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The Reduction of Oximes with Diborane. A New Synthesis of N-Monosubstituted Hydroxylamines

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The reactions of diborane with aliphatic aldoximes and ketoximes lead to intermediates which on basic or acidic hydrolysis afford exclusively the corresponding N-monosubstituted hydroxylamines in yields of 50–90%. The intermediates from the reaction of diborane with α-aryl aldoximes and ketoximes give only on acid hydrolysis the desired hydroxylamines. On basic hydrolysis they disproportionate into amines and oximes.

Reactions of multiple bonds by diborane have been widely explored[1] and include such groups as olefins, acetylenes, nitriles, carbonyl functions, and amides.[2] From these data it seemed quite likely that oximes would also be reduced by diborane. This expectation proved to be correct, for treatment of ketoximes and aldoximes with diborane in tetrahydrofuran gave the corresponding N-monosubstituted hydroxylamines.[3]

$$\underset{\textstyle R'}{R-\overset{|}{C}}=N-OH \xrightarrow[\text{2. hydrolysis}]{\text{1. } B_2H_6} R-\underset{\textstyle R'}{\overset{|}{C}}HNHOH$$

R = H, alkyl, or aryl; R′ = H or alkyl

A survey of the literature revealed that no general method was available for the preparation of N-monosubstituted hydroxylamines. Vavon and co-workers reported that catalytic hydrogenation of aliphatic and alicyclic ketoximes[4-8] led to the corresponding N-monosubstituted hydroxylamines. On the other hand the catalytic reduction of α-phenyl ketoximes, such as acetophenone oxime and benzophenone oxime, gave the corresponding amines,[9] while the reduction of alkyl and aryl aldoximes afforded N,N-disubstituted hydroxylamines.[9] Other methods of preparing N-monosubstituted hydroxylamines include electrolytic reduction of primary and secondary nitroalkanes,[10,11] the controlled oxidation of amines,[12] and the acid cleavage of certain substituted oxaziranes.[13]

The reduction of salts of primary and secondary nitroalkanes with diborane, which is discussed in a subsequent paper,[14] has opened still another attractive synthetic route to N-monosubstituted hydroxylamines.

Our new synthesis provides a facile and convenient preparation of N-monosubstituted hydroxylamines by utilization of the readily available aldoximes and ketoximes. Moreover, it does not require expensive pressure equipment.

Reaction Conditions.—By employing 2-butanone oxime and cyclohexanone oxime as model compounds, many reaction parameters were studied and the following conditions led to optimum yields: (1) during the addition of the borane–THF solution to the oxime, the reaction temperature had to be kept below 5° to prevent excess foaming; (2) a contact time of 4 hr. was found to be sufficient to ensure complete reaction; (3) the yield of hydroxylamine was, over a wide range, independent of the amount of hydride ion per mole of oxime[15]; and (4) basic or acidic hydrolysis of the residue which remained after removal of excess borane and THF *in vacuo*, at reflux temperatures, gave comparable yields in the reduction of aliphatic and alicyclic aldoximes and ketoximes. However, in the case of α-aryl aldoximes and ketoximes, only acid hydrolysis led to high yields of the corresponding hydroxylamine (*vide infra*).

Results

As shown in Table I, the reduction of aliphatic ketoximes and aldoximes gave good to excellent yields

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[1] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

[2] H. C. Brown and P. Heim, *J. Am. Chem. Soc.*, **86**, 3566 (1964).

[3] A preliminary announcement of this work has appeared: H. Feuer and B. F. Vincent, Jr., *J. Am. Chem. Soc.*, **84**, 3771 (1962).

[4] G. Vavon and A. L. Berton, *Bull. soc. chim. France*, **37**, 301 (1925).

[5] G. Vavon and A. Callier, *ibid.*, **41**, 361, 674 (1927).

[6] G. Vavon and P. Anziani, *ibid.*, **41**, 1642 (1927).

[7] G. Vavon and J. Flurer, *ibid.*, **45**, 756 (1929).

[8] G. Vavon and V. M. Mitchovitch, *ibid.*, **45**, 964 (1929).

[9] G. Vavon and Krajcinovic, *ibid.*, **43**, 231 (1928).

[10] P. Pierron, *ibid.*, **21**, 780 (1899).

[11] M. W. Leeds and G. B. L. Smith, *J. Electrochem. Soc.*, **98**, 129 (1951).

[12] H. List, U. S. Patent 2,795,611 (1957).

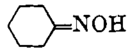
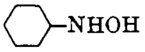
[13] W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 5739 (1957).

[14] H. Feuer, R. S. Bartlett, B. F. Vincent, Jr., and R. S. Anderson, *J. Org. Chem.*, **30**, 2880 (1965).

[15] The reduction of cyclohexanone oxime with 4.4 and with 12.2 equiv. of hydride ion gave N-cyclohexylhydroxylamine in yields of 82 and 78.6%, respectively.

TABLE I

DIBORANE REDUCTION OF ALKYL ALDOXIMES AND KETOXIMES

					Anal., %					
					Calcd.			Found		
Oxime[a]	Hydroxylamine	M.p., °C.	Yield, %	Hydride[b] consumed	C	H	N	C	H	N
$H_2C{=}NOH$[c]	H_3CNHOH	129–130[d]	50	. . .						
$H_3C(CH_2)_2CH{=}NOH$	$H_3C(CH_2)_3NHOH$	54	71	45.7	53.89	12.44	15.71	54.26	12.66	15.47
$H_3CCH_2C(CH_3){=}NOH$	$H_3CCH_2CH(CH_3)NHOH$	67	91	39.5	53.89	12.44	15.71	54.15	12.53	15.37
		140[e]	82	42.1						
$H_3C(CH_2)_5CH{=}NOH$	$H_3C(CH_2)_6NHOH$	62	81	45.5	64.07	13.06	10.68	64.30	13.30	10.79
$H_3C(CH_2)_6CH{=}NOH$	$H_3C(CH_2)_7NHOH$	73.5	87	. . .	66.20	13.10	9.66	65.96	13.16	9.46

[a] 20 mmoles and an excess of diborane were employed. The reaction time was 4 hr. at 25°. [b] Includes 1 equiv. of hydrogen evolved through the action of the oxime on diborane (theory requires 40 mmoles). [c] Formaldehyde oxime polymer was used. The reaction time was 96 hr. at 25°. [d] Isolated and characterized as the picrate; C. Kjellin [*Ber.*, 2382 (1883)] reported m.p. 128–129° for the picrate. [e] Lit.[4] m.p. 142°.

TABLE II

DIBORANE REDUCTION OF α-ARYL ALDOXIMES AND KETOXIMES

					Anal., %					
					Calcd.			Found		
Oxime[a]	Hydroxylamine	Hydrolysis medium	M.p., °C.	Yield, %	C	H	N	C	H	N
$C_6H_5CH{=}NOH$[b]	$C_6H_5CH_2NHOH$	Acid	57[c]	52.1						
$C_6H_5CH{=}NOH$	$C_6H_5CH_2NHOH$[d]	Base	57	19						
p-$NO_2C_6H_5CH{=}NOH$	p-$NO_2C_6H_5CH_2NHOH$	Acid	127	68	50.00	4.80	16.66	50.25	4.82	16.42
p-$NO_2C_6H_5CH{=}NOH$	. . .[e]	Base	. . .	. . .						
$C_6H_5C(CH_3){=}NOH$	$C_6H_5CH(CH_3)NHOH$	Acid	91	54.8	70.07	8.03	10.21	69.83	8.33	9.89
$C_6H_5C(CH_3){=}NOH$	. . .[f]	Base	. . .	. . .						

[a] 20 mmoles and an excess of diborane were employed. The reaction time was 12 hr. at 25°. [b] 40.1 mmoles of hydride was consumed [c] R. Behrend and K. Leuchs [*Ann.*, 214 (1890)] reported m.p. 57°. [d] In addition there were obtained 22% benzylamine and 22% benzaldehyde oxime. [e] Only p-nitrobenzaldehyde oxime was isolated in 15% yield and a black tar. [f] The products of this reaction were α-methylbenzylamine and acetophenone oxime, both in 50% yield.

of the corresponding N-monosubstituted hydroxylamines. The amount of hydride consumed during the reaction was determined by measuring total hydrogen evolution during the course of the reaction and during the final hydrolysis of the reaction mixture.

As shown in Table II, the reduction of α-aryl oximes and ketoximes led to the corresponding N-monosubstituted hydroxylamines in good yield when the reaction time was 12 hr. and when the hydrolysis was carried out in mineral acid. On basic hydrolysis, it was found that, depending on the starting oxime, very little or no hydroxylamine could be isolated and that the products of the reaction consisted of starting material and amine. It was established that the formation of these compounds was due to a dismutation reaction of the hydroxylamine, for refluxing N-benzylhydroxylamine (I) with base afforded benzylamine and benzaldehyde oxime, each in 40% yield.[16] This dismutation reaction also took place when a pure sample of I was allowed to stand for 3 months in a closed vial. Similarly, it has been reported that N-phenylhydroxylamine in converted on standing to aniline and nitrosobenzene.[17]

The reduction of diaryl ketoximes with diborane did not lead to the expected hydroxylamines. Fluorenone oxime (III) and benzophenone oxime (IV) were recovered essentially quantitatively even after reaction times of 12 hr. and reaction temperatures as high as 66°. Quantitative hydrogen evolution measurements indicated that the only reaction which did occur was the replacement of the acidic hydrogens in III and IV by diborane.[18]

Reductions were also carried out with 1,3-diphenyl-2-propanone oxime (V) and its sodium salt, in which the oximino group is out of conjugation with both phenyl groups, but as in the case of III and IV no reduction occurred and V was recovered essentially quantitatively even when a tenfold excess of diborane was employed. The reason for the failure of compounds III, IV, and V to undergo reduction is not apparent, because benzophenone has been reduced by diborane to diphenylcarbinol.[19] Moreover, we have found that O-methyl 1,3-diphenyl-2-propanone oxime was reduced by diborane to 1,3-diphenyl-2-propylamine in 82.6% crude yield[20] and that 1.97 equiv. of hydride per mole of oxime ether was consumed.

$$(C_6H_5CH_2)_2{-}C{=}NOCH_3 \xrightarrow[2.\ OH^-]{1.\ B_2H_6} (C_6H_5CH_2)_2CHNH_2$$

Discussion

On the basis of quantitative measurements of hydride consumption and isolation of intermediates which on subsequent hydrolysis gave hydroxylamines, it is proposed that the reduction of oximes with diborane involves essentially three steps (eq. 1–3). It is realized

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[16] The course of this reaction might involve a base-catalyzed elimination reaction with the formation of imine II, which is subsequently reduced by I to the amine.

$$\underset{\text{I}}{C_6H_5CH_2NHOH} \xrightarrow{OH^-} \underset{\text{II}}{C_6H_5CH{=}NH}$$

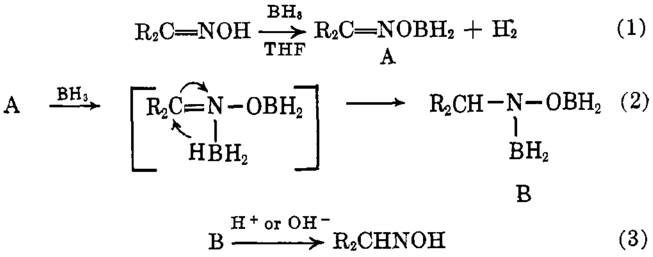
$$\text{I} + \text{II} \longrightarrow C_6H_5CH_2NH_2 + C_6H_5CH{=}NOH$$

[17] N. V. Sidwick, T. W. J. Taylor, and W. Baker, "The Organic Chemistry of Nitrogen," Clarendon Press, Oxford, 1937, p. 163.

[18] Another indication of the stability of 9-fluorenone oxime toward diborane was obtained in the reaction of potassium 9-fluorenitronate with diborane which proceeded only to the oxime stage.[14]

[19] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **82**, 681 (1960).

[20] The reduction of oximino ethers with diborane is being investigated by us.



$$R_2C{=}NOH \xrightarrow[THF]{BH_3} \underset{A}{R_2C{=}NOBH_2} + H_2 \quad (1)$$

$$A \xrightarrow{BH_3} \left[\begin{array}{c} R_2C{=}N{-}OBH_2 \\ HBH_2 \end{array}\right] \longrightarrow \underset{B}{\begin{array}{c} R_2CH{-}N{-}OBH_2 \\ BH_2 \end{array}} \quad (2)$$

$$B \xrightarrow{H^+ \text{ or } OH^-} R_2CHNOH \quad (3)$$

of course that steps 1 and 2 might occur simultaneously. Although intermediates A and B are presented as monomers, it was established that B is certainly polymeric in nature. This was ascertained by the following observations.

The reaction product of diborane with heptanal oxime dissolved in pentane was obtained as a translucent, viscous liquid after removal of the solvent *in vacuo*.[21] Elemental analysis and molecular weight determination with a Mechrolab osmometer of a benzene solution of this liquid gave a molecular formula of $C_{28}H_{70}B_6N_4O_4$, indicating that four molecules of heptanal oxime and three of diborane had combined, with the loss of 4 moles of hydrogen. The infrared spectrum of the liquid showed a broad band at 4.15 (B–H), a sharp peak at 5.95 (B–H), and a medium band at 6.2 μ (B–N).[22] The n.m.r. spectrum in carbon tetrachloride indicated that only methyl protons (δ = 0.9 p.p.m.) and methylene protons (δ = 1.2 p.p.m.) were present,[23] in a ratio of 1:4. There was no indication of a vinyl proton which in the spectrum of heptanal oxime appears as two triplets (δ = 6.7 and 7.4 p.p.m.).[24]

Step 1 in the reduction is based on the well-known reaction of diborane with hydroxyl protons to produce hydrogen and borate esters.[25] For instance 20.4 mmoles of hydrogen was evolved on adding, at 0°, 14 mmoles of diborane in THF to 20 mmoles of cyclohexanone oxime. Step 2 is the actual reduction step wherein the double bond becomes saturated. The four-centered attack is in agreement with present views of the addition of borane to multiple linkages.[1] It was established that, in the reduction, 1 equiv. of hydride ion was consumed (see Experimental). Step 3 presents the hydrolysis of intermediate B to the final product. In order to obtain maximum yield of product, it was necessary to reflux basic or acidic solutions of intermediate B.

Experimental

Apparatus.—All experiments were carried out in a three-necked, 50-ml. flask, equipped with a magnetic stirrer, thermometer, condenser, and either a serum cap or a gas dispersion tube depending on the method of introducing diborane (*vide infra*). A static pressure of high-purity nitrogen was maintained throughout the reaction by means of a Y-tube, connected from the top of the condenser, to a source of nitrogen and an acetone trap. All components of the system were dried at 150° for at least 4 hr. prior to use and flushed with nitrogen while cooling.

Hydrogen evolution was measured by attaching a gas buret through a Dry Ice trap to the outlet of the condenser.

Reagents.—Diborane was generated as described by Brown and solutions of diborane in THF were prepared and standardized.[26] Aldehydes and ketones of Eastman White Label grade were distilled prior to use. Hydroxylamine hydrochloride, Eastman White Label grade, was used as received. All oximes were prepared by methods described in the literature. THF was purified by the method of Feuer and Savides.[27]

Reaction of Diborane with Aliphatic Oximes.—The following experiment is typical of the procedure employed. To 2.26 g. (20 mmoles) of cyclohexanone oxime at 0° was introduced by means of a hypodermic syringe 17 ml. of a 2 *M* solution of borane in THF, at such a rate that the temperature did not exceed 10°. Continuing the reaction for 4 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 10% sodium hydroxide, by means of a syringe, at such a rate that the temperature did not exceed 5°. (*Caution!* The first few drops of base should be added slowly because a considerable exotherm develops; in one case a mild explosion occurred.) Then refluxing the reaction mixture for 1 hr., extracting with pentane for 90 hr., removing the solvent in a nitrogen stream, and subliming the residue at 60° (0.1 mm.) gave 1.89 g. (82%) of **N-cyclohexylhydroxylamine,** m.p. 140° (lit.[5] m.p. 142°).[28]

Similarly, treating 2.26 g. (20 mmoles) of cyclohexanone oxime with 16 ml. of 1.83 *M* solution of borane in THF (87.8 mequiv. of hydride ion) and keeping the reaction mixture 4 hr. at ambient temperature resulted in the evolution of 20.3 mmoles of hydrogen.

Hydrolyzing the reaction mixture at 0° with 2 ml. of water which was added slowly by means of a syringe and then refluxing for 30 min. gave 20.2 mmoles of hydrogen. Then, removing THF *in vacuo*, adding 10 ml. of 10% sodium hydroxide at 0° to the residue, and refluxing for 1 hr. gave an additional 25.2 mmoles of hydrogen. The total amount of hydrogen evolved was 65.7 mmoles, indicating that 1 equiv. of hydride was consumed in the reduction.

N-Methylhydroxylamine.—To 0.9 g. (20 mmoles) of polymeric formaldehyde oxime[29] at 0° was added 20 ml. of a 1.57 *M* solution of borane in THF (94.2 mequiv. of hydride ion) at such a rate that the temperature did not exceed 5°. The reaction mixture was then allowed to warm to room temperature and stirred for 96 hr. After cooling to 0°, a saturated solution of 50 mmoles of sodium hydroxide was added and the mixture was refluxed for 1 hr. The reaction mixture was recooled to 0°, and calcium hydride was added to remove all of the water. All volatile material was distilled off at 40° (3 mm.) and collected in a liquid-nitrogen trap. Evaporating THF from the distillate at 66° and adding a saturated ethanolic solution of picric acid to the residue, gave, after 5 days under refrigeration, 2.76 g. (50%) of **N-methylhydroxylamine picrate,** which after recrystallization from 95% ethanol had m.p. 129–130°.

Reaction of Diborane with α-Aryl Oximes.—The following experiment is typical of the procedure employed. To 2.42 g. (20 mmoles) of benzaldehyde oxime at 0° was introduced by means of a hypodermic syringe 16 ml. of a 2 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 12 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 20% hydrochloric acid by means of a syringe, at such a rate that the temperature did not exceed 5°. The reaction mixture was refluxed for 1 hr. while maintaining pH 1, made basic with 10% potassium hydroxide at 0°, and was then extracted with pentane for 90 hr. Removing the solvent in a nitrogen stream and subliming the residue at room temperature (0.2 mm.) gave 1.28 g. (52.1%) of **N-benzylhydroxylamine,** m.p. 57°.

When the hydrolysis was carried out with 10 ml. of 10% potassium hydroxide and the reaction mixture was worked up as before, except that the pentane extract was cooled in Dry Ice and filtered, 0.47 g. (19%) of N-benzylhydroxylamine was obtained. Evaporation of the filtrate in a nitrogen stream gave

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(21) Alkaline hydrolysis of an aliquot of this intermediate gave N-heptylhydroxylamine in 63.2% yield.

(22) C. N. R. Rao, "Chemical Applications of Infrared Spectroscopy," Academic Press Inc., New York, N. Y., 1963, p. 283.

(23) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press Ltd., London, 1959, p. 51.

(24) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 374.

(25) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **55**, 4020 (1933).

(26) H. C. Brown and B. C. Subba Rao, *ibid.*, **81**, 6428 (1959).

(27) H. Feuer and C. Savides, *ibid.*, **81**, 5826 (1959).

(28) Since hydroxylamines are quite sensitive to oxidation and are hydroscopic, their exposure to air should be limited.

(29) R. Scholl, *Ber.*, **24**, 573 (1891).

1.1 g. (44%) of a liquid which consisted of equal amounts of benzaldehyde oxime and benzylamine as determined by v.p.c.

Treatment of N-Benzylhydroxylamine with Base.—To 0.5 g. (4.1 mmoles) of N-benzylhydroxylamine was added 10 ml. of 10% potassium hydroxide. The reaction mixture was refluxed for 1 hr. and then extracted continuously with pentane for 48 hr. Evaporation of pentane in a nitrogen stream gave 0.42 g. (84% of a liquid which consisted of equal amounts of benzaldehyde oxime and benzylamine as determined by v.p.c.

Preparation of Heptanal Oxime–Diborane Adduct (Isolation of Intermediate).—To a mixture consisting of 2.70 g. (21 mmoles) of analytically pure heptanal oxime and 30 ml. of Phillips pure grade pentane (99 mole % minimum) at 0° was introduced approximately 61 mmoles of gaseous diborane (366 mequiv. of hydride ion) over a 2-hr. period. During the first 0.5 hr. of addition, hydrogen (identified by mass spectrography) was evolved. The mixture was held at room temperature for 7 hr. following diborane addition. Removing pentane and excess diborane *in vacuo* and heating the residue at 80° (0.05 mm.) for 3 hr. afforded 3.0 g. of a viscous, translucent liquid: $\lambda_{\max}^{\text{neat}}$ 4.15 (BH), 5.95 (BH), and 6.2 μ (BN); n.m.r. 0.9 (CH_3, triplet) and 1.3 p.p.m. (CH_2, singlet).

Anal. Calcd. for $C_{28}H_{70}B_6N_4O_4$; C, 56.80; H, 11.80; B, 11.13; N, 9.47; mol. wt., 594. Found: C, 56.89; H, 11.64; B, 10.98; N, 9.28; mol. wt., 638 (in benzene).

Work-up of an aliquot of the heptanal oxime–diborane adduct by the usual procedure gave a 63.2% yield of **N-heptylhydroxylamine**.

O-Methyl 1,3-Diphenyl-2-propanone Oxime.—To a 500-ml. flask, equipped with a magnetic stirrer, were added 150 ml. of absolute ethanol, 10.2 g. (45.3 mmoles) of 1,3 diphenyl-2-propanone oxime, and 1.13 g. (45.3 mg.-atoms) of metallic sodium, the latter in small pieces. After all of the sodium had dissolved, 6.4 g. (45 mmoles) of methyl iodide dissolved in 25 ml. of absolute ethanol was added dropwise, and the reaction mixture was stirred for 18 hr. at room temperature and then refluxed for 2 hr. The ethanol was stripped off *in vacuo* and the remaining material was extracted with anhydrous ether. Evaporating the ether extract in a nitrogen stream and distilling gave 1.50 g. (14%) of **O-methyl 1,3-diphenyl-2-propanone oxime**: b.p. 100–110° (0.3 mm.); $n^{20}\text{D}$ 1.5596; $\lambda_{\max}^{\text{neat}}$ 3.3 and 3.4 (CH), 6.2 (C=N and phenyl), and 9.55 μ (unassigned); n.m.r. 3.4 and 3.6 [$CH_2C(N)CH_2$, two singlets], 3.95 (OCH_3, singlet), and 7.3 p.p.m. (aromatic H, singlet).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 79.94; H, 7.19; N, 6.08.

Reaction of Diborane with O-Methyl 1,3-Diphenyl-2-propanone Oxime.—To 2.88 g. (12 mmoles) of O-methyl 1,3-diphenyl-2-propanone oxime at 0° was introduced by means of a hypodermic syringe 9.0 ml. of a 2.13 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 12 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 10% potassium hydroxide by means of a syringe, at such a rate that the temperature did not exceed 5°. Then refluxing the reaction mixture 1 hr., extracting with pentane for 48 hr., and removing the solvent in a nitrogen stream gave 2.09 g. (82.6% crude yield) of 1,3-diphenyl-2-propylamine. Addition of an aliquot of the crude amine to a saturated ethanolic picric acid solution afforded, after two recrystallizations from absolute ethanol, **1,3-diphenyl-2-propylamine picrate**, m.p. 193° dec. (lit.[30] m.p. 193°).

Anal. Calcd. for $C_{21}H_{20}N_4O_7$: C, 57.37; H, 4.58; N, 12.72. Found: C, 57.73; H, 4.85; N, 12.42.

Bubbling anhydrous hydrogen chloride through an ether solution of the crude amine gave **1,3-diphenyl-2-propylamine hydrochloride**, m.p. 200–202° dec. (lit.[30] m.p. 202°).

Acknowledgment.—We wish to thank the Office of Naval Research for financial support of this work.

[30] B. B. Dev and V. S. Ramanathan, *Proc. Natl. Inst. Sci. Ind.*, **9**, 193 (1943); *Chem. Abstr.*, **43**, 5027*b* (1946).

Diborane Reduction of Nitro Salts. A New Synthesis of N-Monosubstituted Hydroxylamines

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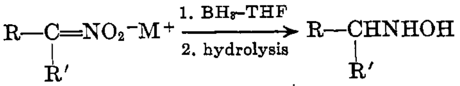
Nitro compounds which are unaffected by diborane interact readily in the form of their salts with this reagent. The reaction leads to intermediates which on basic or acid hydrolysis afford N-monosubstituted hydroxylamines in yields of 30–60%.

A new synthesis of N-monosubstituted hydroxylamines by reduction of the corresponding aldoximes and ketoximes with diborane in tetrahydrofuran has recently been communicated.[1,2] This paper reports on another new and convenient route to hydroxylamines. It has been found that diborane, which does not affect nitro compounds,[3] reduces salts of primary and secondary nitro compounds[4] to the corresponding N-monosubstituted hydroxylamines.[5]



$$\underset{\substack{|\\ R'}}{R\text{—}C}{=}NO_2^-M^+ \xrightarrow[\text{2. hydrolysis}]{\text{1. }BH_3\text{–THF}} \underset{\substack{|\\ R'}}{R\text{—}CH}NHOH$$

R = H or alkyl; R′ = alkyl or aryl; M = Li, K, or NH_4

Results and Discussion

The procedure was similar to that utilized in the reduction of oximes.[2] As shown in Table I, the reduction of aliphatic and alicyclic nitronates gave intermediates which on basic or acidic hydrolysis afforded the corresponding N-monosubstituted hydroxylamines in 30–60% yield. Primary nitronates with the exception of potassium cyclohexylmethanenitronate gave somewhat lower yields than secondary nitronates. It was established that the yield of hydroxylamine was essentially independent of the nature of the cation, for lithium, potassium, and ammonium cyclohexanenitronate were converted to N-cyclohexylhydroxylamine in essentially the same yield.

The reduction of potassium phenylmethanenitronate with diborane gave N-benzylhydroxylamine (I) in 48% yield when the intermediate was hydrolyzed in acid medium. On basic hydrolysis, I underwent a disproportionation reaction to benzylamine and benzaldehyde oxime. This disproportionation was previously

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[1] H. Feuer and B. F. Vincent, Jr., *J. Am. Chem. Soc.*, **84**, 3771 (1962)

[2] H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, *J. Org. Chem.*, **30**, 2877 (1965).

[3] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 249.

[4] The term nitronate is used throughout to denote these compounds.

[5] Other reported methods of preparing hydroxylamines are presented in ref. 2.