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N-HALOGENO COMPOUNDS. PART 12 [1]. SITE-SPECIFIC FLUORINATION OF CARBANIONS WITH PERFLUORO-N-FLUOROPIPERIDINE [2]

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SUMMARY

Perfluoro-N-fluoropiperidine (1) acts as a site-selective electrophilic fluorinating agent towards carbanionic substrates [Me_2CNaNO_2 → Me_2CFNO_2; PhMgBr → PhF; $PhCNa(CO_2Et)_2$ → $PhCF(CO_2Et)_2$; $EtCNa(CO_2Et)_2$ → $EtCF(CO_2Et)_2$; $\overbrace{CH_2(CH_2)_2COCNaCO_2Et}$ → $\overbrace{CH_2(CH_2)_2COCFCO_2Et}$], but in doing so is converted to perfluoro-1-azacyclohexene (2). Unfortunately, this imidoyl fluoride (2) is highly electrophilic and competes with the N-F compound (1) for carbanionic species, as exemplified by the formation of the 2-substituted octafluoro-1-azacyclohexenes $\overbrace{CF_2(CF_2)_3N{=}CR}$, where R = Ph, $CEt(CO_2Et)_2$, and $\overbrace{C(CO_2Et)CO(CH_2)_2CH_2}$ in the respective cases of the last three sodio derivatives listed above.

INTRODUCTION

During the past ten years N-fluoro compounds [3] have featured prominently in the search for easily handled (safe-in-use, storable, transportable), relatively cheap (perhaps via recycling), regio- and enantio-selective electrophilic fluorinating agents as alternatives to perchloryl fluoride [4], O-F reagents (hypofluorites [3b, 4, 5]), xenon difluoride [6], or fluorine itself [7]. This paper concerns the fluorination of carbanions with the prototypical "F^+ transfer" agent of the N-F class, namely perfluoro-N-fluoropiperidine (1), the object

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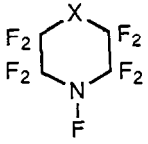
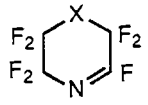
being to provide virtually the first detailed experimental data and thereby to highlight the seemingly little known drawback [8] that the imidoyl fluoride perfluoro-1-azacyclohexene (**2**) produced during fluorination competes with its progenitor for the substrate. Clearly, loss in this manner of perhaps hard-won or costly starting material increases the unattractiveness of the low-yield synthesis of perfluoro-N-fluoropiperidine by the Simons electrochemical fluorination process (8% from pyridine [9]; 13% from 2-fluoropyridine [10]).

Exactly the same problems arise with the morpholino analogue (**3**) of the piperidine (**1**), which we have also used to fluorinate carbanions, e.g. **3** + 2-thienyl-lithium → 2-fluorothiophen [11]. The N-F compound is obtainable only in low yield (8%) by Simons electrochemical fluorination of morpholine [12]; naturally, transfer of "F^+" in this case leads to release of the electrophilic oxa-imine **4**.



(**1**) X = CF_2

(**3**) X = O



(**2**) X = CF_2

(**4**) X = O

For the record, perfluoro-N-fluoropiperidine (**1**) is a seemingly innocuous volatile liquid (b.p. 49.5 °C) which holds the distinction of being only the second compound to be identified as an electrophilic fluorinating agent. Perchloryl fluoride, a hazardous gas (b.p. -46.8 °C) [13], was the first (mid-to-late 1950s), but its manipulation is still judged by many to be too problematical for "general" use [see, however, ref.14].

Initially (early 1960s), perfluoro-N-fluoropiperidine (**1**) was shown to be capable of effecting the conversions Me_2CNaNO_2 → Me_2CFNO_2 and

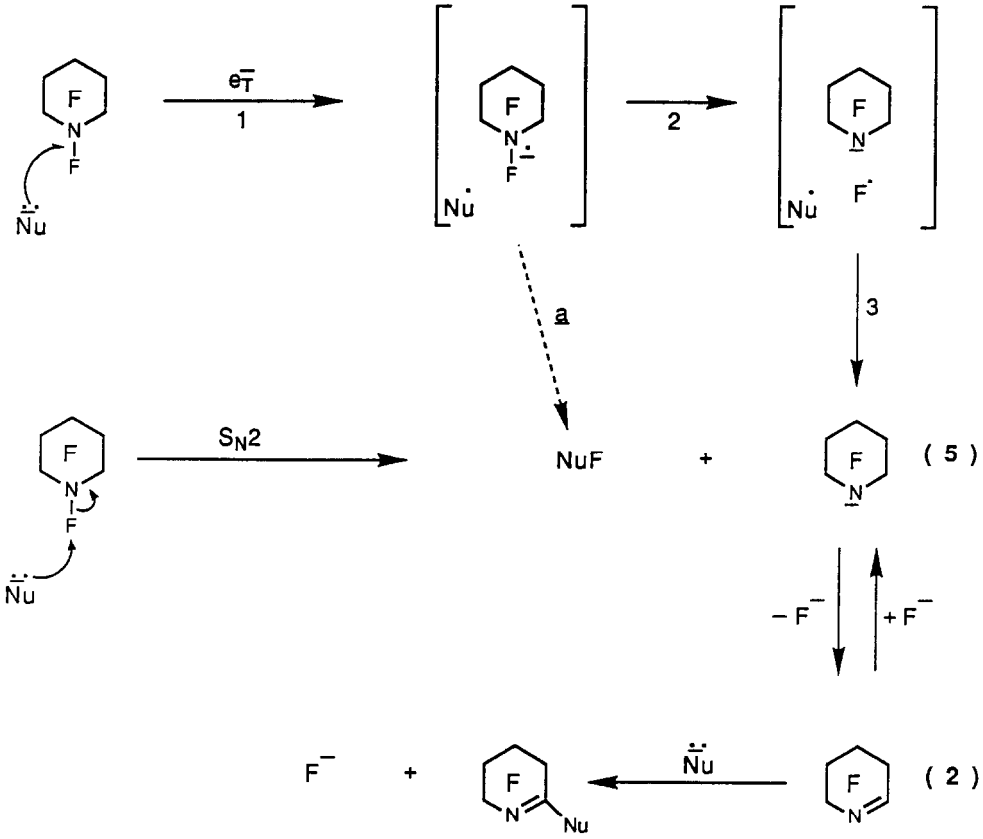
$CHNa(CO_2Et)_2$ → $CF_2(CO_2Et)_2$ [15]. Subsequently, it was employed to convert piperidine itself to N-fluoropiperidine [16], triphenyl-phosphine, -arsine and -stibine to the difluorides Ph_3PF_2, Ph_3AsF_2 and Ph_3SbF_2 respectively [16], perfluoroisopropylcaesium to perfluoropropane [17], NN-dialkylanilines (alkyl = Me or Et) to o-fluoro derivatives [18], sodium phenoxide to o- and p-fluorophenol [19], and lithium 2,4,6-tri-t-butylphenoxide and the corresponding phenoxy radical to 6-fluoro-2,4,6-tri-t-butylcyclohexa-2,4- and 4-fluoro-2,4,6-tri-t-butylcyclohexa-2,5-dienone, respectively [19].

Polymeric analogues of perfluoro-N-fluoropiperidine are known which will fluorinate carbanions, e.g. $PhCNa(CO_2Et)_2$ → $PhCF(CO_2Et)_2$ [20].

RESULTS AND DISCUSSION

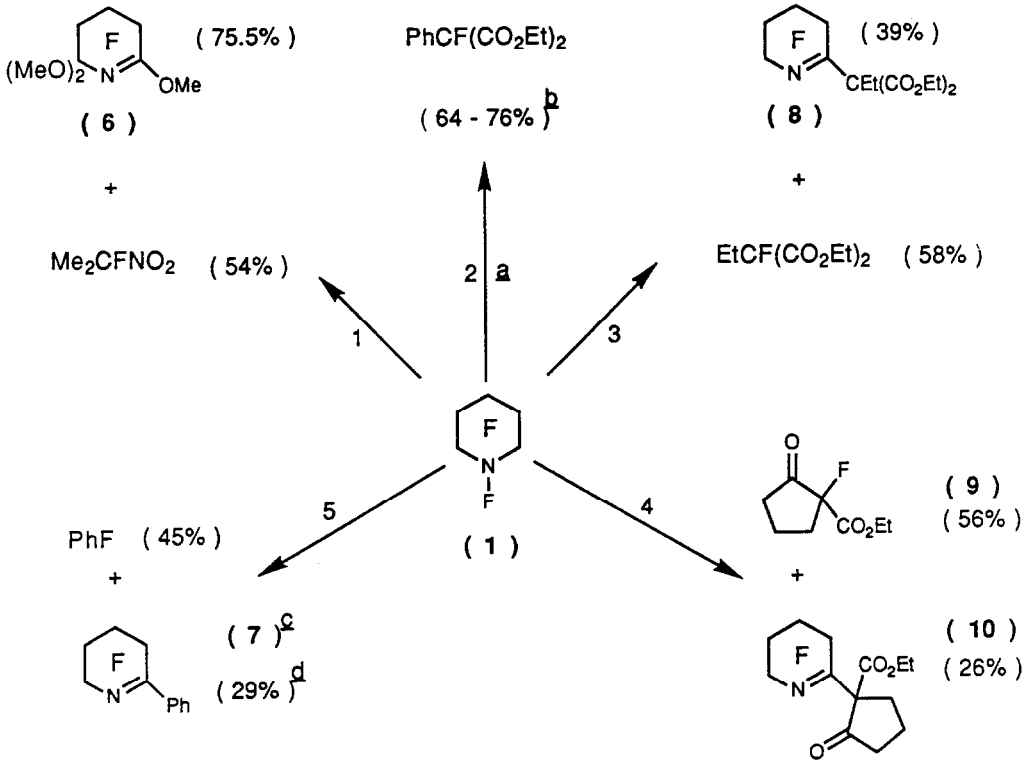
Notionally, as with any N-fluoro-compound, transfer of fluorine in a positive mode from perfluoro-N-fluoropiperidine to an electron-rich (nucleophilic) species can be formulated in terms of either a concerted bimolecular displacement on the fluorine of the N-F bond (i.e. an S_N2 halophilic reaction of type S_NF [21] or a single-electron-transfer (SET or e_T^- process (Scheme 1). Both pathways, which probably compose a mechanistic continuum [22], have been used in the past to rationalise site-specific fluorinations involving perfluoro-N-fluoropiperidine [15-17 (S_NF); 18, 19, 23 (SET)]; and the $S_N2(F)$ process has been discussed in an old review of nucleophilic displacement reactions on fluorine [24]. At present, we have nothing definitive to report about mechanistic processes and wish only to emphasise that a feature common to both mechanisms is the generation of the nitranion $c\text{-}C_5F_{10}N^-$ (**5**), and hence the release of the highly electrophilic imidoyl fluoride, perfluoro-1-azacyclohexene (**2**).

Tangible evidence found in the present study for in situ production of perfluoro-1-azacyclohexene (**2**) during transfer of "F^+" from perfluoro-N-fluoropiperidine (**1**) to carbanionic sources is displayed in Scheme 2. It is well known [25] that nucleophiles readily attack the imidoyl fluoride **2** under the conditions of the fluorination reactions, initially causing the formation of 2-substituted 3,3,4,4,5,5,6,6-octafluoro-1-azacyclohexenes (see footnote c of Scheme



a Note that if steps 2 and 3 of the SET pathway merge, the question of the release of fluorine atom does not arise. Neither does the onset of an $S_{RN}1$ process.

Scheme 1



a No attempt was made to isolate the product expected from attack of the reagent (2) on perfluoro-1-azacyclohexene (2).

b The highest yield was obtained when the reaction was carried out in the presence of caesium fluoride (see text).

c An authentic sample was prepared from perfluoro-1-azacyclohexene as described in the Experimental Section.

d As expected, addition of 1 to the Grignard reagent, rather than vice versa, raised the yield of 7 (78%) at the expense of PhF (10%).

Reagents: 1, Me_2CNaNO_2 in MeOH/MeONa; 2, $PhCNa(CO_2Et)_2$ in THF; 3, $EtCNa(CO_2Et)_2$ in THF; 4, $CH_2(CH_2)_2COCNaCO_2Et$ in THF; 5, PhMgBr in Et_2O.

Scheme 2.

2); with an excess of nucleophilic reagent, fluorine is lost from both the C-2 and C-6 ring sites [25], which accounts for the isolation of 3,3,4,4,5,5-hexafluoro-2,6,6-trimethoxy-1-azacyclohexene (**6**) when perfluoro-N-fluoropiperidine was added to a solution of 2-nitropropan-2-ylsodium prepared from 2-nitropropane and an excess of sodium methoxide in methanol.

Having decided that perfluoro-1-azacyclohexene (**2**) is generated in the fluorinations, attempts were made to restrict its availability to the carbanonic reagents by engaging it in a simple addition reaction with fluoride ion to cause re-formation of the perfluoro-1-azacyclohex-1-yl anion (**5**) (see Scheme 1) [cf. ref. 26 concerning the generation and trapping of $c\text{-}C_5F_{10}N^-Cs^+$ from **2** and CsF]. This ploy was successful to the extent that when the reaction of perfluoro-N-fluoropiperidine with the sodio derivative of diethyl phenylmalonate was repeated in the presence of an excess of caesium fluoride [molar reactant ratio = ca. 1 (NF compound): 1 (carbanion): 3 (CsF)], the yield of $PhCF(CO_2Et)_2$ rose to 76% (from 64%). Addition of caesium chloride worked just as well [75% yield of $PhCF(CO_2Et)_2$]. The presence of a very large amount of sodium chloride in the reaction mixture during the fluorination of 2-nitropropan-2-ylsodium with perfluoro-N-fluoropiperidine [molar ratio: ca. 1 (NF): 1 (carbanion) : 17 (NaCl)] raised the yield of Me_2CFNO_2 by less than 10%, but caused a noticeable decrease (from 75.5 to 56%) in the yield of the trimethoxy-derivative (**6**) of perfluoro-1-azacyclohexene.

EXPERIMENTAL

Spectroscopic Analyses

Unless stated otherwise, details of the instruments used etc. have been given previously [3(a)]. NMR chemical shifts were measured relative to Me_4Si (int., ^1H) or CF_3CO_2H (ext., ^{19}F); positive values were assigned to absorptions appearing downfield from reference signals.

Starting Materials

The sources of the hydrocarbon substrates fluorinated with the NF reagent 1 are indicated in the text. Perfluorinated materials were obtained as follows.

(a) Perfluoro-N-fluoropiperidine (1)

Material (b.p. 48-50 °C) of ca. 97% purity [by GC and ^{19}F NMR analysis; contaminants : perfluoro-n- and iso-pentane, perfluoro-(N-methylpyrrolidine)] was obtained by careful fractional distillation (1.5 m x 2.5 cm adiabatic column packed with 6 mm x 4 mm Pyrex Rashig rings) of volatile 'fluorocarbon' material produced by electrochemical fluorination (Simons Process) of pyridine [3].

(b) Perfluoro-1-azacyclohexene (2)

Defluorination of perfluoro-N-fluoropiperidine (1) with triphenylphosphine [4] by the following modification [5] of a reported procedure [6] gave perfluoro-1-azacyclohexene (2) containing traces (^{19}F NMR analysis) of perfluoro-(N-methylpyrrolidine) and perfluoro-n-pentane. A solution of triphenylphosphine (59.0 g, 0.225 mol) in dry toluene (100 cm^3) was added during 50 min. to a cold (-10 °C) stirred solution of perfluoro-N-fluoropiperidine (61.7 g, 0.218 mol) in dry toluene (100 cm^3) contained in a flask fitted with a double-surface water-cooled condenser surmounted by a cold finger (solid CO_2-methylated spirit) followed by a drying tube ($CaCl_2$). A thick white precipitate of difluorotriphenylphosphorane formed (subsequently isolated in 98% yield). The reaction mixture was stirred for 2 h, then allowed to warm to room temperature and stirred overnight in the now stoppered reaction vessel. Next day, perfluoro-1-azacyclohexene (40.0 g, 0.61 mol, 75%), b.p. 40-42 °C, was distilled directly from the reaction vessel, using a vacuum-jacketed column (15 cm x 1 cm) packed with 2 mm Fenske glass helices.

Fluorination of Organic Substrates with Perfluoro-N-fluoropiperidine

(a) Sodium propane-2-nitronate (with R HATTON)

2-Nitropropane (11.6 g, 0.13 mmol) was added dropwise to a cold (0 °C) stirred solution of sodium methoxide (0.52 mol) in absolute methanol (325 cm^3) under dry nitrogen in a flask equipped with a water-cooled reflux condenser. The stirred mixture was kept at 0 °C for 2 h, then, after the condenser had been replaced by a cold finger device (-72 °C) and guard tube ($CaCl_2$), was treated with perfluoro-N-fluoropiperidine (36.2 g, 0.13 mol) (added dropwise during 1.5 h). The ice bath was removed after 1 h and the mixture left overnight before being poured into iced water (1300 cm^3). Standard work-up [extracted with Et_2O (3 x 600 cm^3); extract washed (H_2O then brine) until neutral (phenolphthalein) then dried ($MgSO_4$); extract concentrated by distillation; residue (250 cm^3) stirred with 20% NaOH aq (18 h) then washed again as above, dried, and concentrated again] culminating in fractional distillation (50 cm^3 Vigreux unit, 15 cm x 1 cm) gave diethyl ether, 2-fluoro-2-nitropropane (6.9 g, 64.5 mmol, 54%), b.r. 108-124 °C at 760 mmHg [pure by GC (2 m Apiezon L/Celite, 150 °C], δ_H [neat.liq.; 60 MHz (Perkin-Elmer R10); benzene interchange ref.] -5.25 p.p.m. (d, $^3J_{HF}$ 19.5 Hz), δ_F (neat; 56.46 MHz) -35.0 p.p.m. (sept., 19.7 Hz), m/z 61 ($M^{+\cdot}$, 100%) (AEI MS/2H instrument), and 3,3,4,4,5,5-hexafluoro-2,6,6-trimethoxy-1-azacyclohexene (**6**) (22.7 g, 98 mmol, 75.7%) [Found: C, 34.4; H, 3.2; N, 4.7%; M (mass spec.), 281. $C_8H_9F_6NO_3$ requires C, 34.2; H, 3.2; N, 5.0%; M, 281], b.r. 62-72 °C at ca. 1 mmHg, δ_H (neat 60 MHz) -3.0 (s, OCH_3), -3.4 [m, $(OCH_3)_2$] p.p.m. (rel.int. 1:2), δ_F (neat; 56.46 MHz) -42.4 (complex, $CF_2C{=}N$), -52.4 (quint., $CF_2CF_2C{=}N$), -56.7 (complex, $CF_2CF_2CF_2C{=}N$) p.p.m. (rel.int. 1:1:1).

The above experiment was repeated exactly, except that anhydrous sodium chloride (100 g, 1.73 mole) was added to the methanolic solution of the sodium propane-2-nitronate before perfluoro-N-fluoropiperidine (26.8 g, 95.0 mmol) was introduced dropwise. The yield of isolated 2-fluoro-2-nitropropane was 60% (6.1 g, 57 mmol) and that of the trimethoxy-compound (**6**) 56% (13.3 g, 53.0 mmol). No 2-chloro-2-nitropropane could be detected in the reaction product by GLC analysis.

(b) Phenylmagnesium bromide

The Grignard reagent in diethyl ether (250 cm^3) [prepared conventionally from PhBr (6.7 g, 42.6 mmol)] was added slowly (30 min), under dry nitrogen, to a cold (0 °C) stirred solution of perfluoro-N-fluoropiperidine (12.0 g, 42 mmol) in sodium-dried diethyl ether (30 cm^3). An exothermic reaction occurred immediately. The mixture was stored overnight at room temperature, then worked-up by decanting the supernatant greenish liquid from a sticky precipitate that had formed and distilling it (Vigreux unit), to give diethyl ether containing unchanged perfluoro-N-fluoropiperidine (10% recovery according to a GLC analysis) and a residue, b.p. > 44 °C, shown by a combination of GLC (calibrated SE 30 column, 80 °C), GC-IR, and NMR (^1H, ^{19}F) analysis to contain traces of diethyl ether, fluorobenzene (19 mmol, 45%), 3,3,4,4,5,5,6,6-octafluoro-2-phenyl-1-azacyclohexene (7) (12 mmol, 29%), and an unidentified fluoro-organic compound.

The reaction was repeated except that the N-fluoro compound (12.1 g, 0.42 mmol) in diethyl ether (20 cm^3) was added to the solution of the Grignard reagent (0.48 mmol). After the mixture had stood at room temperature for 30 min., it was filtered; the greenish precipitate (3 g) (Found: C, 12.9; H, 3.0; N, 0.1; ash 33%), which was insoluble in petroleum ether (b.r. 40-60 °C), dichloromethane, and acetone and reactive towards methanol, was discarded; the filtrate was fractionated to give fluorobenzene (0.4 g, 4 mmol, 10%) and 3,3,4,4,5,5,6,6-octafluoro-2-phenyl-1-azacyclohexene (7) (9.9 g, 33 mmol, 78%).

(c) Diethyl phenylmalonate

Perfluoro-N-fluoropiperidine (2.4 g, 8.4 mmol) was added dropwise (syringe) to a cold (-50 °C) solution of diethyl sodio(phenyl)malonate in anhydrous tetrahydrofuran [prepared in conventional fashion by adding a 50% dispersion of NaH (12.6 mmol) in oil to $PhCH(CO_2Et)_2$ (Aldrich; 2.0 g, 8.4 mmol) in THF (15 cm^3)] held under dry nitrogen. The reaction

mixture was kept at -50 °C for 15 min, then allowed to warm to room temperature slowly, with storage at each point [15 min. at -50°C, -20°C, and 0°C; 30 min at 20°C] before being diluted with diethyl ether (60 cm^3). The mixture was then washed with 0.5M oxalic acid (30 cm^3), 10% aqueous potassium hydrogen carbonate (30 cm^3), and saturated aqueous sodium chloride solution (30 cm^3), dried ($MgSO_4$ overnight), and evaporated (Rotavapor). Chromatographic [DCFC; silica eluted with dichloromethane-hexane] separation of the residue provided (i) a mixture [0.48 g; eluted with 1:4 (v/v) CH_2Cl_2-C_6H_{14}] shown by NMR analysis to contain diethyl phenylmalonate and diethyl fluoro(phenyl)malonate (0.16 g, 0.67 mmol) and (ii) diethyl fluoro(phenyl)malonate [1.19 g, 4.74 mmol, total yield 64%; eluted with 1:2 (v/v) CH_2Cl_2-C_6H_{14}] with spectroscopic properties (IR, NMR, and MS) identical to those of an analytically pure sample prepared by fluorinating diethyl sodio(phenyl)malonate with N-fluoroquinuclidinium fluoride [3(a)].

When the reaction was repeated [$PhCH(CO_2Et)_2$, 17 mmol; $C_5F_{10}NF$, 16.8 mmol; THF, 30 cm^3] except that dry caesium chloride (7.6 g, 45 mmol) was added to the diethyl phenylmalonate solution before the introduction of sodium hydride, the yield of diethyl fluoro(phenyl)malonate (Found: C, 61.7; H, 6.2; Cl, < 0.2; F, 7.1. Calc. for $C_{13}H_{15}FO_4$: C, 61.4; H, 5.9; Cl, 0.0; F, 7.5%) was 75% (3.0 g, 11 mmol). Use of anhydrous caesium fluoride (7.6 g, 50 mmol) instead of caesium chloride gave diethyl fluoro(phenyl)malonate in 76% yield.

(d) Diethyl ethylmalonate

This diester (Aldrich; 1.97 g, 10.5 mmol) was fluorinated with perfluoro-N-fluoropiperidine (2.83 g, 10.0 mmol) in THF (30 cm^3) using the techniques (including work-up procedure) employed in the case of diethyl phenylmalonate [first experiment (c) above, i.e. no caesium halide added]. The products isolated by DCFC were impure (contaminated with hexane according to ^1H NMR) diethyl ethyl(fluoro)malonate (1.2 g,

58 mmol, 58%), m/z (EI) 207 (M + 1, 7%), 187 (M-F, 1%), 178 (M-C_2H_4, 8%), 134 (M-C_2H_4-CO_2, 38%), 106 ($C_4H_7FO_2$, 100%), λ_{max} (liq.film) 1760, 1770 (sh) cm^{-1} (C=O str.), δ_H (in $CDCl_3$) 1.10, 1.18 (overlapping t s, CH_3CH_2CF, CH_3CH_2O resp.), 2.05 (dq, $^3J_{HF}$ 23 Hz, CH_3CH_2CF), 4.17 (q, CH_3CH_2O) p.p.m., δ_F (C_6F_6 ext.ref; same soln.) -6.1 (-93.45 when corrected to TFA) p.p.m. (t, $^3J_{HF}$ 23 Hz), and 2-[1,1-bis(ethoxycarbonyl)propyl]-3,3,4,4,5,5,6,6-octafluoro-1-azacyclohexene (**8**) (n.c.) (1.6 g, 3.9 mmol, 39%) (Found: C, 40.7; H, 3.8, F, 36.6; N, 3.1. $C_{14}H_{15}F_8NO_4$ requires C, 40.7; H, 3.7; F, 36.8; N, 3.4%), a pale orange oil, λ_{max} (liq.film) 1680 (C=N str.), 1745, 1765 (d, C=O str.) cm^{-1}, m/z (EI) 385 (M-C_2H_4, 58%), 368 (M-OC_2H_5, 16%), 340 (M-$CO_2C_2H_5$, 23%), 267 (M-2 x $CO_2C_2H_5$, 100%), δ_H (in $CDCl_3$) 1.11 (t, CH_3CH_2C and CH_3CH_2O), 2.19 (q, CH_3CH_2C), 4.13 (q, CH_3CH_2O) p.p.m. (rel.int. 9:2:2), δ_F -14.6 (br.quint., 6-CF_2), -35.6 (br.quint., 3-CF_2), -54.6 (sept., 4- or 5-CF_2), -58.7 (sept, 5- or 4-CF_2) p.p.m. (rel.int.1:1:1:1).

(e) 2-(Ethoxycarbonyl)cyclopentanone

This cyclic β-keto-ester (1.52 g, 9.74 mmol) was fluorinated with perfluoro-N-fluoropiperidine (2.83 g, 10 mmol) in THF (30 cm^3) as described in experiment (c) above. The same work-up procedure gave a complex oil, shown by NMR analyses to contain 2-(ethoxycarbonyl)-2-fluorocyclopentanone (**9**) and 2-(ethoxycarbonyl)-2-(3,3,4,4,5,5,6,6-octafluoro-1-azacyclohex-1-en-2-yl)cyclopentanone (**10**), the estimated yields being 56 and 26%, respectively. Samples of (**9**) [an oil, m/z (EI) 175 (M + 1, 100%), 155 (M-HF, 83%), λ_{max} (liq.film) 1680 (sh), 1722, 1750, 1765 (t) (C=O str.) cm^{-1}, δ_H (in $CDCl_3$) 1.2 (t, CH_3CH_2O), 1.9-2.8 (complex, ring protons), 4.2 (q, CH_3CH_2O) p.p.m. (rel.int. 3:6:2), δ_F (in $CDCl_3$) -85.3 (dd, $^3J_{HF}$ 21, 18 Hz) p.p.m.] and (**10**) [a reddish oil, λ_{max} (film) 1670 (sh.), 1690 (C=N str.), 1717, 1768 (C=O str.) cm^{-1}, δ_H (in $CDCl_3$) 1.15 (t, CH_3CH_2O), 1.95 (complex) and 2.17 (t) (ring protons), 4.12 (q, CH_3CH_2O) p.p.m. (rel.int.3:6:2), δ_F (in $CFCl_3$)-10.3 (quint, 6-CF_2), -41.8 (quint., 3-CF_2), -55.2 (sept., 4- or 5-CF_2), -56.8 (sept., 5- or 4-CF_2) p.p.m. (rel.int. 2:2:2:2) were isolated by DCFC (silica eluted with dichloromethane-light petroleum, b.p. 40-60 °C).

Reaction of Perfluoro-1-azacyclohexene (2) with Phenylmagnesium Bromide

A solution of this Grignard reagent in diethyl ether (40 cm^3) [prepared conventionally from PhBr (7.9 g, 50 mmol)] was added slowly (2 h), under nitrogen, to a cold (0 °C) stirred solution of perfluoro-1-azacyclohexene (11.0 g, 45 mmol) in diethyl ether (50 cm^3). A reaction occurred immediately with the formation of a sticky green precipitate. The mixture was filtered, and the greenish-brown filtrate was evaporated by distillation [Vigreux column, cold-finger (solid CO_2-EtOH) stillhead] to remove diethyl ether and unreacted perfluoro-1-azacyclohexene (amount not determined); the residue was filtered, to remove a greenish solid which had appeared, then distilled in a Vigreux unit to give 3,3,4,4,5,5,6,6-octafluoro-2-phenyl-1-azacyclohexene (7) (n.c.) (4.0 g, 13 mmol, 30%) [Found: C, 44.3; H, 1.6; F, 49.8; N, 4.6%; M (mass spec.) 303. $C_{11}H_5F_8N$ requires C, 43.6; H, 1.65; F, 50.2; N, 4.6%; M, 303], b.p. 203 °C, λ_{max} (film) 1645 cm^{-1} (C=N str.), δ_H (neat liq.) 6.6-7.0 (complex), 7.4 (mult.) p.p.m., δ_F (neat liq.) -13.5 (quint., 6-CF_2), -33.2 (quint., 3-CF_2), -57.2 (sept., 4- or 5-CF_2), -58.5 (complex, 5- or 4-CF_2) p.p.m. (rel.int. 1:1:1:1).

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