(2 H, q, J = 7 Hz, $-CH_2CH_3$), 6.04 (1 H, t, J = 8 Hz, -CH=), 7.22 (5 H, s, Ph), 9.15 (1 H, s, NH).

Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.77; H, 6.18; N, 12.11.

2-(2,4-Dimethoxybenzylamino)-4-phenyl-3-butenonitrile (13). To an ice-cold stirred solution of cinnamaldehyde (2.64 g) and 2,4-dimethoxybenzylamine hydrochloride (4.07 g) in 40 ml of MeOH, a solution of NaCN (1.0 g) in 10 ml of H_2O was added. The mixture was stirred for an additional 45 min at 5–10 °C, diluted with H_2O, and extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over anhydrous $MgSO_4$, and evaporated in vacuo to give 5.9 (96%) of crude **13** as a colorless oil: ir (neat) 3340 (NH), 2240 (C≡N), 1620 cm^{-1} (C=C); NMR ($CDCl_3$) δ 2.1 (NH), 3.77 (3 H, s, OCH_3), 3.79 (3 H, s, OCH_3), 3.66–4.12 (2 H, d, $-NHCH_2$), 4.36 (1 H, d, d, J = 5, 2 Hz, NHCHCH=), 6.14 (1 H, d, d, J = 5, 15 Hz, =CHCHN), 6.3–7.5 ppm [9 H, m, $C_6H_3(OCH_3)_2$, C_6H_5, and PhCH=CH–). A small portion of the crude oil was dissolved in hexane–dry ether (1:1) and dry HCl was passed into the solution to precipitate **13** HCl. Recrystallization from absolute ethanol–hexane gave colorless crystals, mp 113–115 °C dec.

Anal. Calcd for $C_{19}H_{21}N_2O_2Cl$: C, 66.17; H, 6.14; N, 8.12. Found: C, 65.93; H, 6.19; N, 8.00.

2-Amino-4-phenyl-3-butenonitrile Trifluoroacetate (14). Crude **13** (5.54 g) and *m*-dimethoxybenzene (5 g) were dissolved in 40 ml of CF_3COOH with ice cooling, and the mixture was allowed to stand at room temperature for 15 h. After evaporation of CF_3COOH in vacuo, 20 ml of MeOH was added to the residue and the mixture was evaporated in vacuo. The residual oil was washed with petroleum ether and crystallized from benzene–hexane. The crystal were collected and washed with benzene to give 3.5 g (67%) of **14** as pale yellow prisms, mp 122–125 °C. Recrystallization from EtOAc–hexane gave an analytical sample: mp 122–124 °C dec; ir (KBr) 2260 cm^{-1} (C≡N); NMR (CF_3COOH) δ 5.23 (1 H, d, J = 6 Hz, -CHNH), 6.15 (1 H, d, d, J = 6, 15 Hz, =CHCH), 7.02 (1 H, d, J = 15 Hz, PhCH=), 7.22 ppm (5 H, m, C_6H_5).

Anal. Calcd for $C_{12}H_{11}N_2O_2F_3$: C, 52.94; H, 4.07; N, 10.29. Found: C, 52.79; H, 4.12; N, 10.45.

Styrylglycine (9). A. Direct Hydrolysis of 13. Crude aminonitrile **13**, prepared from 264 mg of cinnamaldehyde, was dissolved in 5 ml of MeOH and added to 30 ml of concentrated HCl and the solution was refluxed for 3 h. The reaction mixture was filtered to remove some resinous product, washed twice with $CHCl_3$, and evaporated to dryness giving a crystalline residue. The crude product was dissolved in a minimum amount of H_2O, and the pH was adjusted to 6.5 with dilute NaOH. After cooling, the precipitate was collected, washed with a small amount of H_2O and EtOH, successively, and dried to give 50 mg (overall yield 13%) of **9** as pale orange crystals, mp 178–183 °C dec. Recrystallization from H_2O gave colorless leaves: mp 198–200 °C dec; ir (Nujol) 3050–2650 (NH_3^+), 1655 cm^{-1} (COO^-); NMR (CF_3COOH) δ 5.06 (m, 1 H, -CHCOOH), 6.25 (1 H, d, d, J = 16, 6 Hz, PhCH=CH–), 7.06 (1 H, d, J = 16 Hz, PhCH=), 7.40 (5 H, s, C_6H_5–), 7.58 ppm (3 H, broad s, NH_3^+).

Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found: C, 67.87; H, 6.37; N, 7.84.

B. Hydrolysis of 14. Three hundred milligrams of **14** was dissolved in 15 ml of concentrated HCl and the solution was refluxed for 3 h. Evaporation of the reaction mixture gave a solid which was dissolved in H_2O. The solution was filtered to remove insoluble material and neutralized with dilute NaOH. After cooling, the precipitate was collected, washed with H_2O and EtOH, successively, and dried to give 75 mg (35%) of **9** as colorless crystals, mp 180–185 °C dec. The ir spectrum was identical with that of the product obtained by method A.

C. Hydrolysis of 14 via the Imino Ester. A solution of **14** (2.91 g) in 30 ml of absolute MeOH was saturated with dry HCl at 0 °C. After 2 h at room temperature, the reaction mixture was diluted with 300 ml of concentrated HCl and refluxed for 2 h. Using the same work-up procedure, 1.31 g (70%) of **9** as colorless crystals was obtained, mp 185–190 °C. The spectrum was identical with that of **9** obtained by method A.

D. From 4b. A solution of 0.92 g (3 mmol) of **4b** in 35 ml of glacial acetic acid and 35 ml of 6 N HCl was refluxed for 24 h. The dark reaction mixture was extracted with three 20-ml portions of diethyl ether and the aqueous solution was concentrated to 4–6 ml on a vacuum pump. After diluting with 20 ml of water, the aqueous solution was clarified with Norit and again evaporated in vacuo giving an extremely hygroscopic residue. The residue was redissolved in 15 ml of water, and the solution was adjusted to pH 5.0–6.0 with 10% ammonium hydroxide solution. After cooling to 0 °C, the precipitated amino acid was filtered and dried in vacuo, giving 0.215 g (41%) of crude product, mp 155–168 °C. Recrystallization from an ammonium acetate buffered solution gave 0.13 g (24%) of **9**, mp 181–190 °C dec (recrystallization raised the melting point to 196–199 °C), identical in all respects with authentic sample.

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Registry No.—**2a,** 58117-73-0; **3b,** 58117-74-1; **3c,** 58117-75-2; **4b,** 58117-76-3; **4c,** 58117-77-4; **5,** 58117-78-5; **6,** 58117-79-6; **7,** 58117-80-9; **8,** 58117-81-0; **9,** 58207-08-2; **10a,** 58117-82-1; **12a,** 58117-83-2; **12b,** 58117-84-3; **13,** 58117-85-4; **13**·HCl, 58117-86-5; **14,** 58117-88-7; β-3,4-dihydroxy-DL-phenylalanine, 63-84-3; (*E*)-α-methylcinnamoyl chloride, 38449-13-7; (*E*)-cinnamaldehyde, 14371-10-9; 2,4-dimethoxybenzylamine hydrochloride, 6967-51-7.

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A Facile Preparation of Highly Fluorinated Diamines

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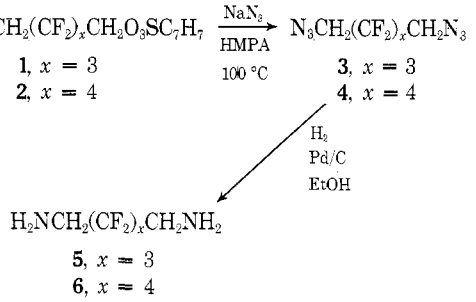
Most highly fluorinated amines and diamines are prepared by lithium aluminum hydride reduction of the corresponding amides[1] or by high-pressure (1000 psi) catalytic hydrogenation of nitriles.[2] The former class of compounds often gives highly explosive reaction mixtures,[1] while the latter reaction is inconvenient and involves an additional dehydration step in the synthesis. Both methods proceed in only moderate yield. Previous attempts to employ the easily obtained 2,2,3,3,4,4-hexafluoropentane 1,5-di-*p*-toluenesulfonate (**1**) with ammonia, methylamine, or diethylamine gave only tarry mixtures from which no amine could be isolated.[1] In one instance,[3] reaction of 1,1-di-*H*-heptafluorobutyl *p*-toluenesulfonate with aniline at 230 °C for 24 h gave a 68% yield of the desired amine, but reaction with ammonia gave only tars.

It has now been found that reaction of **1** with an excess of sodium azide takes place readily to give an almost quantitative yield of diazide **3** when hexamethylphosphoric triamide (HMPA) is employed as solvent. Azide formation was not observed when DMF was used as solvent. The

crude diazide was reduced directly to the diamine **5** in 82–90% yield by catalytic hydrogenation in ethanol at 3 atm using 10% Pd/C catalyst.[4] A similar sequence of reactions led to 2,2,3,3,4,4,5,5-octafluorohexane-1,6-diamine (**6**).



Experimental Section[5]

2,2,3,3,4,4-Hexafluoropentane-1,5-diazide (3). A mixture of 20.0 g (0.038 mol) of ditosylate **1**,[1] 10.0 g (0.15 mol) of sodium azide, and 70 ml of HMPA was stirred and heated in an oil bath[6] at 100–110 °C for 19 h. The mixture was cooled and ca. 300 ml of water was added. The aqueous mixture was extracted three times with ether, washed twice with water, dried over $MgSO_4$, and evaporated in vacuo to leave 10.2 g (99%) of product as a pale yellow oil: ν_{max} (neat) 2100 (s), 2150 (sh), 2210 cm^{-1} (sh); NMR ($CDCl_3$) δ 2.4–4.0 (m). The purity of **3** was estimated by integrating the CH_2 multiplet against a small amount of aromatic resonance still present from unreacted tosylate, and was of the order of 90 ± 3%.

2,2,3,3,4,4,5,5-Octafluorohexane 1,6-Di-*p*-toluenesulfonate (2). To a solution of 100 g (0.38 mol) of 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol[7] in 500 ml of dry pyridine cooled in an ice bath was added 195.0 g (1.0 mol) of *p*-toluenesulfonyl chloride in several portions with strong stirring. The temperature of the reaction was maintained at 30 °C or less until the end of the addition. After the reaction mixture was kept chilled for a further 2 h, it was allowed to equilibrate to room temperature and left overnight. The mixture was poured into 2 l. of cold 1 N HCl and the precipitate collected. Trituration of the moist solid with methanol gave 188.2 g (87%) of white solid, mp 134–136 °C.

Anal. Calcd for $C_{20}H_{18}F_8O_6S_2$: C, 42.08; H, 3.18; F, 26.67. Found: C, 41.65; H, 2.87; F, 26.48.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diazide (4). This was prepared in a like manner as **3** from the ditosylate **2** in 92 ± 3% crude yield.

2,2,3,3,4,4-Hexafluoropentane-1,5-diamine (5). To a solution of 10.7 g of diazide **3** in 60 ml of absolute ethanol was added 1–2 g of 10% palladium on carbon. The mixture was hydrogenated at 48 psi for 5 h and filtered, and the solvent evaporated under reduced pressure. Distillation of the residual oil gave 8.1 g (90%) of colorless oil, bp 65–67 °C (0.7 mm),[8] $n^{25}D$ 1.373, which darkened slightly on standing. A sample in ethanol was treated with ethereal HCl and the precipitate recrystallized from ethanol–ether, mp 305–310 °C dec.

Anal. Calcd for $C_5H_8F_6N_2 \cdot 2HCl$: C, 21.22; H, 2.81; N, 9.90. Found: C, 21.37; H, 3.46; N, 9.91.

2,2,3,3,4,4,5,5-Octafluorohexane-1,6-diamine (6). This compound was prepared similarly as described for **5** in 87% yield, bp 95–98 °C (0.6 mm), mp 44–45 °C (reported[2] 44–45 °C).

Registry No.—**1**, 632-01-9; **2**, 58191-47-2; **3**, 58191-48-3; **4**, 58191-49-4; **5**, 336-33-4; **5** 2HCl, 58191-50-7; 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, 355-74-8.

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(4) For examples of this procedure see J. H. Bayer and F. C. Canter, *Chem. Rev.*, **54**, 38 (1954).
(5) Boiling points and melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 137 Infracord spectrophotometer. NMR spectra were measured on a Varian Associates T-60 spectrophotometer using Me_4Si as an internal standard. Combustion analyses were done by Galbraith Laboratories, Knoxville, Tenn.
(6) The use of a heating mantle is not advisable. In one experiment employing a mantle, superheating occurred which led to a vigorous reaction with concomitant decomposition to dark tarry materials.
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Synthesis and Reactions of Perfluorodialdehydes

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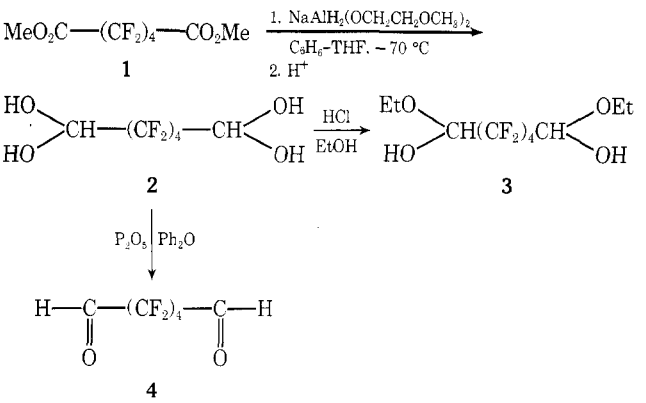
The synthesis of perfluoroaldehydes has generally been accomplished by the lithium aluminum hydride ($LiAlH_4$) reduction of the corresponding esters at low temperatures.[1] Inverse addition has been reported to improve yields.[2,3] Although there have been no reports of perfluorodialdehydes in the literature, we anticipated no difficulty in their preparation by the standard methods described above. However, only traces of the desired product could be detected from the $LiAlH_4$ reduction of dimethyl perfluoroadipate in ether at either 0 °C or −70 °C. Equally unsuccessful was the attempted reduction of perfluoroadipoyl chloride in tetrahydrofuran using lithium tri-*tert*-butoxyaluminum hydride.

Successful synthesis of the desired dialdehyde (as the dihydrate) was achieved in good yield by employing commercially available sodium bis(methoxyethoxy)aluminum hydride (Vitride, 70% in benzene) in tetrahydrofuran solution at −70 °C. The dihydrate **2** reacted with 2,4-dinitrophenylhydrazine in acid solution to give a crystalline yellow bis-2,4-dinitrophenylhydrazone. Treatment of **2** with HCl in ethanol afforded the hemiacetal **3**, while dehydration of **2** to the free dialdehyde **4** was most conveniently carried out using phosphorus pentoxide in diphenyl ether.



When the Vitride reduction of diethyl perfluoroglutarate was effected under similar conditions, the dialdehyde was obtained in the form of the cyclic hemiacetal **8**, formation of which seems best explained by intramolecular cyclization of the initial reduction product **6** to **7** followed by further reduction to **8**. Reaction of perfluoro diesters with Vitride at room temperature afforded consistent yields of greater than 90% of perfluoro diols. Although $LiAlH_4$ reductions were also satisfactory in providing diols,[4] the convenience and greater safety margin of Vitride makes it the reagent of choice—especially in those cases where large quantities of material are required.