yielding 0.28 g. (72%) of buff-colored solid of m.p. 261–264°. Crystallization from dilute acetic acid or Pentasol raised the m.p. to 275°.

Anal. Calcd. for $C_{23}H_{16}O_2N_3Cl$: C, 72.9; H, 3.5; N, 9.1; Cl, 7.7. Found: C, 72.5; H, 3.7; N, 9.2; Cl, 8.1.

4,4′,5,5′-Tetraphenyl-3,3′-bi-*s*-triazole (XVI).—A mixture of 5.9 g. (0.021 mole) of diphenyloxalimidyl chloride[11] and 6.4 g. (0.047 mole) of benzhydrazide in 50 ml. of *o*-dichlorobenzene was stirred for one hour in an oil-bath at 120°. The reaction mixture was cooled overnight, and filtered to remove some yellow salt-like material which was discarded. Dilution of the filtrate with hexane gave 2.6 g. of pale yellow solid with a very indefinite m.p., approximately 270–290°. Crystallization from 60 ml. of chlorobenzene gave 1.15 g. (12%) of product with m.p. 300–306°. Crystallization from Pentasol alternating with chlorobenzene raised the m.p. to 308–309.5°.

Anal. Calcd. for $C_{28}H_{20}N_6$: C, 76.4; H, 4.5; N, 19.1. Found: C, 76.3; H, 4.6; N, 19.1.

This compound showed an absorption maximum in the ultraviolet at 253 mμ (ε 26500) (10 mg. per liter in dimethylformamide buffered with 0.4% ammonium acetate). Under the same conditions, 3,4,5-triphenyl-*s*-triazole showed maximum absorption at 255 mμ (ε 18,800).

Acknowledgment.—The author is indebted to F. C. Dexter for the spectral data and to O. E. Sundberg and his associates for the microanalyses.

BOUND BROOK, N. J.

---

[11] R. Bauer, *Ber.*, **40**, 2650 (1907).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE HOOKER ELECTROCHEMICAL CO.]

Fluorine-containing Secondary Diamines[1,2]

BY BURTON S. MARKS[3a] AND GEORGE C. SCHWEIKER[3b]

RECEIVED DECEMBER 9, 1957

N,N′-Substituted derivatives of 2,2,3,3,4,4-hexafluoropentane-1,5-diamine have been safely prepared by the lithium aluminum hydride reduction of the corresponding N,N′-substituted perfluoroglutaramides. The base strengths of these fluorine-containing secondary diamines have been determined in order to assess the loss of basicity due to the inductive effect of the CF_2 groups.

As part of a study in the preparation of fluorinated polyamides for investigations of special condensation elastomers, it was required to prepare compounds having the general structure $(CF_2)_n(CH_2NHR)_2$, wherein R = alkyl or fluoroalkyl group. It is believed that compounds of this general type have not been prepared before. Primary fluorinated diamines (where R = H) have been previously prepared[4] by reduction of perfluorodinitriles in acetic anhydride over platinum oxide, and then hydrolysis of the acetylated diamines. The attempted preparation of 2,2,3,3-tetrafluorobutane-1,4-diamine by lithium aluminum hydride reduction of perfluorosuccinamide resulted in an explosion.[5] An investigation into the cause of the detonation indicated that an unstable complex formed which could detonate at room temperature. It further was shown that perfluoroadipamide as well as certain fluorinated monocarboxamides formed complexes which also could be detonated; but these compounds decomposed less violently and at elevated temperatures. Similar difficulties with unstable complexes were experienced by Karo[6] in the preparation of 2,2,2-trifluoroethylamine and N-ethyl-2,2,3,3,4,4,4-heptafluorobutylamine.

In the present study, a number of synthetic routes for the preparation of fluorine-containing secondary diamines have been investigated. It has been shown that fluoroalkyl tosylates could be made to react with alkali halides to give the corresponding fluoroalkyl halides.[7] This evidence suggested that an analogous reaction of the tosyl esters with an amine might plausibly produce the substituted secondary amine desired. The reaction of 2,2,3,3,4,4-hexafluoropentane-1,5-di-*p*-toluenesulfonate with methylamine at 165° did not give the desired product, but instead gave a mixture of unidentified products and tars, from which N-methyl-*p*-toluenesulfonamide was isolated in small quantities. Recent work,[8] in which aniline and 2,2,3,3,4,4,4-heptafluorobutyl tosylate have been allowed to react at 230° to yield N-2,2,3,3,4,4,4-heptafluorobutylaniline, has shown the feasibility of this type of reaction for aniline. However, under similar conditions, attempts to treat the tosyl ester with ammonia or diethylamine gave tarry decomposed mixtures from which the desired products could not be isolated.[8] The 2,2,3,3,4,4-hexafluoropentane-1,5-di-*p*-toluenesulfonate was prepared by the reaction of 2,2,3,3,4,4-hexafluoropentane-1,5-diol with *p*-toluenesulfonyl chloride in yields of 45–65%. Small amounts of the corresponding mono-*p*-toluenesulfonate also were obtained. Catalytic reduction of fluorinated amides has not been used widely. A reduction of trifluoroacetamide over copper chromite to yield the corresponding amine has been reported by Henne[9]; however, yields or experimental conditions were not given. Henne also reported a similar reduction of trifluoroacetamide over platinum to yield 2,2,2-trifluoroethanol instead of 2,2,2-trifluoroethylamine.

In an attempt to prepare N,N′-dimethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine, N,N′-dimethylperfluoroglutaramide was treated at 175°

---

[1] This work was supported by the U. S. Air Force under contract AF 33(616)2421 and monitored by Materials Laboratory, Wright Air Development Center, Wright–Patterson Air Force Base, Ohio.

[2] This paper was presented in part at the 133rd Meeting of the American Chemical Society in San Francisco, Calif., April, 1958.

[3] (a) Continental Can Co., Metals Division, Research and Development, Chicago, Ill. (b) Velsicol Chemical Corp., Research and Development Department, Chicago, Ill.

[4] E. T. McBee, P. A. Wiseman and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

[5] T. S. Reid and G. H. Smith, *Chem. Eng. News*, **29**, 3042 (1951).

[6] W. Karo, *ibid.*, **33**, 1368 (1955).

[7] G. V. D. Tiers, H. A. Brown and T. S. Reid, THIS JOURNAL, **75**, 5978 (1953).

[8] H. A. Brown and G. V. D. Tiers, *J. Org. Chem.*, **22**, 454 (1957).

[9] A. L. Henne, R. L. Pelley and R. L. Alun, THIS JOURNAL, **72**, 3370 (1950).

under 2500 p.s.i. of hydrogen and methylamine using copper chromite and also a mixed catalyst of copper chromite and Raney nickel. The reduction was very slow and mainly starting material was obtained even after protracted reaction times. In an endeavor to determine whether fluorine-containing secondary diamines could be prepared *via* an interesting reaction successful with non-fluorinated alcohols and amines,[10] 2,2,3,3,4,4-hexafluoropentane-1,5-diol was treated with aniline. The reaction consisted of heating a mixture of the diol, aniline and a small amount of the sodium salt of the diol, with Raney nickel. The reaction appeared to occur to a limited extent in that both hydrogen and water were eliminated. They would arise from the dehydrogenation of the alcohol to the aldehyde with subsequent reaction of the aldehyde with aniline to yield the Schiff base and water. The work up of the reaction mixture yielded mainly starting material and a small quantity of yellow oil, b.p. 100° (2.5 mm.), with an infrared spectrum consistent with the structure $HOCH_2(CF_2)_3CH{=}NC_6H_5$.

Successful preparation of the fluorine-containing secondary diamines was realized by the lithium aluminum hydride reduction of the appropriate N,N′-substituted diamides. The diamides of the series $(CF_2)_3(CONHR)_2$ wherein R = methyl, ethyl, isopropyl, *n*-butyl, *t*-butyl and 2,2,3,3,4,4,4-heptafluorobutyl were prepared by two different methods: The first method, the reaction of the appropriate primary amine with a diester of perfluoroglutaric acid, was used successfully to prepare the methyl, ethyl and *n*-butyl amides in good yields. In general, this reaction proceeds most readily and in best yield when the ester used is dimethyl perfluoroglutarate as compared to ethyl or butyl perfluoroglutarate.

A second method was used to prepare the amides wherein R = isopropyl, *t*-butyl and 2,2,3,3,4,4,4-heptafluorobutyl. Because of the lower reactivity of the fluorinated amine and the branched amines with esters, perfluoroglutaryl chloride was used in place of methyl perfluoroglutarate. The reactions proceeded readily and in fair yields.

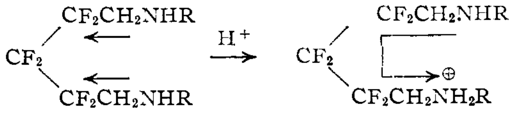
The lithium aluminum hydride reduction of the fluorinated diamides gave the desired amines in yields of 39–53%. The reaction was carried out for relatively long periods of time (72 hours), but even after this protracted period of time starting material still could be isolated. It is felt that the sluggish nature of these reactions is due in part to the insolubility of the starting diamides in ether. Diethyl ether, however, appears to be essential for the fair yields of diamine obtained, since when tetrahydrofuran–diethyl ether mixtures were used as the solvent for the reduction, very poor yields of diamine were produced even though the starting fluorinated diamides were soluble in the tetrahydrofuran. Using tetrahydrofuran–diethyl ether as solvent, increased amounts of by-product and starting material were found. A white crystalline solid, m.p. 103–103.5°, was isolated but not identified. In order to ensure safety, special points of caution in these reductions were observed as noted in the Experimental section, beyond the normal cautions[5,6,11] advocated for lithium aluminum hydride reductions of fluorinated amides.

In the work up of the products of the reductions, the hydrochloride salts of the amines were precipitated from the ether solutions. The fluorinated secondary diamines form insoluble monohydrochloride salts in ether with ease. The dihydrochloride salts are more difficult to obtain and purify. The free bases are obtained by neutralization of the hydrochloride salts and subsequent distillation.

As might be expected, fluorine-containing secondary amines, wherein one nitrogen substituent is an alkyl hydrocarbon, are stronger bases than related fluorine-containing primary amines. This is shown by comparison of pK_B for $C_3F_7CH_2NH_2$[12] = 8.3 with pK_{B1} for $(CF_2)_3(CH_2NHC_2H_5)_2$ = 7.18. On the other hand, it is apparent from the pK_{B1} for $(CH_2)_4(CH_2NHCH_2CH_2CH_2CH_3)_2$ = 2.72 as compared to the pK_{B1} for $(CF_2)_3(CH_2NHCH_2CH_2CH_2CH_3)_2$ = 6.93 that the inductive effect of the CF_2 groups reduces the basicity of the fluorine-containing secondary amine, compared to the hydrocarbon secondary amine, by about 4.2 *pK* units. The pK_{B2}, or the basicity of the second amine function in the fluorinated series, can be compared only roughly with the pK_{B2} of the hydrocarbon series shown, because of the extra methylene group in the latter series. In general, for the fluorinated series, values for pK_{B2} show that the second amine moiety is a weaker base than the first by 0.97 to 1.38 *pK* units.

In the hydrocarbon series of secondary diamines the ΔpK_B values (shown in Table I) vary from −0.02 to 0.27 *pK* unit. It would appear in this series that the *t*-butyl substituents sufficiently shield the two amino groups from each other so that one amino group will not affect the basicity of the other amino group. The *n*-butyl and isopropyl substituted homologs also appear to afford this steric screening but to a lesser extent than the *t*-butyl case. Some idea of the relative degree of this steric effect can be noted by comparison with the ΔpK_B of two unsubstituted hydrocarbon primary diamines included in Table I.

It can be inferred that this type of steric screening effect is also operative in the fluorine-containing secondary diamines. If this inference is correct, then the enhanced ΔpK_B of the two secondary amino groups in the fluorinated series might be ascribed in large part to the increased inductive effect by all the CF_2 groups on the remaining unneutralized amino group, as demonstrated in the formula



Attempts to obtain either pK_{B1} or pK_{B2} for $(CF_2)_3(CH_2NHCH_2CF_2CF_2CF_3)_2$ failed because the diamine is too weakly basic to be measurable by the techniques used to titrate the other secondary diamines listed in Table I.

---

[10] E. F. Pratt and E. J. Frazza, THIS JOURNAL, **76**, 6174 (1954); R. J. Rice and E. J. Kohn, *ibid.*, **77**, 4052 (1955); C. Ainsworth, *ibid.*, **78**, 1635 (1956); Y. Sprinzak, *ibid.*, **78**, 3207 (1956).

[11] D. R. Husted and A. H. Albrecht, U. S. Patent 2,691,043 (Oct. 5, 1954).

[12] A. L. Henne and J. J. Stewart, THIS JOURNAL, **77**, 1901 (1955).

TABLE I

BASE STRENGTHS OF AMINES

Amine	pK_{B1}	pK_{B2}	$\Delta pK_B = pK_{B2} - pK_{B1}$
$(CF_2)_3(CH_2NHC_2H_5)_2$	7.18	8.30	1.12
$(CF_2)_3[CH_2NHCH(CH_3)_2]_2$	6.99	8.28	1.29
$(CF_2)_3(CH_2NHCH_2CH_2CH_2CH_3)_2$	6.93	8.31	1.38
$(CF_2)_3[CH_2NHC(CH_3)_3]_2$	7.11	8.08	0.97
$(CF_2)_3(CH_2NHCH_2CF_2CF_2CF_3)_2$	Too weakly basic to determine either K_1 or K_2 by this method		
$(CH_2)_4[CH_2NHCH(CH_3)_2]_2$[13]	2.79	3.06	0.27
$(CH_2)_4(CH_2NHCH_2CH_2CH_2CH_3)_2$[13]	2.72	2.91	0.19
$(CH_2)_4[CH_2NHC(CH_3)_3]_2$	3.00	2.98	−0.02
$C_3F_7CH_2NH_2$[12]	8.3	..	....
$H_2N(CH_2)_5NH_2$[14]	3.00	4.3	1.3
$H_2N(CH_2)_8NH_2$[14]	3.00	3.9	0.9

Experimental[15]

2,2,3,3,4,4-Hexafluoropentane-1,5-Di-*p*-toluenesulfonate.—The procedure of Tiers, Brown and Reid[7] to prepare monotosylate esters was modified and used to prepare the ditosylate. Into a 1-liter round-bottomed flask was placed 106 g. (0.5 mole) of 2,2,3,3,4,4-hexafluoropentane-1,5-diol, 200 g. of *p*-toluenesulfonyl chloride (1.05 moles) and 225 ml. of water. The mixture was heated to 40°, efficiently stirred and 40 g. (1 mole) of sodium hydroxide dissolved in 160 ml. of water was added over a 1.5-hour interval; addition was regulated to keep the reaction temperature below 50°. After 2 hours the mixture was still basic with a large amount of white precipitate adhering to the sides of the flask; 100 ml. of dioxane was added and stirring was continued for a further 3 hours, and the reaction was allowed to stand over the week-end.

The liquid plus a sizable amount of precipitate was decanted from the flask; however, much precipitate remained on the walls of the flask. To the liquid–solid phase was added petroleum ether, but little or none of the precipitate dissolved. It did help to conglomerate the precipitate and make complete separation *via* filtration more practicable. The white crystalline solid was washed four times with concd. ammonium hydroxide and then with cold water until no further ammoniacal odor could be detected. After drying overnight in a desiccator, the yield of product was 156.5 g., m.p. 84–86°. The precipitate initially remaining in the reaction flask was removed mechanically with the aid of ether in which it was sparingly soluble. It was washed with ammonium hydroxide, followed by water, and dried; m.p. 92–94°, yield 50 g., total yield of crude material 206.5 g. (79.2%). Recrystallization of the lower melting fraction from methylene chloride gave 120 g. of product, m.p. 92–94°, total yield of di-*p*-toluenesulfonate melting at 92–94°, 170 g. (65.4%).

The mother liquor from the recrystallization was evaporated down to an oily solid which was vacuum distilled to yield at 185° (1.3 mm.) (pot temp. 198°) a heavy oil and a small amount of white precipitate, m.p. 95–110°. After filtration, the oil was redistilled twice with the main fraction coming over at 150–151° (0.15 mm.), $n^{29}D$ 1.4629. This analyzed correctly for the corresponding mono-*p*-toluenesulfonate.

Anal. Calcd. for $C_{12}H_{12}F_6O_4S$: C, 39.34; H, 3.28; F, 31.15; S, 8.74. Found: C, 39.56; H, 3.32; F, 31.37; S, 8.73.

The solid material, m.p. 92–94°, was recrystallized four times from ethanol to yield an analytical sample, m.p. 95–96°, of the di-*p*-toluenesulfonate.

Anal. Calcd. for $C_{19}H_{18}F_6O_6S_2$: C, 43.85; H, 3.46; F, 21.92; S, 12.31. Found: C, 44.00; H, 3.26; F, 22.00; S, 12.17.

N,N'-Dimethylperfluoroglutaramide.—One mole (268 g.) of dimethyl perfluoroglutarate was mixed in a 2-liter beaker with 300 ml. of tetrahydrofuran and 250 ml. of ether. As gaseous methylamine was led into the reaction mixture, the beaker was cooled in ice-water. The reaction was over within one hour when no further exotherm was noted; the reaction mixture solidified. The solvent was removed at reduced pressure to yield 251 g. of crude N,N'-dimethylperfluoroglutaramide, m.p. 138–140°. Recrystallization from benzene gave 230 g. (87.5%) of product, m.p. 143°. An analytical sample after three further recrystallizations from benzene melted at 144–144.5°.

Anal. Calcd. for $C_7H_8F_6N_2O_2$: C, 31.58; H, 3.01; F, 42.86; N, 10.53. Found: C, 31.88; H, 3.28; F, 43.06; N, 10.67.

The preparation of the N,N'-dimethyl, N,N'-diisopropyl and N,N'-di-*n*-butyl substituted derivatives of perfluoroglutaramide reported below were run in a fashion similar to the preparation of N,N'-dimethylperfluoroglutaramide, except as noted.

N,N'-Diethylperfluoroglutaramide.—The dibutyl ester was used instead of the dimethyl ester of perfluoroglutaric acid. In general, the reaction was slower than in the preceding example. The yield was 91.3% of a white precipitate melting at 119–120°. An analytical sample was prepared by three recrystallizations from benzene, m.p. 122–122.5°.

Anal. Calcd. for $C_9H_{12}F_6N_2O_2$: C, 36.73; H, 4.08; F, 38.78; N, 9.52. Found: C, 36.79; H, 4.12; F, 38.92; N, 9.17.

N,N'-Diisopropylperfluoroglutaramide.—A 25% excess of isopropylamine was used to ensure reaction with the dibutyl ester of perfluoroglutaric acid. This reaction proceeded more slowly than that of the ethyl homolog. One recrystallization from methanol–water gave 62% of product melting at 132–134°. An analytical sample was prepared by three further recrystallizations from ether–hexane (excess ether was used to solubilize the precipitate, and then was partially boiled off after hexane addition) to yield extremely fine white needles, m.p. 138.8–139.3°.

N,N'-Diisopropylperfluoroglutaramide also was prepared in an analogous fashion to the preparation of N,N'-di-*t*-butylperfluoroglutaramide by the reaction of perfluoroglutaryl chloride with isopropylamine in yields of 75–80%.

Anal. Calcd. for $C_{11}H_{16}F_6N_2O_2$: C, 40.99; H, 4.97; F, 35.40; N, 8.70. Found: C, 41.20, H, 5.18; F, 35.69; N, 8.64.

N,N'-Di-*n*-butylperfluoroglutaramide.—The initial product was obtained as a yellow-white precipitate in 88% yield, m.p. 114.5–115.5°. This was recrystallized from ether–hexane three times to yield a white precipitate melting at 117.3–117.8°.

Anal. Calcd. for $C_{13}H_{20}F_6N_2O_2$: C, 44.57; H, 5.71; F, 32.59; N, 8.00. Found: C, 44.81; H, 6.00; F, 32.48; N, 8.22.

N,N'-Di-*t*-butylperfluoroglutaramide.—Into a solution of 92 g. (0.33 mole) of perfluoroglutaryl chloride and 200 ml. of dry tetrahydrofuran was added dropwise and with stirring 100 g. (1.37 moles) of *t*-butylamine. Reaction was quite vigorous and required external cooling. After the addition, the reaction was allowed to stir over the week-end (66 hours). The reaction mixture was filtered to remove the amine hydrochloride and the solvent was distilled from the filtrate at reduced pressure to yield a white precipitate. This was treated with decolorizing charcoal and recrystallized from ether–hexane, giving 77 g. (66%) of product melting at 119–120°. An analytical sample was prepared by three further recrystallizations from ether–hexane, m.p. 120–121°.

Anal. Calcd. for $C_{13}H_{20}F_6N_2O_2$: C, 44.57; H, 5.71; F, 32.57; N, 8.00. Found: C, 44.76; H, 6.02; F, 32.63; N, 7.99.

N,N'-Di-2,2,3,3,4,4,4-heptafluorobutylperfluoroglutaramide.—To an ether solution containing 150 ml. of ether and 49 g. (0.246 mole) of 2,2,3,3,4,4,4-heptafluorobutylamine (obtained by neutralization of the amine hydrochloride salt with 15% sodium hydroxide followed by ether extraction and drying of the ether extracts over anhydrous magnesium sulfate) was added slowly dropwise 16.12 g. (0.058 mole) of perfluoroglutaryl chloride. Upon completion of addition, 100 ml. of tetrahydrofuran was added to solubilize the diamide. The reaction mixture was allowed to stand overnight and was filtered the next morning to remove 33.5 g. of

---

[13] The preparation of these compounds will be reported in a later paper dealing with their polymerization.

[14] G. Schwarzenbach, *Helv. Chim. Acta*, **16**, 522 (1933); R. Rometsch, A. Marxer and K. Miescher, *ibid.*, **34**, 1611 (1951).

[15] Melting points are corrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

2,2,3,3,4,4,4-heptafluorobutylamine hydrochloride. The filtrate was evaporated to yield 13 g. (45%) of the diamide, m.p. 135–136°.

Anal. Calcd. for $C_{13}H_6F_{20}N_2O_2$: C, 25.91; H, 1.00; F, 63.12; N, 4.65. Found: C, 26.22; H, 1.11; F, 63.03; N, 4.47.

Special note of caution: Beyond general precautions advocated for lithium aluminum hydride reductions of fluorinated amides,[5,6,11] the following points should be observed. 1. Stirring should be effective, and in the event there is a clumping of solid material during the addition of the diamide to the reduction mixture, the addition should be discontinued and the reaction mixture allowed to stir until the clumps disappear. Addition may then be continued. 2. Excess lithium aluminum hydride should not be destroyed if large clumps of solid are noted in the reaction mixture. Water may be used to destroy the lithium aluminum hydride, but special care must be taken to ensure that the dropwise addition of water falls directly into the reaction mixture and not on the sides of the flask.

N,N′-Dimethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine was synthesized by reduction of the corresponding diamide with an ether slurry of lithium aluminum hydride. Before undertaking the reductions, a very small sample of the reaction mixture of N,N′-dimethylperfluoroglutaramide and lithium aluminum hydride was heated cautiously. No sign of decomposition was noted until at about 80° when the reaction product darkened but did not detonate. On a larger scale, 6.9 g. (0.182 mole) of lithium aluminum hydride was slurried in a 3-necked, 3-liter flask with two pounds of anhydrous ether. After one hour, 10 g. (0.0375 mole) of finely powdered and screened N,N′-dimethylperfluoroglutaramide in 250 ml. of anhydrous ether was added dropwise so as to maintain moderate ether reflux. The reaction mixture was allowed to stir at room temperature for 43 hours before the excess lithium aluminum hydride was destroyed by dropwise addition of water. After filtration and drying of the ethereal solution, anhydrous hydrogen chloride was added until no more precipitate formed. About 6.5 g. of hydrochloride salt, m.p. 198–201° dec., was collected. The salt was neutralized with 50% sodium hydroxide solution, and the mixture extracted with five 50-ml. portions of ether. After drying and filtering, and removal of the ether, the residual yellow oil was fractionally distilled to give 4 g. (43.8%) of N,N′-dimethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine, b.p. 55–57° (10 mm.), $n^{25}D$ 1.3779. An analytical sample was redistilled, b.p. 55–56° (10.5 mm.), $n^{26.5}D$ 1.3771.

Anal. Calcd. for $C_7H_{12}F_6N_2$: C, 35.29, H, 5.05, F, 47.90; N, 11.76. Found: C, 35.54; H, 4.82; F, 47.85; N, 11.72.

About 2 g. of starting material was recovered by evaporation of the filtrate from the hydrochloride salt separation.

When the above procedure was modified by using tetrahydrofuran to dissolve the N,N′-dimethylperfluoroglutaramide, lower yields of the desired diamine were obtained, as well as increased amounts of starting material and by-products. A substance melting at 103–103.5°, after four recrystallizations from carbon tetrachloride, was isolated from the reaction when tetrahydrofuran–ether was used as solvent.

N,N′-Dimethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine hydrochloride was prepared by passing anhydrous hydrogen chloride through an ether solution of the fluorinated diamine. Recrystallization of the precipitate from ethanol-ether gave white crystalline product, m.p. 213–215° dec.

Anal. Calcd. for $C_7H_{13}ClF_6N_2$: Cl, 12.93. Found: Cl, 12.62.

When the above salt was dissolved in methanol and treated with further hydrogen chloride, a precipitate was collected which analyzed low in chlorine for the dihydrochloride salt.

Anal. Calcd. for $C_7H_{14}Cl_2F_6N_2$: Cl, 22.83. Found: Cl, 22.01.

N,N′-Diethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine.—The reduction of N,N′-diethylperfluoroglutaramide with lithium aluminum hydride was carried out in an analogous fashion to the preparation of N,N′-dimethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine. Approximately 0.25 mole of diamide was reduced in a comparatively large volume of ether (approximately 3 liters) during a 66-hour reaction time. The hydrochloride salt melted at 243–245° dec. The free base, fractionally redistilled, gave approximately 44% of colorless oil, b.p. 46° (0.05 mm.), $n^{27}D$ 1.3864.

Anal. Calcd. for $C_9H_{16}F_6N_2$: C, 40.60; H, 6.02; F, 42.86; N, 10.52. Found: C, 40.86; H, 6.11; F, 42.92; N, 10.23.

The preparation of several fluorinated diamines by the reduction of the respective fluorinated diamides with lithium aluminum hydride was carried out in an almost identical fashion and molar quantities to the preparation of N,N′-diethyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine.

N,N′-Diisopropyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine.—The hydrochloride salt turned slightly brown at 155° and finally melted at 245–247° dec. From the ether filtrate there was obtained (after removal of the solvent) 40% of starting material. The initial distillation of the free base yielded 41.4% of a light yellow oil, b.p. 66° (0.43 mm.), $n^{26}D$ 1.3924. An analytical sample was prepared by three further fractional distillations, $n^{25}D$ 1.3917, b.p. 70° (0.55 mm.).

Anal. Calcd. for $C_{11}H_{20}F_6N_2$: C, 44.90; H, 6.80; F, 38.78; N, 9.52. Found: C, 44.98; H, 7.03; F, 38.67; N, 9.75.

N,N′-Di-*n*-butyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine.—The hydrochloride salt melted at 250° dec. From the ether filtrate there was obtained, after solvent evaporation, 29% of starting material. The free base, a colorless liquid, was obtained in 39.8% yield, b.p. 70° (0.5 mm.), $n^{25}D$ 1.4038.

Anal. Calcd. for $C_{13}H_{24}F_6N_2$: C, 48.45; H, 7.45; F, 35.40; N, 8.70. Found: C, 48.50; H, 7.70; F, 35.38; N, 8.89.

N,N′-Di-*t*-butyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine.—The hydrochloride salt was a yellow sticky material. The freshly distilled diamine was a colorless oil, b.p. 67° (0.37 mm.), $n^{26}D$ 1.4020, and was obtained in 39.2% yield. From the ether filtrate was derived 25% of the starting material, N,N′-di-*t*-butylperfluoroglutaramide.

Anal. Calcd. for $C_{13}H_{24}F_6N_2$: C, 48.45; H, 7.45; F, 35.40; N, 8.70. Found: C, 48.70; H, 7.72; F, 35.69; N, 8.97.

N,N′-Di-2,2,3,3,4,4,4-heptafluorobutyl-2,2,3,3,4,4-hexafluoropentane-1,5-diamine.—The hydrochloride salt turned brown at 170° and melted to a brown liquid by 180°. The free diamine boiled at 72° (0.04 mm.), $n^{28}D$ 1.3278, and was obtained in 52.5% yield.

Anal. Calcd. for $C_{13}H_{10}F_{20}N_2$: C, 27.18; H, 1.74; F, 66.20; N, 4.88. Found: C, 27.45; H, 1.92; F, 65.94; N, 5.18.

Determination of Base Strengths.—The measurements were made by titration of 0.002 *N* solutions of amine in 0.004 *N* $HClO_4$, with 0.1 *N* NaOH by means of a glass electrode Beckman *p*H meter. The calculations were conventional.[16]

Acknowledgments.—The authors wish to express their appreciation to the Materials Laboratory, Wright Air Development Center, Wright-Patterson Air Force Base, Ohio, for financial support of this work and to the Hooker Electrochemical Co. at whose laboratories and under whose auspices the work was carried out. We wish to thank Dr. Joseph J. Wylegala for the basicity measurements of the amines and for his helpful advice, and Mr. John J. Zedick for his capable assistance.

CHICAGO, ILL.

---

(16) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, pp. 78-94.