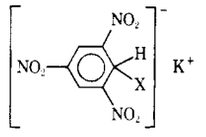
References and Notes

(1) (a) Deceased. (b) NRC Postdoctoral Fellow.
(2) S. K. Yasuda, *J. Chromatog.*, **13**, 78 (1964). An immobile impurity (TLC analysis) present in 2,4,6-trinitrotoluene is assumed to be **1**.
(3) A. N. Parnes, S. M. Shein, M. I. Kalinkin, L. I. Sidelnikova, and D. N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 2350 (1971). Chloranil oxidized I (X = CH_2NO_2) in 20 h at room temperature to give **1** in 12% yield. *Chemical Abstracts* [**76**, 59172e (1972)] indicates that **1** can be formed in 50% yield



I

from I (X = CH_2NO_2) and tropylium tetrafluoroborate. However, the original Russian article claims this reaction only for X = CH_2COCH_3. Analytical data and physical properties of **1** are not given.
(4) K. G. Shipp, L. A. Kaplan, and M. E. Sitzmann, *J. Org. Chem.*, **37**, 1966 (1972).
(5) L. V. Okhlobystina, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **10**, 2339 (1969), states that reaction of fluorotrinitromethane with reducing and nucleophilic reagents (KI, HI, $NaBH_4$, $FeCl_2$, SO_2, H_2O_2–$NaNO_2$) proceeds by a route involving radical intermediates. If radical intermediates are involved in the reaction of **2** with fluorotrinitromethane, one might expect formation of 2,2′,4,4′,6,6′-hexanitrobibenzyl from 2,4,6-trinitrobenzyl radical. However, no bibenzyl is produced in the reaction. In fact, no product other than **1** is detected by thin layer chromatography.
(6) M. J. Kamlet and H. G. Adolph, *J. Org. Chem.*, **33**, 3073 (1968). However, the formation of fluorodinitromethane in the reaction of fluorotrinitromethane with hydroperoxide ion can be explained either by attack of hydroperoxide ion on carbon with displacement of a nitro group or by attack of hydroperoxide ion on oxygen or nitrogen of one of the nitro groups with displacement of fluorodinitromethide ion.
(7) NMR spectra were determined on a Varian HA-100 spectrometer and the chemical shifts are relative to tetramethylsilane. The melting points are uncorrected.
(8) Reference 6, p 3079.

Synthesis of Bis(4-pyridyl)methane[1]

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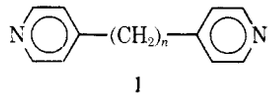
In connection with our studies of intramolecular electron transfer mediated by aromatic nitrogen heterocycles,[2,3] it became important to examine the role of the bridging ligands represented by **1**.



1

Bis(4-pyridyl)methane (compound **1**, where $n = 1$) is not available commercially, but its synthesis via the reaction of chloropyridine with 4-methylpyridine and potassium amide in liquid ammonia has been reported.[4] Unfortunately, repeated (18) attempts (under rigorous exclusion of water and oxygen) to synthesize this compound using the reported method yielded intractable oils, with properties unlike those described by Jampolsky et al.,[4] or those established in the present work for an authentic sample of the desired compound. Therefore, we designed an alternate synthesis of bis(4-pyridyl)methane, and report r results herein.

Bis(4-pyridyl) ketone was prepared using the method of Wibaut and Heeringa.[5] Conversion to the corresponding hydrocarbon was accomplished using the Huang-Minlon[6] modification of the Wolff–Kishner reduction, except that 1-butanol was used as the solvent.

The purified product is a white, crystalline, extremely hygroscopic solid,[7] and, therefore, must be handled by drybox techniques. Proof of the composition and structure of the compound is based on analytical and spectroscopic data reported in detail in the Experimental Section.

Experimental Section

4-Cyanopyridine (Aldrich) was recrystallized from ethanol. Diethyl ether was dried using calcium hydride, and was stored under dry nitrogen. 4-Bromopyridine hydrochloride (Pfaltz and Bauer) and *n*-butyllithium (2.9 M in hexane, Ventron) were used as received.

Visible and ultraviolet spectra were obtained using a Cary 118 spectrophotometer. Infrared spectra were obtained using a 567 Perkin-Elmer spectrophotometer using matched cells (Beckman-RIIC, Ltd). ^1H NMR spectra were obtained on a Varian CFT-20 instrument.[8] The mass spectrum (acetone solution) was obtained using a Hewlett-Packard 5980A mass spectrometer, preceded by a Hewlett-Packard 5710A gas chromatograph. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Inc., Woodside, N.Y.

Bis(4-pyridyl) ketone was synthesized (nitrogen atmosphere) using the literature[5] method, with some modifications. 4-Bromopyridine hydrochloride was neutralized in aqueous solution at 0 °C, and the free base was extracted into ether. The ether solution was dried over magnesium sulfate for 12 h at 5 °C, and then the concentration of 4-bromopyridine was determined gravimetrically.[9] The reaction was allowed to proceed as described[5] and the reported quenching procedure was utilized. The product was isolated as described,[5] except that following the treatment with active carbon, neutralization of the final aqueous phase gave a precipitate of (mostly) potassium sulfate, which was removed by filtration. The faintly yellow filtrate was extracted with ether. Evaporation of the ether gave a white solid which was recrystallized three or four times from ethanol, mp 136–137 °C. The 45% yield of recrystallized product is somewhat higher than that reported.[5]

Bis(4-pyridyl)methane. Bis(4-pyridyl) ketone (4.0 g, 0.022 mol) was added to a solution of 4.0 g of potassium hydroxide in 40 ml of 1-butanol at 60 °C. After stirring for 15 min, 3.7 ml of 85% hydrazine hydrate was added. The solution was refluxed for 1.3 h. Then some solvent was removed by distillation until the temperature of the vapors immediately above the reactant solution had reached 110 °C. Heating was continued under reflux conditions for 8 h. The resulting clear yellow solution was allowed to cool at 60 °C, and then treated with 60 ml of water. The aqueous phase was acidified to pH ~2 by dropwise addition of 6 M hydrochloric acid. The aqueous phase was extracted four times with 50-ml portions of ether, basified to pH 10, and then extracted repeatedly with benzene. The benzene extracts were evaporated at 40 °C to ca. 20 ml in a flash evaporator. The resulting solution was placed on an alumina column (5 × 0.5 in., neutral, activity 1.0, 80–200 mesh), and the column was eluted with 300 ml of benzene. The benzene was removed by evaporation at 40 °C in a flash evaporator to yield a clear, colorless oil. The last traces of benzene were removed at room temperature on a vacuum line, resulting in the crystallization of small, white needles. Since the substance is quite volatile, as a further purification, it was subjected to a short path vacuum distillation at 40 °C onto a cold finger at 15 °C, yielding a white, crystalline solid. The apparatus was filled with dry nitrogen, and then transferred to a dry bag over phosphorus pentoxide. All subsequent manipulations were performed in a glove bag. Yield 3.3 g, 89%; mp 36–37 °C;[10] IR (C_6H_6) 2990 m, 2969 w, 2930 w, 1600 vs, 1565 m, 1420 vs, 1208 w, 1060 w, 982 m, 910 vw, 828 w, 785 m, 770 m, 610 s, 540 m, 475 cm^{-1} w; NMR (C_6D_6/Me_4Si) δ 3.19 (s, 2 H, $-CH_2-$), 6.46 (m, 4 H, aromatic H), 8.40 (m, 4 H, aromatic H); MS *m/e* 170 (P, base), 171 (11.6%) 169 (65%), 168 (11%), 143 (6%), 142 (11%), 141 (4%), 117 (5%), 115 (8%), 92 (3%), 89 (5%), 84 (3%), 65 (5%), 63 (4%), 51 (7%); UV λ_{max} (water) 256 nm.

Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.61; H, 5.93; N, 16.46. Found: C, 77.69; H, 6.10; N, 16.14.

Registry No.—Bis(4-pyridyl) ketone, 6918-15-6; 4-bromopyridine HCl, 19524-06-2; 4-bromopyridine, 1120-87-2; bis(4-pyridyl)methane, 60776-05-8.

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(5) J. P. Wibaut and L. G. Heeringa, *Recl. Trav. Chim. Pays-Bas*, **74**, 1003 (1955).

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(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.
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(10) Compare with the value 138–140 °C reported in ref 4.

Functionalization of 1*H*-Perfluoroalkyl Chains

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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:

$$R_F{-}CF_2{-}CF_2H \xrightarrow{R_2NLi} R_F{-}CF_2{-}CF_2^- Li^+$$
1 **2**

$$\xrightarrow{-LiF} R_F{-}CF{=}CF_2 \xrightarrow{R_2NLi} R_F{-}\bar{C}F{-}CF_2{-}NR_2\ Li^+$$
3 **4**

$$\xrightarrow{-LiF} R_F{-}CF{=}CF{-}NR_2 \xrightarrow{H_3O^+} R_F{-}CHF{-}CONR_2$$
5 **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

^1H NMR spectra were recorded on a Perkin-Elmer R24 spectrometer with Me_4Si as internal standard. ^{19}F NMR spectra were recorded on a JEOL C-60HL spectrometer with $CFCl_3$ as external standard. Chemical shifts are given in parts per million. A downfield displacement is positive for proton, negative for fluorine. Coupling constants are in hertz. The s, d, t, q, m, usual abbreviations are used with the composite form dd, dt, dm, tt, ddd which are doublet of doublets, doublet of triplets, doublet of multiplets, triplet of triplets, and doublet of doublets of doublets. IR spectra were obtained on a Perkin-Elmer 167 spectrometer. Mass spectra data were obtained on a AEI MS 30 spectrometer.

We thank Mr. Foulletier (PCUK)[11] for a sample of 1*H*-perfluorohexane **1a.** 1*H*,6*H*-Perfluorohexane **1b** was prepared according to the method of Brace.[8] Compounds **1c** and **1d** were prepared starting from commercial (PCR)[11] 1*H*,1*H*,7*H*-dodecafluoroheptanol and 1*H*,1*H*,5*H*-octafluoropentanol. The first alcohol was oxidized following Joyce procedure[9] and the acid was transformed as usual in acid chloride, then in amide **1c.** The second alcohol was transformed in ether **1d** with benzyl bromide. Compound **1e** was obtained by transketalization[10] of 7*H*-dodecafluoroheptanal prepared according to the method of Brace.[7] We thank Mr M. Rubinstein for technical assistance and the D.G.R.S.T.[11] for financial support.

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); ^1H 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 ($M - C_2H_5$, 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.

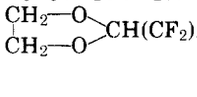
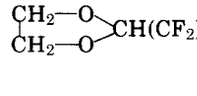
The same general procedure was used to prepare the other amides **6.**

***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); ^1H 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 ($M + 1^{\cdot+}$, 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); ^1H 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 ($M^{\cdot+}$, 10), 404 ($M - C_2H_4 - HF$, 100).

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

Table I

	Substrate		Amide	Yield, %
1a	$CF_3(CF_2)_3CF_2CF_2H$	**6a**	$CF_3(CF_2)_3CHFCONEt_2$	60
1b	$HCF_2CF_2(CF_2)_2CF_2CF_2H$	**6b**	$Et_2NCOCHF(CF_2)_2CHFCONEt_2$	60
1c	$Et_2NCO(CF_2)_4CF_2CF_2H$	**6c**	$Et_2NCO(CF_2)_4CHFCONEt_2$	40
1d	$C_6H_5CH_2OCH_2(CF_2)_2CF_2CF_2H$	**6d**	$C_6H_5CH_2OCH_2(CF_2)_2CHFCONEt_2$	60
1e		**6e**		60