(6) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).
(7) Crystals exposed to an atmosphere of 50–60% humidity absorb water and produce a solution within 15–20 s.
(8) The authors are grateful to Dr. L. Altman for carrying out the measurements.
(9) A. Murray, III, and W. H. Langham, *J. Am. Chem. Soc.*, **74**, 6289 (1952).
(10) Compare with the value 138–140 °C reported in ref 4.

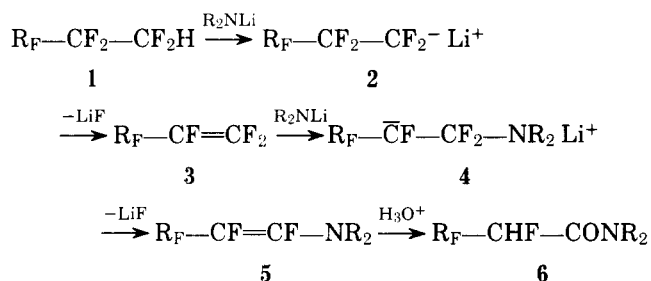## Functionalization of 1*H*-Perfluoroalkyl Chains

Claude Wakselman* and Thoai Nguyen

C.N.R.S.-C.E.R.C.O.A. 2, rue Henri Dunant, 94320 Thiais, France

The terminal hydrogen of 1*H*-perfluoroalkyl chains is known to be extremely inert.[1] These compounds can only be halogenated[2] or oxidized[3] by a radical mechanism at a very high temperature. They are not affected by concentrated potassium hydroxide at 100 °C; however, a slow hydrogen–deuterium exchange has been demonstrated in methanol.[4]

We describe here the mild ionic reaction of lithium dialkylamide on compound 1 yielding the amide **6**. The most probable reaction pathway is as follows:

$$R_F{-}CF_2{-}CF_2H \xrightarrow{R_2NLi} R_F{-}CF_2{-}CF_2^- \; Li^+$$

$$\mathbf{1} \qquad\qquad\qquad \mathbf{2}$$

$$\xrightarrow{-LiF} R_F{-}CF{=}CF_2 \xrightarrow{R_2NLi} R_F{-}\overline{C}F{-}CF_2{-}NR_2 \; Li^+$$

$$\mathbf{3} \qquad\qquad\qquad \mathbf{4}$$

$$\xrightarrow{-LiF} R_F{-}CF{=}CF{-}NR_2 \xrightarrow{H_3O^+} R_F{-}CHF{-}CONR_2$$

$$\mathbf{5} \qquad\qquad\qquad \mathbf{6}$$

The lithium dialkylamide initially reacts as a strong base, abstracting a proton from the CHF_2 group, then as a nucleophile which adds readily on the fluorinated alkene **3**. This attack occurs on the difluoromethylene group and yields the most stable anion **4**. Carbanions **2** and **4** produce respectively the perfluoroalkene **3** and the fluorinated enamine **5**, both by loss of F^-. This enamine **5** may be isolated in aprotic media. For instance, $C_6H_5CH_2OCH_2CF_2CF_2CF{=}CFN(CH_2CH_3)_2$ (**5d**) was enough stable to be recovered unchanged after 1 month at 0 °C; its ^{19}F NMR spectrum shows a cis configuration (J_{FF} = 7 Hz). Using the lithium reagent (1–2 molar equiv) we have found that the reaction needs 2 molar equiv to go to completion and not any olefin **3** could be detected during the reaction by ^{19}F NMR on the crude reaction medium.

Amide **6** can be obtained from 1*H*-perfluoroalkyl chains containing a variety of functional groups such as ether, ketal, amide, etc. This type of compounds is readily available by a radical addition on tetrafluoroethylene.[5] The compounds with R_F = $-(CF_2)_nCH_2OH$ can be obtained commercially.[6] The results obtained with various substrates, using 2 equiv of lithium diethylamide in diethyl ether, are listed in Table I.

Bifunctional fluorinated compounds are relatively rare synthetic intermediates.[7] They are generally symmetrical. The functionalization of 1*H*-perfluoroalkyl chains by lithium dialkylamide constitutes a smooth access to symmetrical or unsymmetrical bifunctional fluorinated intermediates.

Experimental Section

Preparation of N,N-Diethyl-2*H*-decafluorohexanoic Acid Amide (6a). Into a 250-ml three-neck flask equipped with a mechanical stirrer, a condenser–drying tube system, and addition funnel fitted to provide an argon atmosphere was placed 5 g (15 mmol) of 1*H*-perfluorohexane in 30 ml of anhydrous diethyl ether. The flask was cooled at −10 °C with a CCl$_4$–dry ice bath. With stirring, a white suspension of lithium diethylamide [prepared by addition of 3.5 g (48 mmol) of diethylamine in 100 ml of ether on 31 mmol of a butyllithium solution in pentane at 0 °C] was added dropwise. After stirring the mixture for 1 h, it was acidified with 30 ml of 20% HCl solution. The mixture was extracted with diethyl ether. The organic layer was dried over MgSO$_4$ and filtered, and the solvent was evaporated under reduced pressure. The residue was distilled under vacuum to give 3.5 g of **6a**: bp 95–96 °C (12 mm); IR (neat) 1660 cm^{-1} (amide); ^{1}H NMR (CDCl$_3$) 3.45 (q, 4 H, J = 7 Hz), 1.2 (t, 6 H), 5.5 (ddd, 1 H, J = 46, 16, 7 Hz); ^{19}F NMR (CDCl$_3$) 79 (3 t, 3 F, J = 11, 2 Hz), 124 (m, 2 F), 121 (m, 2 F), 117 (dm, 1 F, J = 280 Hz), 121 (dm, 1 F), 194 (ddd, 1 F); mass spectrum m/e (rel intensity) 351 (M$\cdot^+$, 67), 336 (M − CH$_3$, 96), 332 (M − F, 100), 322 (M − C$_2$H$_5$, 48).

Anal. Calcd for C$_{10}$H$_{11}$F$_{10}$NO: C, 34.15; H, 3.12; F, 54.10. Found: C, 34.06; H, 3.10; F, 54.23.
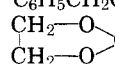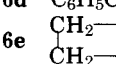
The same general procedure was used to prepare the other amides **6**.

N,N,N',N'-Tetraethyl-2*H*,5*H*-hexafluorohexanedioic Acid Amide (6b): bp 160–161 °C (0.1 mm); IR (neat) 1670 cm^{-1} (amide); ^{1}H NMR (CDCl$_3$) 3.4 (q, 8 H, J = 7 Hz), 1.2 (t, 12 H), 5.65 (ddd, 1 H, J = 45, 8, 14 Hz); ^{19}F NMR (CDCl$_3$) 122–123 (m, 4 F), 197 (dm, 2 F); mass spectrum m/e (rel intensity) 365 (M + 1·$^+$, 12), 345 (M − F, 15), 292 (M − NEt$_2$, 63), 264 (M − CONEt$_2$, 100).

N,N,N',N'-Tetraethyl-2*H*-nonafluoroheptanedioic Acid Amide (6c): bp 169–170 °C (0.1 mm); IR (neat) 1670 cm^{-1} (amide); ^{1}H NMR (CDCl$_3$) 1.2 (2 t, 12 H, J = 7 Hz), 3.42 (q, 8 H), 5.65 (ddd, 1 H, J = 46, 12, 9 Hz); ^{19}F NMR (CDCl$_3$) 119–121 (3 m, 6 F), 117 (dm, 1 F, J = 310 Hz), 122 (dm, 1 F), 197 (ddd, 1 F, J = 46, 25, 12 Hz); mass spectrum m/e (rel intensity) 432 (M·$^+$, 10), 404 (M − C$_2$H$_4$, 10), 344 (M − C$_2$H$_4$ − HF, 100).

N,N-Diethyl-2*H*,5*H*,5*H*-5-benzyloxypentafluoropentanoic

Table I

	Substrate		Amide	Yield, %
1a	CF$_3$(CF$_2$)$_3$CF$_2$CF$_2$H	**6a**	CF$_3$(CF$_2$)$_3$CHFCONEt$_2$	60
1b	HCF$_2$CF$_2$(CF$_2$)$_2$CF$_2$CF$_2$H	**6b**	Et$_2$NCOCHF(CF$_2$)$_2$CHFCONEt$_2$	60
1c	Et$_2$NCO(CF$_2$)$_4$CF$_2$CF$_2$H	**6c**	Et$_2$NCO(CF$_2$)$_4$CHFCONEt$_2$	40
1d	C$_6$H$_5$CH$_2$OCH$_2$(CF$_2$)$_2$CF$_2$CF$_2$H	**6d**	C$_6$H$_5$CH$_2$OCH$_2$(CF$_2$)$_2$CHFCONEt$_2$	60
1e	CH$_2$—O ⟩CH(CF$_2$)$_4$CF$_2$CF$_2$H CH$_2$—O	**6e**	CH$_2$—O ⟩CH(CF$_2$)$_4$CHFCONEt$_2$ CH$_2$—O	60

Acid Amide (6d): bp 140–141 °C (0.1 mm); IR (neat) 1660 (amide), 1600, 1580, 1500 cm^{-1} (aromatic); ^{1}H NMR (CDCl$_3$) 7.3 (s, 5 H), 4.6 (s, 2 H), 3.95 (t, 2 H, J = 14 Hz), 5.55 (ddd, 1 H, J = 47, 15, 7 Hz), 3.35 (q, 4 H, J = 7 Hz), 1.1 (t, 6 H); ^{19}F NMR (CDCl$_3$) 121 (dt, 2 F, J = 10, 14 Hz), 122 (ddd, 1 F, J = 294, 15, 16 Hz), 127 (ddd, 1 F, J = 13, 7 Hz), 200 (m, 1 F); mass spectrum m/e (rel intensity) 353 (M·$^+$, 43), 334 (M − F, 12), 297 (M − 2C$_2$H$_4$, 10), 262 (M − C$_7$H$_7$, 42), 247 (M − C$_7$H$_7$ − CH$_3$, 100).

Anal. Calcd for C$_{16}$H$_{20}$F$_5$NO$_2$: C, 54.38; H, 5.70; N, 3.96. Found: C, 54.65; H, 5.55; N, 3.77.

The enamine **5d** (1-diethylamino-5H,5H-5-benzyloxyhexafluoropentene-1) was isolated from the crude reaction mixture by evaporation of the solvent before hydrolysis: ^{19}F NMR 117 (tt, 2 F), 122 (m, 2 F), 120 (dt, 1 F, J = 12, 7 Hz), 115 (dt, 1 F, J = 12 Hz).

N,N-Diethyl-2H,7H-7-ethylenedioxynonafluoroheptanoic Acid Amide (6e): bp 139–140 °C (0.1 mm); IR (neat) 1660 cm^{-1} (amide); ^{1}H NMR (CDCl$_3$) 3.5 (q, 4 H, J = 7 Hz), 1.25 (t, 6 H), 3.95 (m, 4 H), 4.9 (ddd, 1 H, J = 34, 13, 6 Hz), 5.1 (m, 1 H); ^{19}F NMR 119–121–124 (m, 8 F), 197 (dm, 1 F); mass spectrum m/e (rel intensity) 405 (M·$^+$, 10), 361 (M − OC$_2$H$_4$, 18), 346 (M − OC$_2$H$_3$, 100), 332 (M − C$_3$H$_5$O$_2$, 36).

Anal. Calcd for C$_{13}$H$_{15}$F$_9$NO$_3$: C, 38.53; H, 3.98; N, 3.46. Found: C, 38.68; H, 3.84; N, 3.46.

Registry No.—**1a**, 355-37-3; **1b**, 336-07-2; **1c**, 60895-94-5; **1d**, 60895-95-6; **1e**, 60895-96-7; **5d**, 60895-97-8; **6a**, 60895-98-9; **6b**, 60895-99-0; **6c**, 60934-65-8; **6d**, 60896-00-6; **6e**, 60896-01-7.

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Synthesis and Activity of 29-Hydroxy-3,11-dimethyl-2-nonacosanone, Component B of the German Cockroach Sex Pheromone

Albert W. Burgstahler,* Leland O. Weigel,
Mark E. Sanders, and Craig G. Shaefer

*Department of Chemistry, The University of Kansas,
Lawrence, Kansas 66045*

William J. Bell and Susan B. Vuturo

*Department of Entomology, The University of Kansas,
Lawrence, Kansas 66045*

In a previous report,[1] we described a synthesis of 3,11-dimethyl-2-nonacosanone (**1**), an active component of the contact mating pheromone present in the cuticle of the female German cockroach (*Blattella germanica*). Recently, Ishii and co-workers, who first isolated and synthesized this substance,[2] have identified a closely related second component, 29-hydroxy-3,11-dimethyl-2-nonacosanone (**2**).[3] In connection with
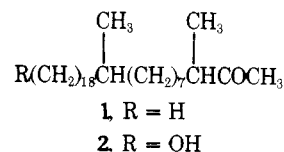
studies on the behavioral responses of cockroaches to pheromones,[4] we undertook and now describe a synthesis of **2** together with some preliminary bioassays.

As shown in Chart I, the benzyl ether (**3**) of 4-bromo-1-butanol was used to assemble the terminal hydroxy chain.

Chart I
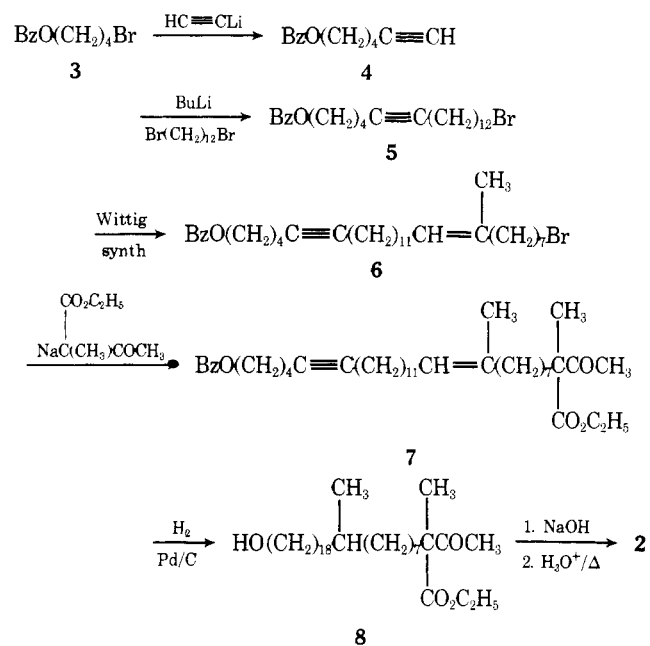
This derivative was selected because of its greater stability and convenience for removal compared to the alternative tetrahydropyranyl ether and because its distinctive spectral features made it especially useful for monitoring subsequent steps. The preparation of **3** was achieved in 88% yield by the phase-transfer catalyzed reaction[5] of 1,4-dibromobutane (5 equiv) with sodium benzyloxide. By alkylation with lithium acetylide (as the ethylenediamine complex), **3** was converted almost quantitatively into the acetylenic ether **4**. Monoalkylation of 1,12-dibromododecane (3 equiv) with the lithium salt of **4** then provided the acetylenic bromo ether **5** in 84% yield.

In the next step, a Wittig reaction of 9-bromo-2-nonanone[2] with the triphenylphosphorane derivative of **5** gave the olefinic bromo ether **6** as a mixture of Z and E isomers in 56% yield. Alkylation of **6** with ethyl 2-methylacetoacetate then furnished the required benzyloxy keto ester **7** in 91% yield. Finally, hydrogenation–hydrogenolysis of **7** gave the saturated hydroxy keto ester **8** (97% yield), mp 30–32 °C, which, when hydrolyzed and decarboxylated, afforded, in 71% yield from **8**, the desired hydroxy ketone **2** as a mixture of diastereoisomers, mp 41.5–43 °C.

Bioassay by antennation[1,2] showed that synthetic **2** readily evoked the characteristic precopulatory wing raising and 180°-turning response in isolated adult male German cockroaches. Male roaches isolated from their parent colonies were housed and tested in groups of five. In the tests their antennae were stroked intermittently (~10 s/min) with freshly ablated American cockroach (*Periplaneta americana*) antennae that had been dipped for 1–2 s into a carbon tetrachloride solution of the test substance and then allowed to dry.[6] All tests were performed at 24–25 °C during a period of 2.5–4.0 h into the dark phase of a 12/12-h photocycle.