The nitrolysis of *N*-butyl-*N*-fluorocarbamate most likely proceeds by the electrophilic displacement of carbomethoxycarbonium ion by nitronium ion (eq 3).

$$C_4H_9NFCOOCH_3 + NO_2^+ \longrightarrow C_4H_9NFNO_2 + [^+COOCH_3] \quad (3)$$

This mechanism is analogous to that proposed for the fluorinalysis of *N*-alkyl-*N*-fluorocarbamates to the corresponding *N*,*N*-difluoroalkylamines.[9] The nitrolysis of *N*,*N*-dialkylformamides has also been reported.[10]

Experimental Section

Fluorinations were conducted in a three-necked flask following the previously described technique.[5,6] *Adequate safety shielding* should be used when handling *N*-fluoro-*N*-nitrobutylamine.

Fluorination of Butylnitramine.—Butylnitramine (11.8 g, 0.1 mol) and 0.1 mol of potassium hydroxide in 250 ml of water were fluorinated with 0.1 mol of fluorine over a period of 45 min. A yellow liquid separated. The product was extracted with 70 ml of methylene chloride, and was washed with 75 ml of cold saturated aqueous sodium bicarbonate and 75 ml of water. The methylene chloride solution was dried with sodium sulfate and distilled to give 11.5 g (86% yield) of *N*-fluoro-*N*-nitrobutylamine: bp 40° (25 mm); proton nmr (CCl_4) δ 0.98 (m, CH_3), 1.62 (m, two internal CH_2's), and 6.07 (d, t, J_{HF} = 35, J_{HH} = 11 Hz, $-CH_2$); fluorine nmr ϕ −1.10 (t, J_{HF} = 33.5 Hz); ir 3.39 (m), 3.50 (m), 6.18 (sh), 6.35 (sh), 6.84 (w), 7.01 (w), 7.25 (w), 7.55 (sh), 7.76 (s), 7.93 (sh), 8.14 (w), 8.96 (w), 9.40 (w), 9.61 (w), 10.05 (w), 11.35 (m), and 12.10 μ (m).

Anal. Calcd for $C_4H_9N_2FO_2$: C, 35.3; H, 6.7; N, 20.6; F, 14.0. Found: C, 35.0; H, 6.3; N, 21.2; F, 14.3.

Nitration of Methyl *N*-Butyl-*N*-fluorocarbamate.—Methyl *N*-butyl-*N*-fluorocarbamate (4.0 g, 0.027 mol) was added dropwise over a 15-min period to 25 ml of 100% nitric acid at −5°. Carbon dioxide was evolved. The mixture was stirred for 20 min and then poured on 100 g of crushed ice. The product was extracted with two 20-ml portions of methylene chloride, dried over sodium sulfate, and distilled to give 3.1 g (84% yield) of *N*-fluoro-*N*-nitrobutylamine, bp 40° (25 mm).

Registry No.—*N*-Fluoro-*N*-nitrobutylamine, 14233-86-4.

[10] J. H. Robson, *J. Amer. Chem. Soc.*, **77**, 107 (1955).

Amine Hydrochlorides by Reduction in the Presence of Chloroform[1]

John A. Secrist III*[2] and Marshall W. Logue

Department of Chemistry, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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We have developed a new method for the preparation of amine hydrochlorides from azides, nitriles, oximes, and nitro compounds. Catalytic reduction of these compounds in a solvent containing a small amount of chloroform leads directly to the corresponding amine hydrochlorides. In addition to trapping unstable amines as the hydrochloride, an important advantage of the present procedure lies in the fact that it provides a method for the preparation of amine hydrochlorides that contain functional groups which might be unstable to reduction conditions employing acidic media. As can be seen from Table I, reduction in the presence of chloroform affords comparable yields to those afforded by reduction in the presence of hydrochloric acid.

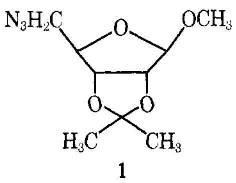
Table I

Reduction Data[a]

Compd	Proton source	Catalyst	Time, hr	Yield, %
1	$CHCl_3$	Pd/C	1.5	92
n-PrCN	$CHCl_3$	PtO_2	4	96
	HCl	PtO_2	1.75	95
C_6H_5CN	$CHCl_3$	PtO_2	2	98
	HCl	PtO_2	1.5	97
p-$CH_3C_6H_5NO_2$	$CHCl_3$	Pd/C	1.5	89[b]
	HCl	Pd/C	1.5	93[c]
n-$PrNO_2$	$CHCl_3$	PtO_2	18	40[d]
	$CHCl_3$	PtO_2	15	61[e]
	HCl	PtO_2	24	59[f]
n-$C_6H_{13}CH{=}NOH$	$CHCl_3$	PtO_2	1	97
	HCl	PtO_2	2	60

[a] Standard conditions are 3 atm, 2 mmol of starting material, 50 ml of absolute EtOH, 1 ml of $CHCl_3$ or 1 ml of concentrated HCl, 100 mg of 10% Pd/C or 50 mg of PtO_2, except as noted.[g] [b] 83% after sublimation. [c] After sublimation. [d] 0.2 ml of $CHCl_3$. [e] 0.1 ml of $CHCl_3$. [f] 0.2 ml of concentrated HCl. [g] Only 1.0 mmol of 1 was employed.

Methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-*β*-D-ribofuranoside (1),[3] which contains the acid-labile isopropylidene and acetal functions, was found to be reduced cleanly in the presence of chloroform to the corresponding amine hydrochloride 2 without affecting either of these acid-sensitive groups. By contrast, reduction in the presence of methanolic hydrogen chloride also resulted in removal of the isopropylidene group and anomerization, as judged by nmr. Attempts at reduction of 1 under similar conditions in ether containing hydrogen chloride resulted in recovery of unchanged 1.



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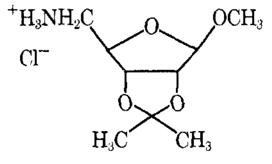

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Reduction of aromatic and aliphatic nitriles as well as *p*-nitrotoluene occurred readily in the presence of either chloroform or hydrochloric acid. In the absence of a proton source the reduction of 1-nitropropane produced propylamine, characterized as the hydrochloride, in 95% yield after 1.75 hr. Under the standard conditions with either chloroform or hydrochloric acid, 1-nitropropane was not reduced to any appreciable extent.[4] Upon decreasing the quantity of chloroform and hydrochloric acid, however, reduction was facilitated.

Heptaldoxime was reduced readily in the presence of either chloroform or hydrochloric acid, although the yield in hydrochloric acid was considerably lower. In both cases an additional ether-soluble product was formed.

As a mechanistic test, a blank solution of absolute ethanol, chloroform, and catalyst was hydrogenated for 1 hr. The resulting solution gave a positive silver ni-

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[1] Generously supported by a research grant (GM 05829) from the National Institutes of Health.

[2] National Institutes of Health Predoctoral Fellow, 1969–1971.

[3] J. A. Secrist III and N. J. Leonard, *J. Amer. Chem. Soc.*, in press.

[4] Nitroalkanes are known to be reduced with difficulty in the presence of acids; see P. N. Rylander, "Catalytic Hydrogenation over Platinum Metals," Academic Press, New York, N. Y., 1967, pp 168–174.

trate test,[5] indicating the presence of ionic chloride. It appears, therefore, that the reaction occurs by hydrogenolysis of the chloroform to produce very small quantities of hydrogen chloride, which combines immediately with the amine as it is formed by reduction.

Experimental Section[6]

General Procedure.—The hydrogenations were carried out on a Parr apparatus as indicated in Table I followed by filtration through Hyflo-Supercel and evaporation of the solvent under reduced pressure. Unless otherwise indicated, the material left after evaporation to dryness was used for characterization.

Methyl 5-amino-5-deoxy-2,3,-*O*-isopropylidene-β-D-ribofuranoside hydrochloride (2) was obtained as a colorless solid, mp 189.5–190° dec. Recrystallization from absolute EtOH gave **2**, mp 200.5–201.5° dec (lit.[7] 201.5–202°).

***n*-Propylamine hydrochloride, *n*-butylamine hydrochloride, and benzylamine hydrochloride** were obtained as colorless solids, mp 153–154° (lit.[8] 155–158°), 201–203° (lit.[9,10] 195 and 215°), and 253–254° (lit.[11] 255–256°), respectively.

***p*-Toluidine hydrochloride** was obtained as a gray solid, mp 233.5–237.5°. Sublimation gave colorless material, mp 238.5–239.5° (lit.[12] 238–240°).

***n*-Heptylamine Hydrochloride.**—After filtration of the hydrogenation mixture through Hyflo-Supercel, the filtrate was evaporated to dryness. The residue was then washed with ether to give a colorless solid, which turned to a gel (200°) and became fluid at 256–259°. An authentic sample prepared by a Gabriel synthesis behaved identically.

Registry No.—2, 14131-79-2; chloroform, 67-66-3; *n*-propylamine HCl, 556-53-6; *n*-butylamine HCl, 3858-78-4; benzylamine HCl, 3287-99-8; *p*-toluidine HCl, 540-23-8; *n*-heptylamine HCl, 142-93-8.

[5] Pretested chloroform gave a negative silver nitrate test.

[6] All melting points were determined on a Thomas-Hoover capillary melting point apparatus in sealed capillaries and are corrected.

[7] N. J. Leonard and K. L. Carraway, *J. Heterocycl. Chem.*, **3**, 485 (1966).

[8] E. Linnemann and V. Zotta, *Justus Liebigs Ann. Chem.*, **161**, 45 (1872).

[9] E. Linnemann and V. Zotta, *ibid.*, **162**, 4 (1872).

[10] W. H. C. Rueggenberg and M. M. Falkof, *J. Amer. Chem. Soc.*, **67**, 2052 (1945).

[11] M. Konowalow, *Ber.*, **28**, 1861 (1895).

[12] C. A. Bischoff and P. Walden, *Justus Liebigs Ann. Chem.*, **279**, 130 (1894).

Metal-Amine Reactions.[1a,b] Selective 1,2′-Reductive Dimerization of Naphthalene

L. E. Harris[2] and E. J. Eisenbraun*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

P. W. Flanagan, M. C. Hamming, and G. W. Keen

Research and Development Department, Continental Oil Company, Ponca City, Oklahoma 74601

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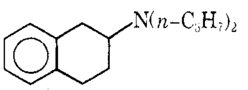
The reduction of naphthalene with sodium and amines yields numerous products, including 1,2-dihydronaphthalene (1), 1,4-dihydronaphthalene (2), 1,2,3,4-tetrahydronaphthalene (3), reductive amination products, C_{20} dimers, and decreasing amounts of C_{30} and C_{40} products.[1a–c] The product distribution varies considerably depending on reaction conditions and the selection of the amine.[1a,b] If steric effects are present in the amine, reductive amination diminishes and reductive dimerization may increase; *e.g.*, piperidine gave 46% reductive amination of naphthalene and 11% of a mixture of C_{20} dimers, whereas dipropylamine caused formation of 6% of **4** and 55% of a mixture of reductive dimerization products[1a] now known to be **5**, **6**, and **7**. In our current work with sodium and dipropylamine using a specialized apparatus,[3a] the yield of **4** is 12% and the combined yield of **5**, **6**, and **7** is 62%. In the earlier work, two C_{20} dimers, 1,1′,2,2′,3,3′,4,4′-octahydro-2,2′-binaphthyl and 5,6,6a,6b,11,12,12a,12b-octahydrodibenzo[*a,g*]biphenylene, were frequently observed, particularly with primary diamines.[1b] We now know there are, however, systems in which they are minor products or may not appear. One of these, sodium and dipropylamine, was chosen for detailed study because the resulting C_{20} dimer mixture was less complex. Indeed, we have learned that in this system a remarkably selective formation of 1,2′-coupled C_{20} dimers results. The major component of the dimer fraction,[3b] a colorless crystalline hydrocarbon, is shown to be 1′,2′,3′,4′-tetrahydro-1,2′-binaphthyl (**5**). It gives a molecular ion *m/e* 258.1408 and both analytical and spectral data are consistent with structure **5**. Hydrocarbon **5** shows uv absorption characteristic of an aliphatic-substituted naphthalene and forms a picrate that can be decomposed by stirring with petroleum ether and eluting through a column of basic alumina. The hydrocarbons **6** and **7** did not form picrates.



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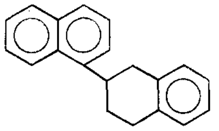

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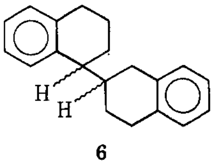

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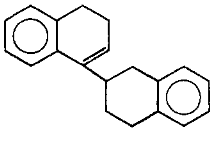

7

At room temperature, dimers **5**, **6**, and **7** were formed in the ratio 73:11:16, respectively. At higher temperatures (40–80°) dimer **5** was the C_{20} hydrocarbon formed almost exclusively.

To obtain pure **6**, a mixture of **5**, **6**, and **7** was treated with Pd/C in refluxing toluene[3c] and the resulting mixture of **5** and **6** was separated by column chromatography. The ir spectrum of **6** thus prepared from **7** is very similar[4a] to that of **6** obtained by hydrogenation

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[1] (a) E. J. Eisenbraun, R. C. Bansal, D. V. Hertzler, W. P. Duncan, P. W. K. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **35**, 1265 (1970); (b) R. C. Bansal, E. J. Eisenbraun, and P. W. K. Flanagan, *J. Amer. Chem. Soc.*, **88**, 1837 (1966); (c) L. Reggel, H. W. Sternberg, and I. Wender, *Nature (London)*, **190**, 81 (1961).

[2] Continental Oil Company Fellowship, 1970–1971, and National Aeronautical and Space Administration Trainee, 1969–1970.

[3] (a) E. J. Eisenbraun and H. Hall, *Chem. Ind. (London)*, 1158 (1971). (b) Correspondence regarding this reference hydrocarbon and other samples should be addressed to Mr. A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213. (c) L. E. Harris, W. P. Duncan, M. J. Hall, and E. J. Eisenbraun, *Chem. Ind. (London)*, 403 (1971).

[4] (a) Dimer **6** from both sources is a liquid. It should be recognized that **6** may possibly be a mixture of racemates and hence minor differences in the infrared spectra of samples from independent sources are to be expected. (b) J. M. Springer, C. W. Hinman, E. J. Eisenbraun, P. W. K. Flanagan, and M. C. Hamming, *J. Org. Chem.*, **35**, 1260 (1970). (c) H. L. Retcofsky, L. Reggel, and R. A. Friedel, *Chem. Ind. (London)*, 617 (1969). (d) We thank Mr. J. W. Burnham for a sample of **8** prepared by acid-catalyzed dimerization of 1-tetralone.