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REACTIONS OF DIETHYLCARBAMOYL-LITHIUM AND BIS(DIETHYLCARBAMOYL)MERCURY WITH HIGHLY FLUORINATED SUBSTRATES

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Summary

Nucleophilic acylations have been carried out using a species reacting as diethylcarbamoyl-lithium. With pentafluorobenzaldehyde it gave the addition product, *N*,*N*-diethylpentafluoromandelamide, and with hexafluorobenzene, octafluorotoluene, decafluorocyclohexene and pentadecafluoro-octanoyl chloride it gave products which are formed by the nucleophilic replacement of fluorine or chlorine by the $-CONEt_2$ group, though in poor yield. Reaction of bis(diethylcarbamoyl)mercury with decafluorocyclohexene, pentafluorobenzyl chloride and pentadecafluoro-octanoyl chloride afforded aminated products in low yields.

Introduction

Although there are numerous reported examples of indirect nucleophilic acylations [1], there have been only a few publications concerning the one-stage nucleophilic introduction of carbonyl groups [2 - 6]. One, in particular [3], describes some reactions of a species which was generated at —78 °C by the reaction of bis(diethylcarbamoyl)mercury with n-butyl-lithium and which undergoes reactions as if it were diethylcarbamoyl-lithium*. Thus, reaction with benzaldehyde was reported to give *N*,*N*-diethylmandelamide in good yield, together with dibutylmercury.

We have studied some reactions of diethylcarbamoyl-lithium with highly fluorinated substrates and have prepared, in one step, several new compounds which otherwise would have required lengthy syntheses. (The reactions are summarised in Figs. 1 and 2.) We have also reacted bis(diethylcarbamoyl)mercury with some fluorocarbon substrates and confirmed the report [7] that the amino group of the organomercurial can be transferred in a nucleophilic manner.

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* For convenience, throughout this paper the reagent will be referred to as diethylcarbamoyl-lithium, thereby indicating its nucleophilic character but not implying that this is the reactive species.

$$C_6F_5CHO \xrightarrow{LiCONEt_2} C_6F_5CH(OH)CONEt_2$$

$$C_6F_6 \xrightarrow{LiCONEt_2} C_6F_5CONEt_2 + o\text{- and } p\text{-}C_6F_4(CONEt_2)_2$$

$$C_6F_5CF_3 \xrightarrow{LiCONEt_2} p\text{-}CF_3C_6F_4CONEt_2$$

$$C_7F_{15}COCl \xrightarrow{LiCONEt_2} C_7F_{15}COCONEt_2 \text{ (I)}$$

Fig. 1. Reactions of $LiCONEt_2$.

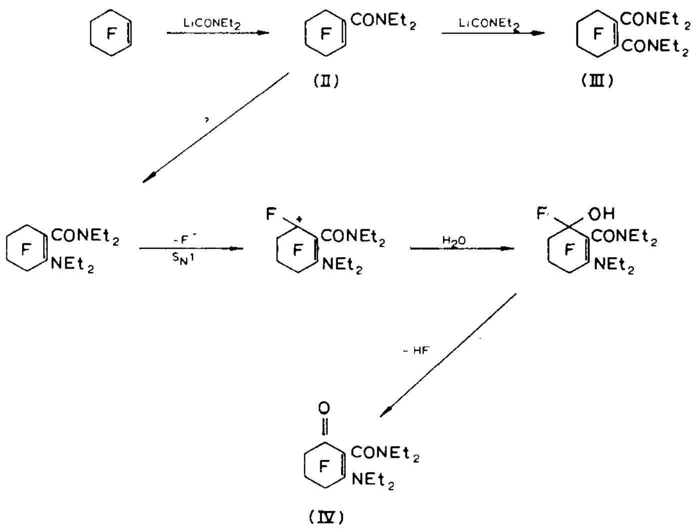


Fig. 2. Reaction of decafluorocyclohexene with $LiCONEt_2$.

Results and discussion

The experimental procedures of Schöllkopf and Gerhart [3, 7] were followed and reaction of butyl-lithium with bis(diethylcarbamoyl)mercury at —78 °C gave a clear yellow solution of the reactive species. On reaction of this solution with 2,3,4,5,6-pentafluorobenzaldehyde at —78 °C, the addition product, *N*,*N*-diethyl-2,3,4,5,6-pentafluoromandelamide, was isolated in 27% yield, together with dibutylmercury and unreacted aldehyde. No products arising from nucleophilic aromatic substitution or haloform cleavage were observed, although these products predominated in the reaction [8] of the aldehyde with sodium methoxide and sodium ethoxide respectively.

Reaction of diethylcarbamoyl-lithium with hexafluorobenzene gave three products, *N,N*-diethyl-2,3,4,5,6-pentafluorobenzamide and an inseparable equimolar mixture of the *ortho*- and *para*-disubstituted isomers, clearly arising from further nucleophilic substitution of the monosubstituted product. That *ortho*- and *para*-disubstitution was observed is in accordance with previous nucleophilic substitutions [9] of an aromatic nucleus bearing an electron-withdrawing substituent, but usually *para*-disubstituted isomers predominate. In our case the large amount of *ortho* attack might suggest some form of interaction between the attacking entity and the carboxamido substituent already present, similar to the interaction postulated [10] to explain the high percentage of *ortho* attack when pentafluoronitrobenzene was treated with certain nucleophiles.

Diethylcarbamoyl-lithium was also reacted with octafluorotoluene and the *para*-disubstituted compound, *N,N*-diethyl-2,3,5,6-tetrafluoro-4-trifluoromethylbenzamide, was isolated in 21% yield. This is in agreement with previous nucleophilic substitutions of octafluorotoluene [11], where only the *para*-disubstituted isomers were obtained.

The susceptibility of polyfluoroalkenes to attack by nucleophiles is well known and the possible mechanisms have been fully discussed by Park [12]. When diethylcarbamoyl-lithium was reacted with decafluorocyclohexene two products were isolated in small yield, 1,2-bis(diethylcarbamoyl)octafluorocyclohexene [(III), Fig. 2] and 3-diethylamino-2-diethylcarbamoyl-hexafluorocyclohex-2-en-1-one [(IV), Fig. 2]. The former compound clearly arises by a two-step substitution of the vinylic fluorine atoms of decafluorocyclohexene. After monosubstitution the resulting compound (II) is activated towards further nucleophilic attack, possibly explaining why no monosubstituted product was observed. Compound (IV) could also be derived from the monosubstituted olefin by the scheme shown in Figure 2, the olefin reacting with some entity acting as a source of the diethylamino group to effect further substitution. This entity might be either unreacted bis(diethylcarbamoyl)mercury or some complex species formed in solution at −78 °C (see later discussion). It is likely that during the work-up the disubstituted olefin eliminates fluoride ion by an S_N1 process; this is aided by the stabilisation which the diethylamino group affords the resulting carbonium ion. Quenching of the carbonium ion with hydroxyl ion, followed by elimination of hydrogen fluoride, yields the observed product. An analogous process has been observed [13]; thus 1-pyrollidino-nonafluorocyclohexene was found to convert rapidly into 3-pyrollidino-heptafluorocyclohex-2-en-1-one.

Finally, diethylcarbamoyl-lithium was reacted with pentadecafluorooctanoyl chloride and the product resulting from substitution of the chlorine atom by $-CONEt_2$, *i.e.* the α-keto-nonamide (I), was obtained in 5% yield. In this experiment the reaction medium contained a large amount of ether, due to the insolubility of the acyl chloride in THF at −78 °C, and this may have contributed to the low yield. Also the bulkiness of the C_7F_{15} group would be expected to hinder attack at the carbonyl carbon.

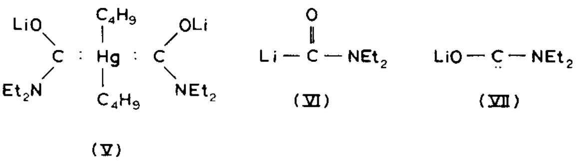


Fig. 3. Possible reactive species.

We have not arrived at any definite conclusions concerning the nature of the reactive species, in common with the earlier workers [3] in the field. They suggested that the addition of butyl-lithium to bis(diethylcarbamoyl)-mercury could form the complex (V) (Fig. 3). This complex might then itself react with the substrate or decompose to the tautomers (VI) and (VII), which might react to effect the addition or substitution. We favour the first route. Although the reactivity of the reagent at low temperatures suggests that some highly reactive species (such as a carbene) is involved, the yields of dibutylmercury are not quantitative, implying that this compound is only formed when a reaction has occurred.

We have carried out several experiments to investigate the reactivity of the species. When the "anion" was allowed to warm from −78 °C to ambient temperature, the clear yellow solution became cloudy and white at *ca.* −40 °C to −30 °C, and no longer effected nucleophilic acylations. It was not possible to investigate the decomposition route of the unreacted complex due to the inseparable mixtures formed. Furthermore, when the fluorocarbon substrate was added at −78 °C, the length of time for which the reaction mixture was stirred at this temperature did not significantly affect the yield of acylated product. We tentatively conclude that the reactive species is a complex, which gives dibutylmercury and acylated products on reaction with the substrate.

We have reacted bis(diethylcarbamoyl)mercury with decafluorocyclohexene, pentafluorobenzyl chloride and pentadecafluoro-octanoyl chloride, and the expected amination products were obtained in each case. A possible reaction scheme is illustrated in Figure 4 and requires little further comment. The formation of diethylcarbamoyl fluoride in the reaction with decafluorocyclohexene could be explained by the decomposition of a species $FHgCONEt_2$. From a synthetic viewpoint, it should be noted that these reactions could have been accomplished in better yield using diethylamine.

The structures of the products described in this paper followed from their elemental analyses, mass spectra and nuclear magnetic resonance spectra (data summarised in Table 1). The NMR spectra are quite straightforward, with chemical shifts and couplings having expected values apart from two points. Firstly, the two ethyl groups in each $—CONEt_2$ group are diastereotopic at *ca.* 35 °C (the temperature of the spectrometer) because of restricted rotation around the C—N bond, a feature normally shown by

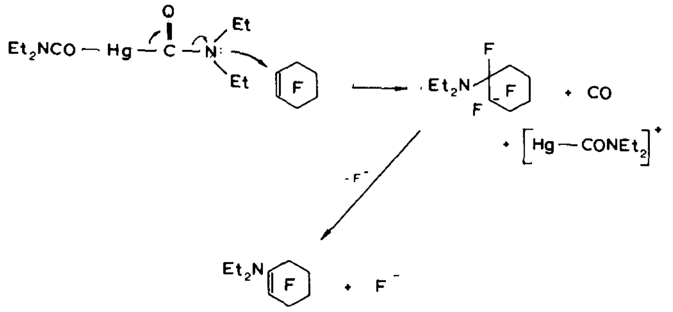


Fig. 4. Reaction of bis(diethylcarbamoyl)mercury with decafluorocyclohexene.

—$CONR_2$ groups [14]. The second point is less expected; the fluorines in each CF_2 group of both decafluorocyclohexene substitution products [(III) and (IV)] are non-equivalent. Once again, we associate this with some form of restricted rotation of the substituent —$CONEt_2$ and —NEt_2 groups; this restriction could involve any one or several of a variety of molecular shapes, and we can see no way of distinguishing between the possibilities.

Experimental

Bis(diethylcarbamoyl)mercury was prepared by a previously reported route [7]. n-Butyl-lithium in n-hexane was obtained from Alpha Inorganics Ltd., and was standardised before use. Product mixtures were examined by TLC using MN-silica gel G/UV_{254} and column chromatography was performed using silica gel (M.F.C., Hopkin and Williams Ltd.) contained in a glass column (25 mm diameter) packed to a depth of *ca.* 75 cm. All solvents were dried and distilled before use. GLC equipment was a Pye Series 104 Gas Chromatograph containing the following columns (9.1 m × 10 mm):

Unit 1: Silicone gum SE30 on Chromosorb P (1:6).
Unit 2: Ucon oil 50-HB-2000 on 60 - 80 mesh brick dust (1:9).
Unit 3: Silicone gum SE30 on celite (1:6).

When these units are referred to, the operating temperature and nitrogen pressure are quoted.

Reactions of diethylcarbamoyl-lithium

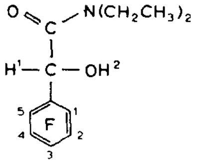
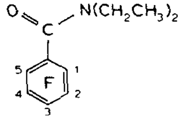
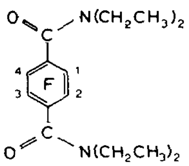
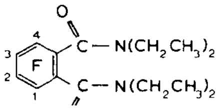
Diethylcarbamoyl-lithium solution was prepared at —78 °C by the addition of the n-butyl-lithium solution (2*y* mol) to a stirred suspension of bis(diethylcarbamoyl)mercury (*x* g, *y* mol) in THF (10*x* cm^3) at —78 °C. The clear yellow solution was then reacted at —78 °C with the chosen substrate. The work-up procedure described for the reaction with pentafluorobenzaldehyde is typical of the other reactions of this type.

(a) Reaction with 2,3,4,5,6-pentafluorobenzaldehyde

To a solution of diethylcarbamoyl-lithium, prepared from bis(diethyl-

TABLE 1

NMR spectra of reported compounds

Compound	^{19}F spectra			^{1}H spectra		
	Shifts*	Group(s)	Comments	Shifts**	Group(s)	Comments
	143.2	F^1, F^5		1.03	CH_3 (2X)	Two triplets 0.25 ppm apart
	161.7	F^2, F^4		3.27	CH_2 (2X)	Two quartets 0.33 ppm apart
	154.1	F^3				$J(CH_3—CH_2) = 7.1$ Hz
				4.77	H^1	
				5.36	H^2	
	142.5	F^1, F^5		1.18	CH_3 (2X)	Two triplets 0.12 ppm apart
	161.4	F^2, F^4		3.35	CH_2 (2X)	Two quartets 0.35 ppm apart
	154.5	F^3				$J(CH_3—CH_2) = 6.5$ Hz
	142.8	F^1, F^2, F^3, F^4		1.10***	CH_3 (4X)	
				3.35***	CH_2 (4X)	
	141.9	F^1, F^4		1.10***	CH_3 (4X)	
	155.5	F^2, F^3		3.35***	CH_2 (4X)	

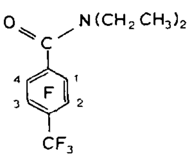
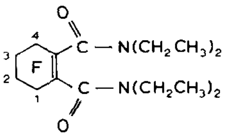
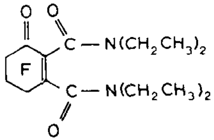
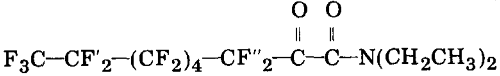
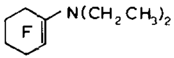
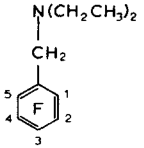
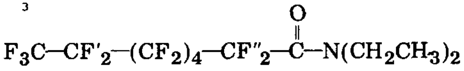
	141.3	F^1, F^4		1.20	CH_3 (2×)	Two triplets 0.15 ppm apart
	140.1	F^2, F^3		3.36	CH_2 (2×)	Two quartets 0.33 ppm apart
	57.4	CF_3	Triplet (J = 21.4 Hz)			$J(CH_3{-}CH_2)$ = 6.8 Hz
	104.6 115.9	F_2 (1 and 4)	AB quartet $J(AB)$ = 270 Hz	1.10	CH_3 (4×)	Two triplets 0.06 ppm apart $J(CH_3{-}CH_2)$ = 7.2 Hz
				3.30***	CH_2 (4×)	
	131.5 138.9	F_2 (2 and 3)	AB quartet $J(AB)$ = 265 Hz			
	109.2 116.1	CF_2	AB quartet $J(AB)$ = 288 Hz	1.20 3.35***	CH_3 (4×) CH_2 (4×)	
	122.5 128.9	CF_2	AB quartet $J(AB)$ = 298 Hz			
	131.4 137.9	CF_2	AB quartet $J(AB)$ = 265 Hz			
 $F_3C{-}CF'_2{-}(CF_2)_4{-}CF''_2{-}\overset{O}{\overset{\Vert}{C}}{-}\overset{O}{\overset{\Vert}{C}}{-}N(CH_2CH_3)_2$						
	81.6	CF_3		1.21***	CH_3 (2×)	
	127.2	CF'_2		3.41***	CH_2 (2×)	
	122.1***	$(CF_2)_4$				
	118.3	CF''_2				
	154.7	$=C{-}F$		1.15	CH_3 (2×)	Triplet
	111.0	CF_2		3.28	CH_2 (2×)	Quartet
	115.5	CF_2				$J(CH_3{-}CH_2)$ = 7.3 Hz
	135.0	CF_2(2×)				

TABLE 1 *(continued)*

Compound	^{19}F spectra			^{1}H spectra		
	Shifts*	Group(s)	Comments	Shifts**	Group(s)	Comments
	144.0	F^1, F^5		1.03	CH_3 (2×)	Triplet
	164.1	F^2, F^4		2.48	CH_2 (2×)	Quartet
	157.4	F^3				$J(CH_3—CH_2) = 7.1$ Hz
				3.65	$C_6F_5CH_2N$	
 $F_3C—CF'_2—(CF_2)_4—CF''_2—\overset{\overset{O}{\parallel}}{C}—N(CH_2CH_3)_2$						
	80.0	CF_3		1.21***	CH_3 (2×)	
	125.0	CF'_2		3.45***	CH_2 (2×)	
	120.0***	$(CF_2)_4$				
	110.0	CF''_2				

*Shifts in ϕ (ppm upfield from CCl_3F).

**Shifts in δ (ppm downfield from TMS).

***Overlapping signals, centre of absorptions quoted.

carbamoyl)mercury (1.0 g) in THF (10 cm^3) and butyl-lithium in hexane (2.1 mol l^{-1}, 2.4 cm^3) at −78 °C, was added a solution of the aldehyde (1.0 g) in THF (10 cm^3), also at −78 °C. The mixture was warmed to ambient temperature and volatiles removed by rotary evaporation. Water (50 cm^3) was added to the residue and the mixture extracted with ether (4 × 30 cm^3). The combined ethereal extracts were dried ($MgSO_4$), filtered and most of the ether removed by distillation. After TLC examination, the product was separated by column chromatography (using ether/benzene 6:1 as eluant) to give, after the removal of solvents by rotary evaporation, (i) a mixture (0.5 g) of dibutylmercury and unreacted aldehyde, and (ii) a cream-coloured solid (0.5 g), which was recrystallised (light petroleum b.p. 40 - 60 °C) to give (±)-*N*,*N*-diethyl-2,3,4,5,6-pentafluoromandelamide (nc) (0.4 g), m.p. 64 - 65 °C. (Found: C, 48.8; H, 4.1; N, 4.7%. $C_{12}H_{12}F_5NO_2$ requires C, 48.5; H, 4.1; N, 4.7%).

(b) Reaction with hexafluorobenzene

Diethylcarbamoyl-lithium, prepared from bis(diethylcarbamoyl)mercury (4.0 g) in THF (40 cm^3) and butyl-lithium solution (2.1 mol l^{-1}, 9.6 cm^3), was reacted with hexafluorobenzene (3.8 g) in THF (10 cm^3) in the manner previously described. After work-up and TLC examination, the product was separated by column chromatography, using benzene followed by benzene/ether (6:1) as eluants, to give (i) dibutylmercury (1.73 g) (ii) a liquid (0.7 g) which was distilled *in vacuo* (160 °C/15 mmHg) to give *N*,*N*-diethyl-2,3,4,5,6-pentafluorobenzamide [15] (0.5 g), b.p. 260 °C (Found: C, 49.2; H, 3.8; F, 35.5%. $C_{11}H_{10}F_5NO$ requires C, 49.4; H, 3.8; F, 35.6%), top mass peak at 267 corresponding to M^+, and (iii) a white solid (0.26 g) which was recrystallised (light petroleum b.p. 60 - 80 °C) to give a further white solid (0.15 g), m.p. 132 - 134 °C, identified by NMR spectroscopy as a mixture (1:1) of *ortho*- and *para*-bis(diethylcarbamoyl) tetrafluorobenzenes. (Found: C, 55.4; H, 5.9; N, 8.0%. $C_{16}H_{20}F_4N_2O_2$ requires C, 55.2; H, 5.8; N, 8.0%), top mass peak at 348 corresponding to M^+.

(c) Reaction with octafluorotoluene

Diethylcarbamoyl-lithium, prepared from bis(diethylcarbamoyl)mercury (4.0 g) in THF (40 cm^3) and butyl-lithium solution (2.4 mol l^{-1}, 8.75 cm^3), was reacted in the usual way with octafluorotoluene (4.7 g) in THF (10 cm^3). Separation of the product by column chromatography using benzene, followed by benzene/ether (4:1), as eluants gave (i) a mixture (1.9 g) of dibutylmercury and octafluorotoluene, and (ii) a liquid which was distilled *in vacuo* (y-piece) to give *N*,*N*-diethyl-2,3,5,6-tetrafluoro-4-trifluoromethylbenzamide (nc) (1.3 g), b.p. 270 °C. (Found: C, 45.2; H, 3.1; F, 41.7%. $C_{12}H_{10}F_7NO$ requires C, 45.4; H, 3.2; F, 41.9%), top mass peak at 317 corresponding to M^+.

(d) Reaction with decafluorocyclohexene

Diethylcarbamoyl-lithium, prepared from bis(diethylcarbamoyl) mercury (3.0 g) in THF (30 cm^3) and butyl-lithium solution (2.2 mol l^{-1}, 6.8 cm^3), was reacted with decafluorocyclohexene (4.0 g) in THF (10 cm^3). Separation by column chromatography using benzene, followed by benzene/ether (4:1) and benzene/ether (1:1) as eluants gave (i) dibutylmercury (1.2 g), (ii) an oil (0.4 g) which slowly solidified to give a solid which was recrystallised from light petroleum (b.p. 60 - 80 °C) to give 1,2-bis(diethylcarbamoyl)octafluorocyclohexene (nc) (0.28 g), m.p. 50 - 52 °C. (Found: C, 45.6; H, 4.8; N, 6.5%. $C_{16}H_{20}F_8N_2O_2$ requires C, 45.3; H, 4.8; N, 6.6%), top mass peak at 424 corresponding to M$^+$, and (iii) a solid (0.29 g) which, after recrystallisation from light petroleum (b.p. 60 - 80 °C), afforded 3-diethylamino-2-diethylcarbamoyl-hexafluorocyclohex-2-en-1-one (nc) (0.15 g), m.p. 78 °C. (Found: C, 48.1; H, 5.3; N, 7.0%. $C_{15}H_{20}F_6N_2O_2$ requires C, 48.1; H, 5.4; N, 7.5%), top mass peak at 374 corresponding to M$^+$. The UV spectrum in ethanol showed $\lambda_{max} = 330$ nm, $\epsilon = 23\ 050$.

(e) Reaction with pentadecafluoro-octanoyl chloride

Diethylcarbamoyl-lithium, prepared from bis(diethylcarbamoyl)mercury (2.0 g) in THF (20 cm^3) and butyl-lithium solution (1.9 mol l^{-1}, 5.5 cm^3), was reacted with pentadecafluoro-octanoyl chloride (4.3 g) in ether (150 cm^3). Work-up, followed by separation by column chromatography using benzene and benzene/ether (4:1) as eluants, gave (i) dibutylmercury (0.3 g), (ii) a yellow oil (0.31 g) which after further purification by preparative GLC (Unit 1, 190 °C, 1.1 atm) gave *N*,*N*-diethylpentadecafluoro-2-keto-nonamide (nc) (0.26 g), b.p. 260 - 262 °C. (Found: C, 31.0; H, 1.9%. $C_{13}H_{10}F_{15}NO_2$ requires C, 31.4; H, 2.0%), top mass peak at 497 corresponding to M$^+$, and (iii) bis(diethylcarbamoyl)mercury (0.1 g).

Reactions of bis(diethylcarbamoyl)mercury

(a) Reaction with decafluorocyclohexene

A mixture of bis(diethylcarbamoyl)mercury (2.0 g), decafluorocyclohexene (4.0 g) and THF (15 cm^3) was refluxed for 5 days. Water (50 cm^3) was added and volatiles were removed by rotary evaporation. The residue was extracted with ether (3 × 40 cm^3), the combined extracts dried ($MgSO_4$), filtered and most of the ether removed by distillation up a 30 cm column packed with glass helices. The residue was distilled *in vacuo* (y-piece) and the distillate (1.4 g) separated by preparative GLC (Unit 2, 160 °C, 1.4 atm) to give (i) a mixture of ether and THF, (ii) 1-diethylaminononafluorocyclohexene (nc) (0.48 g), b.p. 168 °C. (Found: C, 38.1; H, 3.1; N, 4.6; F, 54.7%. $C_{10}H_{10}F_9N$ requires C, 38.1; H, 3.2; N, 4.4; F, 54,3%), top mass peak at 315 corresponding to M$^+$, and (iii) diethylcarbamoyl fluoride (0.13 g), b.p. 158 °C (lit. [16] : 154 °C). ^{19}F NMR spectroscopy showed a singlet at 23.9 ϕ and ^{1}H NMR spectroscopy showed a triplet ($J = 7.5$ Hz) at 1.20 δ and a quartet ($J = 7.0$ Hz) at 3.28 δ, relative intensity 3:2. Mass spectroscopy showed a large peak at 119 corresponding to M$^+$.

(b) Reaction with 2,3,4,5,6-pentafluorobenzyl chloride

A mixture of bis(diethylcarbamoyl)mercury (1.5 g), the title compound (1.5 g) and THF (4.0 cm^3) was refluxed for 9 days. The mixture was worked-up as before and separation of the products by preparative GLC (Unit 3, 180 °C, 1.1 atm) gave (i) a mixture (0.27 g) of ether, THF and the title compound, and (ii) *N*,*N*-diethyl-2,3,4,5,6-pentafluorobenzylamine (nc) (0.37 g), b.p. 205 °C. (Found: C, 52.5; H, 4.55%. $C_{11}H_{12}F_5N$ requires C, 52.2; H, 4.8%).

(c) Reaction with pentadecafluoro-octanoyl chloride

A mixture of the title compound (0.9 g) in THF (5 cm^3) and bis(diethylcarbamoyl)mercury (0.5 g) in DMF (5 cm^3) was stirred for 2 days and finally refluxed for 4 h. Sodium hydroxide solution (1 mol l^{-1}, 20 cm^3) was added and the mixture worked-up as usual. Separation of the products by preparative GLC (Unit 1, 160 °C, 1.1 atm) gave (i) ether (0.27 g) and (ii) *N*,*N*-diethyl-pentadecafluoro-octanamide (nc) (0.12 g) b.p. 235 °C. (Found: C, 31.0; H, 2.2%. $C_{12}H_{10}F_{15}NO$ requires C, 30.7; H, 2.1%), top mass peak at 469 corresponding to M^+.

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