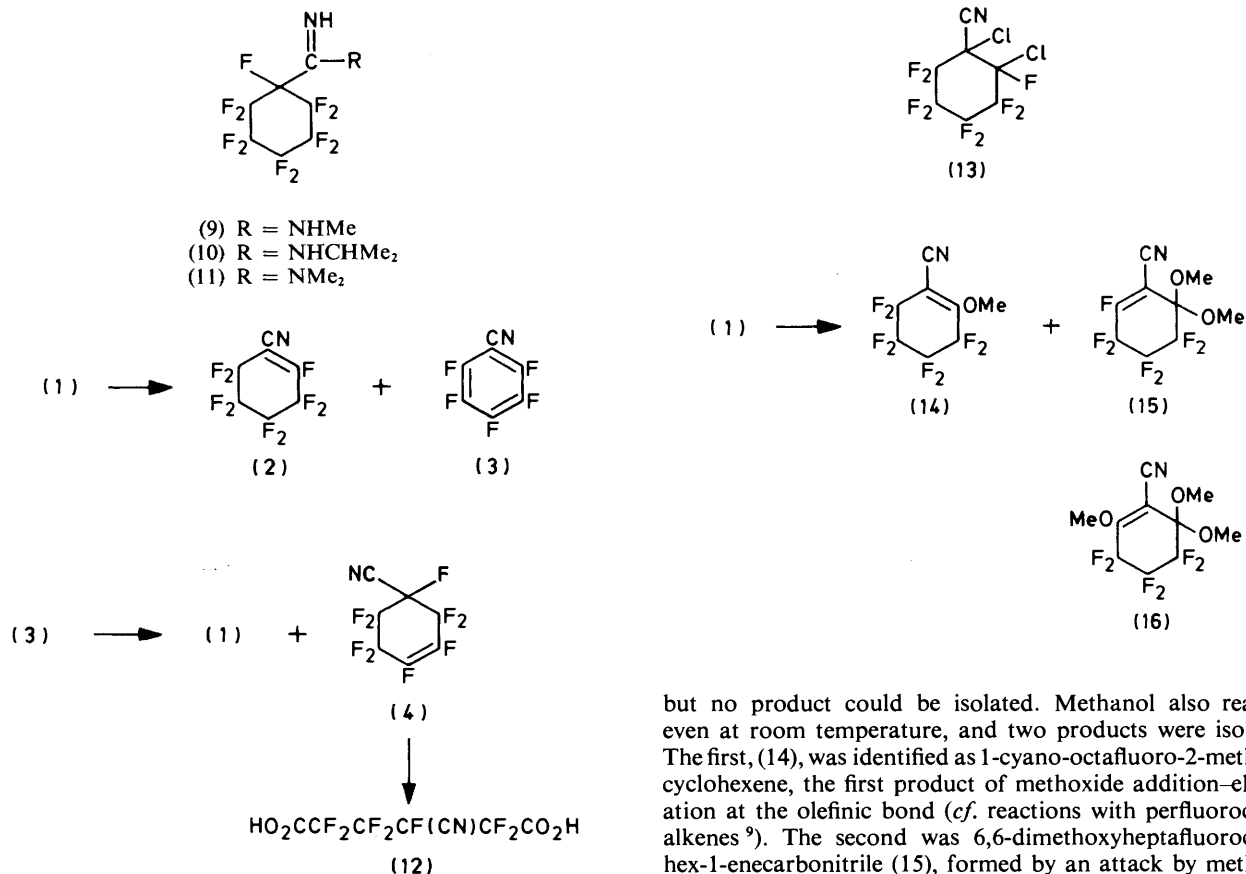
conditions, following fluorination at the carbon of the nitrile group, the reaction intermediate, presumably a radical species, dimerises and adds further fluorine to give the azo compound (7). In the vapour phase reactions further fluorination of this intermediate at nitrogen takes precedence to give product (5) and thence (6). The azomethane (7) showed, on g.l.c. analysis, two close peaks (ratio 9 : 1) for which mass spectrometry gave identical top masses and very similar fragmentation patterns. Product (7) therefore consisted of a mixture of *syn*- and *anti*-stereoisomers.

Saturation of the triple bond of trifluoroacetonitrile using cobalt(III) fluoride has been reported,⁴ and also the formation⁵ of dimers and trimers from this nitrile and its homologues by mercury and silver fluorides. In conformity, the nitrile (1) was found to give 2,4,6-tris(undecafluorocyclohexyl)-1,3,5-triazine (8) when treated with silver(I) fluoride in a sealed tube. This product was known⁶ from an alternative synthesis.

The cyano group of the nitrile (1) would be expected to react readily with nucleophiles. Methylamine, isopropylamine, and dimethylamine each reacted smoothly in aqueous solution, to give the appropriate carboxamidines [(9), (10), and (11) respectively]. By analogy with trifluoromethyl-substituted amidines,⁷ the alkyl groups were assumed to be attached to the saturated nitrogen.

Defluorination of the saturated nitrile (1) with iron gauze or iron(III) oxide afforded³ nonafluorocyclohex-1-enecarbonitrile (2) in moderate yield, together with pentafluorobenzonitrile (3). The first attack would be expected at the tertiary fluorine, to give (2).

It was of interest to subject the nitrile (3) to vapour phase



fluorination by cobalt(III) fluoride. Fluorinations of several pentafluoroaryl compounds (C₆F₅X) have yielded⁸ polyfluorocyclohexenes and -hexadienes, with the substituent X carried on the double bonds. The result with the nitrile (3) did not follow this pattern; the products were the saturated nitrile (1), unidentified material (probably mainly dienes), and nonafluorocyclohex-3-enecarbonitrile (4). The structure of (4) followed from its ¹⁹F n.m.r. spectrum, there being only one vinylic fluorine signal (at -160 p.p.m.), and the chemical shifts of the >CF₂ groups fitted the 3-ene structure better than the 2-ene. The fluorination over potassium tetrafluorocobaltate(III) went much better, and a higher yield of compound (4) was obtained.

This is the first occasion that a structure such as (4), with a CF=CF double bond, has been obtained as the major product from the fluorination of a pentafluorophenyl derivative. A comparable fluorination of octafluorotoluene, for example,⁸ gives the product corresponding to compound (2). However, the cyano group is the first unsaturated function to be involved in a fluorination of this type; it may conjugate with intermediate radicals in a way that CF₃ cannot.

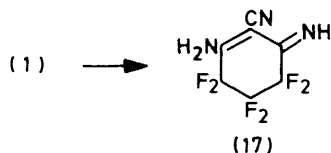
The nitrile (4) was oxidised in the standard way with potassium permanganate in acetone. The 3-cyanoheptafluorohexane-1,6-dioic acid (12) obtained was isolated as its dianilinium salt and the structure was confirmed by its ¹⁹F n.m.r. spectrum.

Though the cyano-3-ene (4) has isolated unsaturated centres, presumably reacting independently, it was of interest to try the effect of addition reactions on the cyano-1-ene (2), with its conjugated unsaturation. Chlorine under u.v. irradiation proceeded, though only very slowly, to give a mixture of *cis*- and *trans*-1,2-dichlorononafluorocyclohexanecarbonitrile (13). Nucleophilic additions with the nitrile (2) went extremely readily however. Even water alone reacted at 100 °C,

but no product could be isolated. Methanol also reacted, even at room temperature, and two products were isolated. The first, (14), was identified as 1-cyano-octafluoro-2-methoxycyclohexene, the first product of methoxide addition-elimination at the olefinic bond (*cf.* reactions with perfluorocycloalkenes⁹). The second was 6,6-dimethoxyheptafluorocyclohex-1-enecarbonitrile (15), formed by an attack by methanol on the double bond of the primary product (14), followed by regeneration of a double bond in a different position. Both structures were clear from the analyses and spectroscopic characteristics of the respective compounds. There was also a trace of a third product, which was the only one isolated when sodium methoxide was used as the attacking nucleophile. This was hexafluoro-2,6,6-trimethoxycyclohex-1-enecarbonitrile (16).

These three products [(14)–(16)] were formed by progressive attack of methoxide on the appropriate olefinic bond and no attack on the cyano group was detected. Addition to the double bond was always directed so that the negative charge of the anionic intermediate was located on the carbon carrying the cyano group. This is clearly the expected direction of attack on the C=C double bond (*cf.* addition reactions of the analogous nonafluoro-1-trifluoromethylcyclohex-1-ene¹⁰). The parent 1-cyano-ene (2) itself shows³ evidence of conjugation (appropriate u.v. spectrum; no i.r. absorption for the nitrile group) and, furthermore, the nitrile group of the saturated compound (1) readily forms³ carboximidate esters with sodium alkoxides. However, it seems that the only significant effect of the nitrile group in (2) is to activate the olefinic bond towards classical nucleophilic attack; it neither distorts the pattern of this attack, nor is it as reactive itself towards the reagents. This double bond reactivity gives rise to products (15) and (16), interesting dimethoxy acetals arising by methoxide attack on a carbon already bearing a methoxy group, and followed by double bond migration with loss of fluoride ion. Reaction stops at (16) since further migrations of this type cannot take place.

Ammonia attacks olefinic bonds in polyfluorocycloalkenes with formation^{11,12} of imino-enamines. Such a reaction occurred with the nitrile (2), the product being 2-aminoheptafluoro-6-iminocyclohex-1-enecarbonitrile (17). This is analogous to the product¹² from the above-mentioned nonafluoro-1-trifluoromethylcyclohexene. Again, the nitrile group in (2)



promotes a very rapid reaction, but does not get involved itself, despite ready amidine formation from (1) and ammonia.

Experimental

Fluorinations, spectroscopy, and g.l.c. separations were carried out as previously described.³ An additional g.l.c. column was used; Unit F, silicone rubber SE30–Universal Support B (1:9). Given for each separation are the Unit used,³ the temperature (°C), and the nitrogen overpressure (lb in⁻²). The n.m.r. results are recorded in the order: chemical shift in p.p.m., then type of signal, coupling constants and relative intensity in brackets. Samples were dissolved in tetrachloromethane, unless stated otherwise, with tetramethylsilane (¹H) and trichlorofluoromethane (¹⁹F) as internal standards. Ether refers to diethyl ether.

Fluorinations of Undecafluorocyclohexanecarbonitrile (1).—

(a) *In the vapour phase over cobalt(III) fluoride.* In a typical run, the nitrile (1) (3.1 g) in a stream of nitrogen (2 l h⁻¹) was passed during 30 min through a small stirred nickel reactor (150 g CoF₃) at 230–245 °C. The reactor was then swept with nitrogen (4 l h⁻¹) for 45 min and the product was collected in a glass trap cooled by liquid nitrogen. The product was washed with iced water and saturated aqueous sodium hydrogen carbonate, and dried (MgSO₄). After being filtered, part (1.9 g) of the product (10.1 g) from four such runs was separated by g.l.c. (Unit C, 50 °C, 20 lb in⁻²) to give (i) dodecafluorocyclohexane (0.02 g); (ii) undecafluoro(trifluoromethyl)cyclohexane (0.71 g); and (iii) recovered (1), all of which were identified by g.l.c. and i.r.; (iv) [difluoroamino(difluoro)methyl]undecafluorocyclohexane (6) (0.05 g), b.p. 100–102 °C (Found: C, 22.0; F, 74.8. C₇F₁₅N requires C, 21.9; F, 74.4%), *m/z* (*M*⁺ not detected) 364 (*M* – F), δ(¹⁹F) *ca.* 19.5 (br, 2 F), –108.0 (c, 2 F), –119.8 and –130.0 (AB, *J* 300 Hz, 4 F), –122.9 and –139.9 (AB, *J* 288 Hz, 4 F), –124.7 and –142.4 (AB, *J* 288 Hz, 2 F), and –188.1 (c, 1 F); (v) fluoroimino(fluoro)methylundecafluorocyclohexane (5) (0.07 g), b.p. 86–89 °C (Found: *m/z* 344.9830. C₇F₁₃N requires 344.9823), *v*_{max.} 1 680 cm⁻¹ (C=N), δ(¹⁹F) –6.2 (cd, *J*_d 45 Hz, 1 F), –70.6 (c, 1 F), –118.0 and –131.2 (AB, *J* 284 Hz, 4 F), –123.1 and –139.3 (AB, *J* 289 Hz, 4 F), –124.2 and –142.0 (AB, *J* 288 Hz, 2 F), and –184.3 (c, 1 F).

(b) *In the vapour phase over silver(II) fluoride.* Under conditions similar to those in (a), but at reactor temperature 80–85 °C, the product (1.33 g) was separated (Unit C, 70 °C, 15 lb in⁻²) into (i) undecafluoro(trifluoromethyl)cyclohexane containing some dodecafluorocyclohexane (0.30 g); (ii) recovered (1) (0.10 g) together with (6) (0.10 g) and (5) (0.02 g); all were identified by g.l.c. and i.r.

(c) *With silver(II) fluoride in a sealed tube.* The nitrile (1) (5.0 g) and freshly prepared silver(II) fluoride (7.14 g) were sealed in a hard-glass Carius tube and shaken at 130 °C for 4 days. The solid product was distilled (0.1 mmHg) and the volatile portion 'sublimed' onto a cold finger to give perfluoro- $[\alpha, \alpha'$ -bis(cyclohexyl)azomethane] (7) (1.76 g), m.p. 29–32 °C, b.p. 107–110 °C (Found: C, 24.4; F, 71.9; N, 4.1. C₁₄F₂₆N₂ requires C, 24.4; F, 71.6; N, 4.1%); *m/z* (*M*⁺ not detected), 671 (*M* – F), and 331 (C₆F₁₁CF₂); *v*_{max.} 1 550 cm⁻¹ (vw); δ(¹⁹F) –99.7 (t, *J* 14.7 Hz, 2 F), –119.6 and –129.4 (AB, *J* 299 Hz, 4 F), –123.0 and –140.0 (AB, *J* 282 Hz, 4 F), –125.3

and –142.2 (AB, *J* 280 Hz, 2 F), and –189.5 (s, 1 F). G.l.c. showed two close peaks (9:1) and the g.l.c. (OV25 column)–mass spectrum showed that each had the same (*M* – F) and very similar cracking patterns.

(d) *With silver(I) fluoride in a sealed tube.* The nitrile (1) (5.0 g) and silver(I) fluoride (2.9 g) were sealed under vacuum in a hard-glass Carius tube, which was shaken at 104 °C for 65 h. After being cooled by liquid N₂, the tube was opened, and vacuum distillation afforded recovered (1) (0.79 g). The residue was extracted with dry acetone (50 cm³), the solution filtered, dried (MgSO₄), and evaporated to leave a pale yellow solid (1.93 g). A portion (0.5 g) dissolved in acetone gave by g.l.c. (Unit F, 150 °C, 15 lb in⁻²) (i) acetone; (ii) undecafluorocyclohexylcarboxamide³ (0.6 g) (by i.r.); (iii) 2,4,6-tris(undecafluorocyclohexyl)-1,3,5-triazine (8) (0.26 g), m.p. 143–145 °C (lit.,⁶ 95–97 °C) (Found: C, 27.5; N, 4.7. Calc. for C₂₁F₃₃N₃: C, 27.4; N, 4.6%) (Found: *m/z* 920.9655. Calc. for C₂₁F₃₃N₃: *M* 920.9565), i.r. and δ(¹⁹F) values as reported.⁶

Amidines from the Undecafluoronitrile (1).—

(a) The nitrile (7.7 g) was added during 15 min to aqueous methylamine (25% w/v; 5 cm³). After being refluxed for 2 h, the mixture was cooled, the solid filtered off, dried, and sublimed (50 °C/18 mmHg) to give N¹-methylundecafluorocyclohexanecarboxamidine (9) (5.0 g), m.p. 49–51 °C (Found: C, 28.6; H, 1.4; F, 61.4; N, 8.6. C₈H₅F₁₁N₂ requires C, 28.4; H, 1.5; F, 61.8; N, 8.3%); *v*_{max.} 1 675 and 1 640 cm⁻¹; τ [(CD₃)₂SO] 3.2 (2 H, br, NH) and 7.15 (3 H, s, NMe); δ(¹⁹F) –118.6 and –133.9 (AB, *J* 293 Hz, 4 F), –122.7 and –139.3 (AB, *J* 290 Hz, 4 F), –123.2 and –142.5 (AB, *J* 297 Hz, 2 F), and –175.7 (c, 1 F).

(b) The nitrile (1) (3.0 g), isopropylamine (1.0 g), and water (5 cm³) were mixed and refluxed for 15 min, cooled and the liquid product separated off. After being seeded by the product from (a), this crystallised and was dried and sublimed (60 °C/18 mmHg) to give N¹-isopropylundecafluorocyclohexanecarboxamidine (10) (2.6 g), m.p. 36–40 °C (Found: C, 32.5; H, 2.4; F, 57.4; N, 7.4. C₁₀H₉F₁₁N₂ requires C, 32.8; H, 2.5; F, 57.1; N, 7.6%); *v*_{max.} 1 620 cm⁻¹; τ 3.5 (1 H, br, NH), 5.45 (1 H, br, NH), 5.85 (1 H, c, CH), and 8.76 (6 H, m, Me); δ(¹⁹F) –118.8 and –133.1 (AB, *J* 318 Hz, 4 F), –122.6 and –138.4 (AB, *J* 275 Hz, 4 F), –122.9 and –142.3 (AB, *J* 287 Hz, 2 F), and –175.6 (c, 1 F).

(c) The nitrile (1) (3.0 g) and aqueous dimethylamine (30% w/v; 4 cm³) gave a liquid product, distillation affording N¹,N¹-dimethylundecafluorocyclohexanecarboxamidine (11) (2.4 g), b.p. 155–160 °C (Found: C, 30.6; H, 1.9; F, 59.4; N, 7.7. C₉H₇F₁₁N₂ requires C, 30.7; H, 2.0; F, 59.4; N, 8.0%); *v*_{max.} 1 625 cm⁻¹; τ 2.0 (1 H, br, NH), and 7.04 (6 H, d, *J* 3 Hz, NMe); δ(¹⁹F) –118.0 and –133.0 (AB, *J* 296 Hz, 4 F), –122.6 and –139.0 (AB, *J* 287 Hz, 4 F), –122.6 and –142.3 (AB, *J* 286 Hz, 2 F), and –171.4 (c, 1 F).

Fluorination of Pentafluorobenzonitrile (3) in the Vapour Phase.—

(a) *Over cobalt(III) fluoride.* The nitrile (3) (2.0 g) in a stream of nitrogen (2 l h⁻¹) was passed during 30 min through the reactor at 165–170 °C [as for the nitrile (1), expt. (a)]. A portion (0.9 g) of the product (2.0 g) gave by g.l.c. (Unit C, 45 °C, 20 lb in⁻²) (i) a mixture (0.19 g) comprising mainly nitrile (1), but also containing an unidentified cyclohexadiene; (ii) a solid (0.16 g) mixture of at least three compounds; (iii) nonafluorocyclohex-3-enecarbonitrile (4) (0.28 g), b.p. 84–85 °C (Found: C, 31.0; F, 63.9; N, 4.9. C₇F₉N requires C, 31.2; F, 63.6; N, 5.2%); *m/z* 269 (*M*⁺); *v*_{max.} 2 260 (C≡N) and 1 750 cm⁻¹ (C=C), δ(¹⁹F) (also at 100 MHz) –99.9 and –117.5 (AB, *J* 290 Hz, 2 F), –108.6 and –124.7 (AB, *J* 190 Hz, 2 F), –117.8 and –129.5 (AB, *J* 283 Hz, 2 F), –160.0 (c, 2 F), and –172.3 (c, 1 F).

(b) *Over potassium tetrafluorocobaltate(III)*. This was carried out as in (a) above but at 210 °C, to give a comparable yield of crude product. Separation (0.7 g) as before gave (i) a mixture (0.05 g) of the nitrile (1) and hexadiene; (ii) a solid mixture (0.02 g); and (iii) the nitrile (4) (0.41 g), identified by g.l.c. and i.r.

Oxidation of Nonafluorocyclohex-3-enecarbonitrile (4).—Compound (4) (0.5 g) was added to stirred potassium permanganate (0.3 g) in dry acetone (100 cm³) at 25 °C. After 30 min, water (100 cm³) was added, and the bulk of the acetone distilled off under reduced pressure. After being acidified with aqueous sulphuric acid (2M; 5 cm³), and decolourised by sulphur dioxide, the solution was extracted with ether (5 × 10 cm³). To the dried (MgSO₄) and filtered extracts, freshly distilled aniline (2 cm³) was added. The resultant precipitate was recrystallised from trichloromethane-acetone to give the *dianilinium salt* of 3-cyanoheptafluorohexane-1,6-dioic acid (0.54 g), m.p. 155–156 °C (Found: C, 47.5; H, 3.2; F, 27.5; N, 8.8. C₁₉H₁₆F₇N₃O₄ requires C, 47.2; H, 3.3; F, 27.5; N, 8.7%); τ 2.5–3.1 (br, Aryl H), and 8.0 (br, NH); δ(¹⁹F) –110.7 (c, 2 F), –115.6 (c, 4 F), and –175.3 (c, 1 F).

Reactions of Nonafluorocyclohex-1-enecarbonitrile (2).—(a) *With chlorine*. The nitrile (2) (1.73 g) and chlorine (2.7 g) were sealed in a hard-glass Carius tube and irradiated with u.v. light for 1 week at ca. 15 °C. Distillation (at 15 mmHg) of the product afforded 1,2-dichlorononafluorocyclohexanecarbonitrile (13) (2.04 g), m.p. 78–80 °C (Found: C, 24.9; Cl, 20.9; F, 50.0; N, 4.0. C₇Cl₂F₉N requires C, 24.7; Cl, 20.9; F, 50.3; N, 4.1%); ν_{max.} 2 260 cm⁻¹; δ(¹⁹F) –108 to –141 (overlapping ABs etc.).

(b) *With methanol*. The nitrile (2) (0.5 g) was added slowly with stirring to dry methanol (2 cm³), heat being evolved. After 1 h at 15 °C, the mixture was poured into water (10 cm³), and the fluorocarbon layer separated by g.l.c. (Unit F, 70 °C, 15 lb in⁻²) to give (i) methanol; (ii) octafluoro-2-methoxycyclohex-1-enecarbonitrile (14) (0.11 g), b.p. 168–170 °C (Found: C, 33.1; H, 1.0; N, 4.6. C₈H₃F₈NO requires C, 34.2; H, 1.1; N, 5.0%); ν_{max.} 1 635 (C=C), 2 215 cm⁻¹ (C≡N); τ 5.55 (3 H, s, OMe); δ(¹⁹F) –105.3 (s, 2 F), –117.6 (s, 2 F), and –134.8 (s, 4 F); (iii) heptafluoro-6,6-dimethoxycyclohex-1-enecarbonitrile (15) (0.05 g), m.p. 48 °C (Found: C, 37.0; H, 2.1; N, 5.1. C₉H₆F₇NO₂ requires C, 36.9; H, 2.1; N, 4.8%); ν_{max.} 1 680 (C=C), 2 315 cm⁻¹ (C≡N); τ 6.37 (m, OMe); δ(¹⁹F) –110.5 (tt, J 25 and 5 Hz, 1 F), –120.4 (dp, J 25 and 5 Hz,

2 F), –124.1 (m, 2 F), and –127.9 (m, 2 F); (iv) a mixture (0.05 g) containing product (16).

(c) *With sodium methoxide*. Compound (2) (1.35 g) was added during 15 min to a solution of sodium (0.12 g) in dry methanol (10 cm³) at 25 °C. After being stirred for 4½ h, the mixture was poured into water (30 cm³) which was cooled to 0 °C, and the precipitate (1.33 g) was filtered off and dried to give hexafluoro-2,6,6-trimethoxycyclohex-1-enecarbonitrile (16), m.p. 34–36 °C, b.p. 165–167 °C (Found: C, 39.0; H, 2.9; F, 37.4; N, 4.4. C₁₀H₉F₆NO₃ requires C, 39.3; H, 3.0; F, 37.4; N, 4.6%); ν_{max.} 1 630 (C=C), 2 240 cm⁻¹ (C≡N); τ 5.74 (3 H, s, OMe), 6.48 (6 H, s, OMe); δ(¹⁹F) –116.4 (m, 2 F), –128.0 (m, 2 F), and –131.2 (m, 2 F).

(d) *With ammonia*. The nitrile (2) (1.0 g) in water (3 cm³) was added dropwise with shaking to aqueous ammonia (d 0.88; 2 cm³). A solid was formed in an exothermic reaction and was filtered off, washed with water and aqueous ethanol, and dried to yield 2-aminoheptafluoro-6-iminocyclohex-1-enecarbonitrile (17) (0.35 g), m.p. 160–162 °C (Found: C, 34.9; H, 1.1; F, 46.7; N, 17.6. C₇H₃F₆N₃ requires C, 34.6; H, 1.2; F, 46.9; N, 17.3%); ν_{max.} 1 660–1 680 (C=C), 2 220 cm⁻¹ (C≡N); λ_{max.} 290 nm (ε 30 400); τ 1.05 (br, NH); δ(¹⁹F) –119.4 (ct, J 10 and 10 Hz, 4 F), –135.8 (p, J 10 Hz, 2 F).

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