alkylamines may be obtained by lithium aluminum hydride reduction of perfluoronitriles. This latter method overcomes the complications caused by carbonyl-containing by-products.

In view of the possibly troublesome nature of routes to these amines utilizing lithium aluminum hydride it was deemed desirable to investigate methods using less reactive complex metal hydrides. Because of the ease of handling sodium borohydride, it was the reagent of choice.

A search of the literature revealed that amine formation from the sodium borohydride reduction of neither nitriles nor primary amides containing polyfluoroalkyl groups has been reported.[6,8a,b,10]

Addition of three representative polyfluoroalkyl nitriles to a stirred slurry of sodium borohydride in the dimethyl ether of diethylene glycol (diglyme) gave moderate to high yields of the corresponding amines after the reaction mixture was treated with aqueous acid or, preferably, sodium hydroxide. Apparently the amine is formed *via* some type of boron-containing complex since gas chromatographic examination of the mixture of sodium borohydride and perfluorocaprylonitrile in diglyme immediately after refluxing but prior to alkaline hydrolysis revealed, in addition to diglyme and minute amounts of free amine and unchanged nitrile, a large amount of an unknown material which is assumed to be the intermediate complex. Subsequent steam distillation of the alkaline reaction mixture gave the free amine which could be isolated either by ether extraction or by conversion to the hydrochloride salt.

At least 2 moles of sodium borohydride/mole of nitrile were employed to ensure complete reduction of the nitriles. The reductions were carried out for 1–1.5 hr. at the reflux temperature of diglyme in the case of the higher boiling nitriles, while perfluorobutyronitrile was reduced at room temperature.

Since nitriles are normally not reduced by sodium borohydride,[8b,10] it is assumed that strong electron withdrawal by a polyfluoroalkyl group is sufficient to render the nitrile function amenable to attack by the hydride.

Experimental Section[11]

1,1-Dihydroperfluorobutylamine.—An intimate mixture of 25.0 g. (0.117 mole) of perfluorobutyramide and 50 g. (0.35 mole) of phosphorus pentoxide in a flask surmounted by a Dry Ice–acetone cooled condenser was heated for about 1.5 hr. at 140–170° and the nitrile formed was slowly transferred by means of a nitrogen stream into two traps cooled by Dry Ice–acetone. The nitrile was then led during about 1.5 hr. into a three-necked flask surmounted by a Dry Ice–acetone cooled condenser. The reaction flask contained a magnetically stirred slurry of 8.85 g. (0.234 mole) of sodium borohydride in 140 ml. of dry diglyme at about 25°. The addition was slow enough to maintain the reaction temperature at about 32°. After the addition, about 150 ml. of ice–water and 10 ml. of 50% sodium hydroxide were cautiously added before steam distilling the mixture. About 450 ml. of distillate was collected and extracted with ether, and the extract was saturated with hydrogen chloride. The 1,1-dihydroperfluorobutylamine hydrochloride weighed 12.33 g. after washing with ether: m.p. 310–314° dec. (sealed capillary); its neutralization equivalent was 235 (calcd. 234.5). Recrystallization from an absolute ethanol–ether mixture gave an analytical sample, m.p. 317–319° dec. (sealed capillary preheated to 300°).

Anal.[12] Calcd. for $C_4H_5ClF_7N$: 20.40; H, 2.14; N, 5.95. Found: C, 20.23; H, 2.11; N, 5.99.

About 0.6 g. of unchanged amide was recovered from the phosphorus pentoxide by an ether wash, giving a 46.1% yield of amine salt based on amide utilized. Treatment of the salt with sodium hydroxide gave the pure amine, b.p. 69°,[3b] upon distillation from barium oxide.

Anal.[12] Calcd. for $C_4H_4F_7N$: C, 24.13; H, 2.02; F, 66.81; N, 7.04. Found: C, 24.45; H, 2.26; F, 66.64; N, 7.10.

Its acetyl derivative melted at 50.5–52°.[13]

1,1,9-Trihydroperfluorononylamine.—Ethyl 9-hydroperfluoropelargonate, b.p. 112° at 40 mm., $n^{25}D$ 1.3203, C=O at 5.64 μ ($CHCl_3$), was formed in 46% yield by esterification of the acid with concentrated sulfuric acid as catalyst.

Anal. Calcd. for $C_{11}H_6F_{16}O_2$: C, 27.86; H, 1.28; F, 64.11. Found: C, 26.25; H, 1.29; F, 63.02.

Treatment of the ester with gaseous ammonia gave the amide, m.p. 136–138°,[3a] which was then dehydrated with phosphorus pentoxide to give an 86% yield of 9-hydroperfluoropelargononitrile, b.p. 144°, C≡N at 4.44 μ ($CHCl_3$).

Anal. Calcd. for $C_9HF_{16}N$: C, 25.31; H, 0.24; F, 71.18; N, 3.28. Found: C, 24.38; H, 0.15; F, 72.84; N, 3.23.

Reaction of the nitrile with excess sodium borohydride for 1.5 hr. at the reflux temperature of diglyme gave a 61.8% yield of 1,1,9-trihydroperfluorononylamine hydrochloride, m.p. 264–266° dec. (sealed capillary), neut. equiv. 476 (calcd. 467.5). The free amine distilled at 84–90° at 12–14 mm.[3a]

1,1-Dihydroperfluorooctylamine.—Reduction of perfluorocaprylonitrile with excess sodium borohydride for 1 hr. at the reflux temperature of diglyme gave a 73% yield of 1,1-dihydroperfluorooctylamine, b.p. 75–75.5° (50 mm.),[3b] $n^{27}D$ 1.3051.

Anal.[12] Calcd. for $C_8H_4F_{15}N$: C, 24.07; H, 1.01; F, 71.41; N, 3.51. Found: C, 24.11; H, 1.08; F, 71.34; N, 3.80.

The hydrochloride salt decomposed in a sealed capillary at 278–280°.

Anal.[12] Calcd. for $C_8H_5ClF_{15}N$: C, 22.06; H, 1.16; F, 65.43. Found: C, 21.70; H, 1.65; F, 65.62.

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[6] In a patent specification[3a] it is stated that sodium borohydride is effective in reducing polyfluoroalkylcarboxamides to amines but no supporting experimental data are given. In our hands reaction of $CF_3(CF_2)_6CONH_2$ with excess sodium borohydride in the dimethyl ether of diethylene glycol (diglyme) either at room temperature or at reflux gave $CF_3(CF_2)_6CH_2OH$ and only traces of the amine.[7]

[7] S. E. Ellzey, Jr., and J. S. Wittman, III, unpublished data.

[8] (a) H. P. Johnston [U. S. Patent 3,026,355 (1962)] reported that acetamide and benzamide were reduced to the corresponding amines by *deficient* amounts of sodium borohydride in a solvent-free system. (b) In our hands, a variety of nonfluorinated primary amides gave mainly the corresponding *nitriles* upon treatment with *excess* sodium borohydride in refluxing diglyme.[9]

[9] S. E. Ellzey, Jr., Charles H. Mack, and W. J. Connick, Jr., unpublished results.

[10] N. G. Gaylord, "Reduction with Complex Metal Hydrides," Interscience Publishers, Inc., New York, N. Y., 1956, p. 750.

[11] Melting points and boiling points are uncorrected. Analyses were performed by Midwest Microlab, Inc., Indianapolis, Ind., and Galbraith Laboratories, Inc., Knoxville, Tenn.

[12] This compound was reported without analytical data in ref. 3b.

[13] D. R. Husted and A. H. Ahlbrecht, U. S. Patent 2,743,297 (1956).

Synthesis and Base Strength of 2,4,6-Tri-*t*-butylphenylhydrazine

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We have synthesized 2,4,6-tri-*t*-butylphenylhydrazine (I) in order to determine the effects of the *t*-butyl groups on the basicity. Our work can be regarded as an extension of observations by others on the basicity of 2,4,6-tri-*t*-butylaniline[1] (II) and 2,6-di-*t*-butylpyridine[2] (III).

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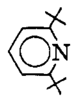
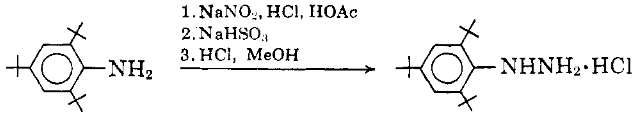
[1] (a) P. D. Bartlett, M. Roha, and R. M. Stiles, *J. Am. Chem. Soc.*, **76**, 2349 (1954); (b) B. M. Wepster, *Rec. trav. chim.*, **76**, 357 (1957); (c) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *ibid.*, **77**, 491 (1958).

[2] H. C. Brown and B. Kanner, *J. Am. Chem. Soc.*, **75**, 3865 (1953).



III

For the synthesis, the already known 2,4,6-tri-*t*-butylaniline (II) was prepared and diazotized. The diazonium salt was reduced with freshly prepared sodium bisulfite (eq. 1). The product I was obtained as an oil. With hydrochloric acid, however, it formed a crystalline salt with limited solubility in aqueous methanol, which gave a correct elemental analysis.



II I·HCl (1)

During the preparation of II, we found it convenient to nitrate a mixture of 1,3,5-tri-*t*-butylbenzene and 1,4-di-*t*-butylbenzene, obtained by *t*-butylation of benzene. These two hydrocarbons have similar melting points, boiling points, and solubilities and are difficult to separate, except by use of an efficient fractionating column[1] or by preparative gas–liquid chromatography.[3] The 1,3,5-tri-*t*-butylbenzene was nitrated preferentially, however, in spite of its having fewer available positions and more steric hindrance for nitration than 1,4-di-*t*-butylbenzene. These factors are more than offset by accumulation of the activating influences of the *t*-butyl groups. The result is consistent with calculations based on data for *t*-butylbenzene, which indicate that 1,3,5-tri-*t*-butylbenzene would be nitrated about 80 times as rapidly as 1,4-di-*t*-butylbenzene.[4]

2,4,6-Tri-*t*-butylphenylhydrazine was found to have a pK_a of 3.66 in 50% ethanol at 30° and to be a weaker base than phenylhydrazine by about 1.4 pK units under these conditions. The result is discussed in detail elsewhere.[5] It is believed that a base-weakening effect of steric hindrance to hydration more than offsets base-strengthening inductive effects of the *t*-butyl groups and, possibly, a base-strengthening steric inhibition of resonance.

Experimental Section

2,4,6-Tri-*t*-butylaniline (II) was prepared as described by Bartlett, Roha, and Stiles[1a], except that we found it was possible and convenient to obtain 2,4,6-tri-*t*-butylnitrobenzene by nitration of the difficultly separable mixture of 1,3,5-tri-*t*-butylbenzene and 1,3- and 1,4-di-*t*-butylbenzene obtained by alkylation of benzene (1 mole) with *t*-butyl chloride (2.1 moles) and aluminum chloride (1.1 mole) in carbon disulfide as a solvent. A semisolid fraction boiling at 118–135° at 12 mm. was filtered with suction, and 11.2 g. of the solid was dissolved in 8 ml. of acetic acid and 6 ml. of acetic anhydride. The mixture was cooled in an ice–salt bath, and 1.6 g. of fuming nitric acid was added dropwise at 0°. The solid product precipitated from the reaction mixture with each addition of nitric acid. After 1 hr. of standing, the mixture was filtered with suction and the crude product was recrystallized from petroleum ether (b.p. 30–60°): yield 3.4 g., m.p. 198–200°.

Reduction of 2,4,6-tri-*t*-butylnitrobenzene with sodium amalgam and methanol[1a] gave II contaminated with sodium carbonate. The II was readily purified, however, by crystallization from methanol–acetic acid: m.p. 143.5–144.5°.

2,4,6-Tri-*t*-butylphenylhydrazine (I).—To a mixture of 5 g. of II, 50 ml. of glacial acetic acid, and 13 ml. of concentrated hydrochloric acid, cooled to 0°, there was added with stirring a precooled solution of 1.3 g. of sodium nitrite in 7 ml. of water. A yellow precipitate was observed. To the mixture was then added a solution of sodium bisulfite, freshly prepared from 4 g. of sodium hydroxide in 30 ml. of water and sulfur dioxide to a phenolphthalein end point.[6] The mixture was heated at reflux overnight, cooled, and made basic with sodium hydroxide. An oil separated and was extracted into ether. After efforts to crystallize the product failed, it was converted to a solid hydrochloride by treatment with a small amount of 4 *M* hydrochloric acid in methanol solution, and the solid was purified by recrystallization from aqueous methanol: m.p. 208–210° dec.

Anal.[7] Calcd. for $C_{18}H_{33}ClN_2$: C, 69.09; H, 10.63; N, 8.95. Found: C, 69.49; H, 10.63; N, 8.87.

For determination of its pK_a, a solution of 0.1405 g. of the hydrochloride in 20 ml. of 50% aqueous ethanol was titrated with a 0.104 *N* solution of carbonate-free sodium hydroxide in 50% ethanol at 30°. A Beckman Model H2 pH meter was used with a glass electrode and calomel half-cell. The pH at the point of half-neutralization was 3.68. A correction for hydrolysis amounts to −0.02 pK unit. When freshly prepared phenylhydrazine hydrochloride was titrated under similar conditions (50% ethanol), but at 27°, its pK_a was found to be 5.09. A correction for the activity coefficient of the hydrazinium ion may amount to about −0.15 pK unit in each case,[8] but was not applied.

Acknowledgment.—We are indebted to Dr. J. L. Goldberg for use of a pH meter and advice on its operation and to the Research Committee of The City College for a grant-in-aid.

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(3) G. A. Olah, C. G. Carlson, and J. C. Lapiere, *J. Org. Chem.*, **29**, 2687 (1964).

(4) The calculations follow. *t*-butylbenzene is nitrated 15.7 times as rapidly as benzene, and the product is 12.0% *o*-, 8.5% *m*-, and 79.5% *p*-nitro-*t*-butylbenzene [H. Cohn, E. D. Hughes, M. H. Jones, and M. G. Peeling, *Nature*, **169**, 291 (1952)]. The partial rate factors (rates relative to that for any one position in benzene) are therefore *ortho* 5.6, *meta* 4.0, and *para* 75. For each position in 1,3,5-tri-*t*-butylbenzene, a partial rate factor may be calculated as a product of partial rate factors, one relating to each substituent and its position [F. E. Condon, *J. Am. Chem. Soc.*, **70**, 1963 (1948)]; that is $75 \times 5.6 \times 5.6 = 2350$. The rate for the molecule as a whole would be $3 \times 2350 = 7050$, relative to that for any one position in benzene. Similarly, the relative rate of nitration of 1,4-di-*t*-butylbenzene is calculated as $4 \times 4.0 \times 5.6 = 89.6$, and that for 1,3-di-*t*-butylbenzene is 887. The rate of nitration of 1,3,5-tri-*t*-butylbenzene therefore is estimated to be about 80 times that of 1,4-di-*t*-butylbenzene and about 8 times that of 1,3-di-*t*-butylbenzene (a minor component of the mixture nitrated.)

(5) F. E. Condon, *J. Am. Chem. Soc.*, **87**, 4491 (1965).

(6) H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 443.

(7) Analysis were by Carl Tiedcke Laboratory of Microchemistry, Teaneck, N. J.

(8) See J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937), and available data for hydrazine: G. Schwartzenbach, *Helv. Chim. Acta*, **19**, 178 (1936); N. Yui, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **20**, 256 (1941); *Chem. Abstr.*, **35**, 4660 (1941); R. L. Hinman, *J. Org. Chem.*, **23**, 1587 (1958).

The Absolute Configuration of Thujopsene[1]

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Thujopsene, a tricyclic sesquiterpene, has been shown to be a constituent of the wood oil and heartwood of many genera belonging to the natural order Cupressales.[3] In the past few years the chemistry of

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(2) Roche Anniversary Foundation Postdoctoral Fellow, 1963–1965.

(3) For a summary of the numerous isolations of thujopsene, see T. Norin, *Acta Chem. Scand.*, **15**, 1676 (1961).