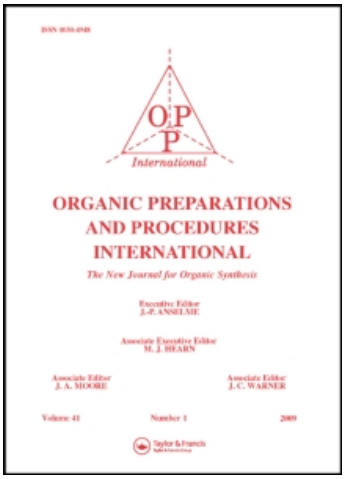

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SYNTHESIS OF N,N-DIALKYLHYDROXYLAMINES. A REVIEW

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SYNTHESIS OF N,N-DIALKYLHYDROXYLAMINES. A REVIEW

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Introduction and Scope of the Review

N,N-Dialkylhydroxylamines have been obtained from:

1. The reaction of organometallic compounds with various compounds having nitrogen-oxygen bonds (p. 136).
2. The pyrolysis of trialkylamine oxides (Cope reaction p. 141).
3. The oxidation of secondary amines (p. 146).
4. The alkylation of hydroxylamine or N-alkylhydroxylamine (p. 147).
5. The reduction of nitrones (p. 149).

However, many of these reactions give other products in addition to the desired N,N-dialkylhydroxyamine and often the nature and the yield of these side-products are omitted by the investigators. This short survey will cover mainly the preparation of N,N-dialkylhydroxylamines. Hydroxylamines with aryl groups are included only if the synthesis is suitable for both types of compounds. In addition experimental details for reactions carried out in the authors' laboratories are given in the sections involved.

1. REACTION OF ORGANOMETALLIC COMPOUNDS WITH N-O CONTAINING COMPOUNDS

a) Grignard Reagents

i) Nitrosyl Chloride and Nitrogen Dioxide

When Grignard reagents are added to an ethereal solution of nitrosyl chloride or nitrogen dioxide, dialkylhydroxylamines are formed. The first compound when treated with t-butylmagnesium chloride gives di-t-butylhydroxylamine in a 2.6% yield.[2] The reverse addition yields the monoalkylhydroxylamine[2] or a mixture of the monosubstituted derivative and the N-nitrosoalkylhydroxylamine.[3] Treatment of a Grignard solution with an ethereal solution of nitrogen dioxide has been used to prepare diethylhydroxylamine[4] and di-n-butylhydroxylamine.[5] The yield of the former was reported to be very good. In a similar fashion, nitric oxide gave the monoalkylhydroxylamine from cyclohexylmagnesium halide and the dialkylhydroxylamine from benzylmagnesium chloride.[3]

ii) Alkyl Nitrates and Nitrites

The reaction of Grignard reagents with alkyl nitrates yields mainly the dialkylhydroxylamine if 3.5 fold excess of Grignard are used.[6] The same reaction with alkyl nitrites gives lower yields of the product. The yields obtained are listed in Table I. The product from all these reactions is a hydroxylamine in which both alkyl groups are the same. Variation of the alkyl groups can be accomplished by the reaction of Grignard reagents with nitroalkanes, nitrones, esters of nitronic acid and gem-halonitrosoalkanes.

Table I

N,N-Dialkylhydroxylamine from Alkyl Nitrates and Alkyl Nitrites

Grignard(Substrate)	Product(% Yield)	Ref.
$CH_3MgI(C_2H_5ONO_2)$	$(CH_3)_2NOH(49)$	6
$((CH_2ONO_2)_2)$	$(CH_3)_2NOH(76)$	6
(Nitroglycerin)	$(CH_3)_2NOH(76)$	6
$(C(CH_2ONO_2)_4)$	$(CH_3)_2NOH(na)$	6
$C_2H_5MgBr(C_2H_5ONO_2)$	$(C_2H_5)_2NOH(67)$	6
$((CH_2ONO_2)_2)$	$(C_2H_5)_2NOH(76)$	6
(Nitroglycerin)	$(C_2H_5)_2NOH(76)$	6
$(C(CH_2ONO_2)_4)$	$(C_2H_5)_2NOH(na)$	6
$\underline{n}\text{-}C_3H_7MgI(\underline{i}\text{-}C_3H_7ONO)$	$(C_3H_7)_2NOH(66)$	7
$\underline{t}\text{-BuMgCl}(C_2H_5ONO)$	$(\underline{t}\text{-Bu})_2NOH(11)$	2

iii) Nitroalkanes

The addition of Grignard reagents to nitroalkanes leads usually to the formation of two different hydroxylamines.

$$EtMgBr + CH_3NO_2 \longrightarrow Et(Me)NOH + Et(\underline{n}\text{-Pr})NOH$$

One of these products results from addition of the reagent directly to the nitro group and the other is formed by the addition to the nitro group and substitution of the α-hydrogen by the Grignard reagent; the actual mechanism for the formation of these compounds is not known. Other products reported for this reaction are amines, oximes,

nitrones, hydrazines, azo and azoxy compound. Reports of the formation of only one hydroxylamine in this reaction should be suspect since the two hydroxylamines are difficult to separate by ordinary distillation.

Studies in this laboratory[1] have shown that the maximum total yield of hydroxylamines was obtained when 2.5-3.0 fold excess of Grignard reagent was used. The experimental details are given below. This observation was based on a gas chromatographic study of the trimethylsilyl derivatives of the products from nitromethane and ethyl magnesium bromide. The yields of dialkylhydroxylamines obtained by this method are given in Table II.

Reaction of Nitromethane and Butylmagnesium Bromide. General Procedure.

A solution containing 2.7 moles of n-butylmagnesium bromide in 600 ml of ether was added to a stirred solution of 54 ml (1 mole) of nitromethane in 600 ml of ether at 0-5° at a rate which maintained the solution at constant reflux. The resulting solution was refluxed for 4 hrs and then allowed to stand overnight. Addition of water to the reaction mixture was followed by the addition of dilute hydrochloric acid to give a solution with a pH of 9-10. The resulting mixture was steam distilled into dilute hydrochloric acid and ~19 l of distillate were collected. The hydrochloric acid solution was concentrated to about 300 ml, made basic with concentrated sodium hydroxide and extracted several times with ether. Removal of the ether after drying using an efficient column was followed by distillation through a spinning band column. The products obtained were n-butylmethylhydroxylamine (22.0 g), bp. 33-36° (0.3 mm) and n-butyl-n-pentylhydroxylamine (25.4 g), bp. 59-61° (0.1 mm).

n-Butylmethylhydroxylamine: IR(neat) 3.06μ (OH); nmr(neat) δ 7.91 (s, OH), 2.53 (s, NCH_3) 2.54 (t,-NCH_2; J = 7 cps), 1.4 (m, CH_2CH_2), 0.88 (t, CH_3-C, J = 6 cps).

Anal. Calcd for $C_5H_{13}NO$: C, 58.21; H, 12.62. Found: C, 58.49; H, 13.03.

n-Butyl-n-pentylhydroxylamine: IR(neat) 3.06μ (OH); nmr($DCCl_3$)δ 7.91 (s, OH), 2.65 (distorted triplet $N(CH_2)_2$, J = 7 cps), 1.4 (m, five CH_2), 0.92 (t, two CH_3, J = 6 cps).

Anal. Calcd for $C_9H_{21}NO$: C, 67.92; H, 13.20; N, 8.80. Found: C, 67.72; H, 13.43; N, 8.61.

Data for the other dialkylhydroxylamines prepared by this method are given below.

From Nitromethane and Ethylmagnesium Bromide.

Ethylmethylhydroxylamine, bp. 40° (16-20 mm) (Lit.[8] 26-20° (10 mm); IR(neat) 3.03μ (OH); nmr(neat) δ 10.83 (s, OH), 2.60 (q, CH_2N, J = 7 cps), 2.53 (s, NCH_3) and 1.10 (t, CH_3, J = 7 cps).

Ethyl-n-propylhydroxylamine, bp. 50° (8 mm) (Lit.[9] 55-8° (10-11 mm); IR(neat) 3.04μ (OH); nmr(neat) δ 8.10 (s, OH), 2.3-2.9 (m, $-N(CH_2)_2$), 1.49 (sextet C-CH_2-C, J = 8 cps), 1.11 (t, CH_3, J = 7 cps) and 0.90 (t, CH_3 J = 8 cps).

From Nitromethane and n-Propylmagnesium Bromide.

Methyl-n-propylhydroxylamine, bp. 51-53° (11 mm); IR(neat) 3.11μ (OH); nmr(neat) δ 8.30 (broad, s, OH); 2.49 (s, NCH_3), 2.48 (t, NCH_2, J = 7 cps); 2.53 (sextet, CH_3CH_2, J = 7 cps), 0.85, (t, CH_3, J = 7 cps).

Anal. Calcd for $C_4H_{11}NO$: C, 53.89; H, 12.44. Found: C, 53.64; H, 11.90.

n-Butyl-n-propylhydroxylamine, bp. 83-83° (11 mm); IR(neat) 3.04μ (OH); nmr(DCCl3)δ 7.58 (broad, s, OH), 2.57 (distorted t, $N(CH_2)_2$, J = 7 cps); 1.0-2.0 (m, CH_2, $-CH_2CH_2-$) and 0.89 (t, two CH_3, J = 7 cps).

Anal. Calcd for $C_7H_{17}NO$: C, 64.12; H, 12.97. Found: C, 64.31; H, 12.68.

The above procedure could be adapted to the preparation of other dialkylhydroxylamines using organometallic compounds.

iv) Nitrones, Nitronic Esters and Halonitroso Compounds

Nitrones derived from benzaldehyde,[13] and Δ^1-pyrroline N-oxides[14,15] are converted by Grignard reagents into

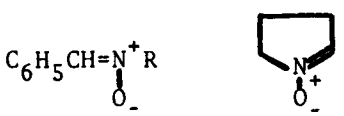


Table II

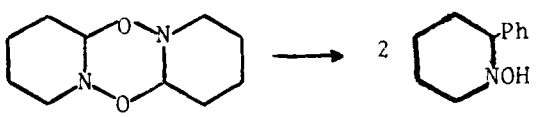
N,N-Dialkylhydroxylamines from

Nitroalkanes and Grignard Reagents

Grignard(Substrate)	Product(% Yield)	Ref.
MeMgI(CH_3NO_2)	Me_2NOH(23)	10
EtMgBr[a](CH_3NO_2)	Et(Me)NOH(10), n-Pr(Et)NOH(25)	1
n-PrMgBr[b](CH_3NO_2)	n-Pr(Me)NOH(15), n-Pr(n-Bu)NOH(7.6)	1
n-BuMgBr(CH_3NO_2)	See Experimental Part	1
EtMgI($C_2H_5NO_2$)	Et_2NOH[c], Et(2-Bu)NOH[c]	7
EtMgBr($C_2H_5NO_2$)	Et_2NOH(46)	11
n-PrMgI($C_2H_5NO_2$)	n-Pr(Et)NOH[c], Et(2-C_5H_{11})NOH[c]	7
EtMgI(1-$NO_2C_3H_7$)	n-Pr(Et)NOH[c], Et(3-C_5H_{11})NOH[c]	7
i-PrMgCl($PhCH_2NO_2$)	i-Pr($PhCH_2$)NOH[c]	12
PhMgBr($PhCH_2NO_2$)	Ph_2CH(Ph)NOH(32.5)	12
i-PrMgCl(NO_2CH_2COOEt)	$(i\text{-Pr})_2\overset{\overset{OH}{|}}{C}CH_2$(i-Pr)NOH(8)	12

a) 2 fold excess. b) 2.5 fold excess. c) Yield was not reported.

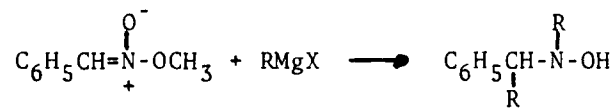
disubstituted hydroxylamines. Dimers of tetrahydropyridine N-oxides behave similarly with phenylmagnesium bromide to give cyclic hydroxylamines.[16] More highly substituted



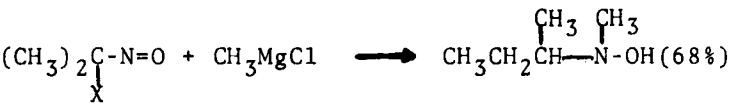
(93%)

nitrones such as N,α,α-triphenylnitrone are reduced by isopropylmagnesium chloride to the Schiff base.[12]

Methyl α-phenylnitronate reacts with Grignard reagents (R=CH_3, C_2H_5, C_3H_7, C_6H_5) to yield N,N-dialkylhydroxylamines in better than 50% yields.[17]



Only methylmagnesium chloride reacts with 2,2-halonitrosopropane (X=Cl,Br) in the following manner.[18] Other



Grignard reagents cause elimination of hydrogen halide.

b) Organozinc Compounds and Other Organometallics

The use of other organometallic compounds in the formation of dialkylhydroxylamines from various nitrogen oxygen compounds has dealt mainly with dialkylzinc and alkylzinc iodides.

With nitroalkanes, dialkylzinc compounds and alkylzinc iodides are reported to give only one dialkylhydroxylamine; alkylzinc iodides are the preferred reagent. The examples which have been studied are listed in Table III.

The results obtained with miscellaneous organometallic compounds are given in Table IV.

2. PYROLYSIS OF AMINE OXIDES

The pyrolysis of trialkylamine oxides, known as the Cope reaction, though mainly used for the preparation of

Table III

N,N-Dialkylhydroxylamines from

Organozinc Compounds

Reagent(Substrate)	Product(% Yield)	Ref.
EtZnI(i-$C_5H_{11}ONO$)	Et_2NOH(33)	4,7
EtZnI($C_2H_5NO_2$)	Et(2-Bu)NOH(13)	7
n-PrZnI(i-C_3H_7ONO)	(n-Pr)$_2$NOH(28)	7
i-PrZnI(i-$C_5H_{11}ONO$)	(i-Pr)$_2$NOH(61)	7
i-PrZnI($C_2H_5NO_2$)	$Me_2CHCH(Me)$(i-Pr)NOH(77)	7
Et_2Zn(NOCl)	Et_2NOH(44)	19
Et_2Zn(i-C_3H_7ONO)	Et_2NOH(78)	20
Et_2Zn(i-$C_5H_{11}ONO$)	Et_2NOH(46)	20
Et_2Zn(Ph_2NNO)	Et_2NOH(30)	21
Et_2Zn(CH_3NO_2)	n-Pr(Et)NOH(low)	9
Et_2Zn($C_2H_5NO_2$)	Et(2-Bu)NOH(43)	9
Et_2Zn(1-$C_3H_7NO_2$)	$Et_2CH(Et)NOH$(53)	9
Et_2Zn(2-$C_3H_7NO_2$)	$EtC(CH_3)_2NOH(Et)$(49)	9
Et_2Zn($(CH_3)_2CH(CH_2)_2NO_2$)	$Me_2CHCH_2CH(Et)NOH(Et)$(46)	9
(n-Pr)$_2$Zn(n-C_3H_7ONO)	(n-Pr)$_2$NOH(43)	20
(n-Pr)$_2$Zn($C_2H_5NO_2$)	n-Pr(2-C_5H_{11})NOH(33)	9
(n-Pr)$_2$Zn(1-$C_3H_7NO_2$)	n-Pr(3-C_6H_{13})NOH(52)	9
(n-Pr)$_2$Zn(2-$C_3H_7NO_2$)	n-$PrC(CH_3)_2$N(n-Pr)-OH(38	9

Table IV

N,N-Disubstituted Hydroxylamines from

Miscellaneous Organometallics

Reagent(Substrate)	Product(% Yield)	Ref.
$PhNa((CH_3)_3CNO_2)$	t-Bu(Ph)NOH(3.6)	22
$PhLi((CH_3)_3CNO_2)$	t-Bu(Ph)NOH(3.6)	22
$2,6\text{-}(MeO)_2C_6H_3Li((CH_3)_3CNO_2)$	$t\text{-Bu}(2,6(MeO)_2C_6H_3)NOH(18)$	22
$PhMgBr((CH_3)_3CNO)$	t-Bu(Ph)NOH(56)[a]	23
$Et_3Al\cdot Et_2O(NO_2)$	$Et_2NOH(\sim 50)$	24

a) The yields with other aryl Grignard reagents varied from 16-62%.

olefins, is also useful for the synthesis of N-alkyl-N-methylhydroxylamines and dialkylhydroxylamines in which the alkyl groups are the same. If the amine oxide possesses more than one type of alkyl group capable of forming an olefin, a mixture of hydroxylamines is obtained. Amine oxides possessing an allyl group rearrange to the corresponding O-allylhydroxylamine.

Tertiary amine oxides are readily prepared by oxidation of the corresponding amines with hydrogen peroxide. Their decomposition normally takes place at temperatures of 100-120° and is carried out on small amounts under reduced pressure.[25] Examples for which the dialkylhydroxylamine yield was given are listed in Table V.

Table V

N,N-Dialkylhydroxylamines from

Amine Oxides

Amine Oxide	Product(% Yield)	Ref.
Me_2,n-Pr	$(CH_3)_2NOH$(20)	8
Me_2,cyclohexyl	$(CH_3)_2NOH$(61)	8
Me_2,cyclohexylmethyl	$(CH_3)_2NOH$(78-90)	26
Me,Et_2	$CH_3(C_2H_5)NOH$(82)	8
Et_3	$(C_2H_5)_2NOH$(41-91)	8,27,28
n-Pr_3	$(n\text{-}C_3H_7)_2NOH$(50-84)	8,28
1-Etpiperidine	1-Hydroxypiperidine(42-65)	8,29,30
Me,-$(CH_2)_6$-	CH_2=CH$(CH_2)_4$(Me)NOH(53)	31
Me,-$(CH_2)_4CH(CH_3)$-	CH_2=CH$(CH_2)_4$(Me)N-OH(12)	32
Me,-$(CH_2)_7$-	CH_2=CH$(CH_2)_5$(Me)NOH(79)	31
Me,$(n\text{-}C_7H_{15})_2$	$CH_3(n\text{-}C_7H_{15})NOH$(80)	31
$(n\text{-Bu})_3$	$(n\text{-}C_4H_9)_2NOH$(79)	28
$(n\text{-}C_5H_{11})_3$	$(n\text{-}C_5H_{11})_2NOH$(75)	28
$(i\text{-}C_5H_{11})_3$	$(i\text{-}C_5H_{11})_2NOH$(53)	28
$(n\text{-}C_6H_{13})_3$	$(n\text{-}C_6H_{13})_2NOH$(70)	28
$(n\text{-}C_7H_{15})_3$	$(n\text{-}C_7H_{15})_2NOH$(76)	28
Et_2,$PhCH_2$	$PhCH_2$(Et)NOH(34),Et_2NOH(21)	33

A modification of the Cope reaction which involves a retrograde Michael reaction offers the possibility for the preparation of all types of dialkylhydroxylamine. This method is based on the preparation of ethyl β-dialkylamino propionates by the condensation of a dialkylamine with ethyl

acrylate. The resulting tertiary amine is oxidized with monoperthalic acid ($C_8H_6O_5$) to the corresponding amine oxide which precipitates out of ether solution as the phthalate salt. Treatment of the salt with acid or base causes decomposition of the amine oxide to ethyl acrylate and the corresponding dialkylhydroxylamine.[8]

$$R_2NH + CH_2{=}CHCOOEt \longrightarrow R_2NCH_2CH_2COOEt$$

$$R_2NCH_2CH_2COOEt + C_8H_6O_5 \longrightarrow R_2N(O)CH_2CH_2COOEt \cdot C_8H_6O_4$$

$$R_2N(O)CH_2CH_2COOEt \cdot (C_8H_6O_4) \longrightarrow R_2NOH + CH_2{=}CHCOOEt$$

The yields of dialkylhydroxylamine from diethylamine and dipropylamine were 50 and 56% respectively; no yields were reported for the hydroxylamines prepared from dibutylamine, morpholine and piperidine.

An analogous reaction occurs with β-cyanoethyldimethylamine and forms dimethylhydroxylamine in 22% yield.[8]

3. OXIDATION OF SECONDARY AMINES

Secondary amines when treated with hydrogen peroxide or acyl peroxides form N,N-dialkylhydroxylamines. The reaction appears to be general and has even been used with primary amines. However, this method is erratic and yields of the product have not exceeded 50%. Oxidation of the α-carbon atoms often occurs to yield a complex mixture of products.

The reaction is usually conducted by addition of the calculated amount of oxidant to the amine dissolved in alcohol. The solution is then allowed to stand until all the peroxide has been consumed. Examples of hydroxylamines prepared by this method are listed in Table VI. This method

Table VI

N,N-Dialkylhydroxylamines from Secondary Amines

Amine	Oxidizing Agent	% Yield	Ref.
$(CH_3)_2NH$	H_2O_2	12	32
$CH_3(C_2H_5)NH$	H_2O_2	16	34
$(C_2H_5)_2NH$	H_2O_2	40-50	35,36
$(\underline{n}\text{-}C_3H_7)_2NH$	H_2O_2	40-50	36,37
$(\underline{i}\text{-}C_3H_7)_2NH$	H_2O_2	17	32
$\underline{n}\text{-}C_{12}H_{25}(CH_3)NH$	H_2O_2	—	10
$(CH_2)_6NH$	H_2O_2	20.5	35
$PhCH_2(CH_3)NH$	H_2O_2	—	34
$EtOCH_2CH_2(CH_2{=}CHCH_2)NH$	H_2O_2	—	38
$EtOCH_2CH_2(Et)NH$	H_2O_2	10.5	38
$(MeOCH_2CH_2)_2NH$	H_2O_2	15.8-22	35
$(EtOCH_2CH_2)_2NH$	H_2O_2	24	35,38
Morpholine	H_2O_2	4-19	32,39
4-Ethoxypiperidine	$(PhCOO)_2$	8	38
	H_2O_2	24	38
$(MeOCH_2CH_2OCH_2CH_2)_2NH$	H_2O_2	12.5	38

in our laboratory gave no isolable yield of product from di-n-butylamine.

4. ALKYLATION OF HYDROXYLAMINES

Disubstituted hydroxylamines may also be prepared by alkylation of hydroxylamine or of N-alkylhydroxylamines with alkyl halides. Formation of trimethylamine oxide is the

preferred reaction with methyl iodide and hydroxylamine. The formation of amine oxides becomes less important as the alkyl group becomes larger. This reaction has also been used to prepare monoalkylhydroxylamines but the yields are low.

The reaction is carried out by treatment of hydroxylamine with the alkyl halide in aqueous alcohol in the presence of base; the reaction time can be reduced by heating under reflux.

Studies in this laboratory[1] have shown that this method always yields a mixture of the N,N-dialkylhydroxylamine and N-alkylhydroxylamine irrespective of the ratio of the alkyl halide and hydroxylamine employed. Experimental details are given for the reaction of n-butyl bromide and hydroxylamine; the latter was used in excess and served as the base in the reaction.

Reaction of n-Butyl Bromide and Hydroxylamine.

General Procedure.

A solution of n-butyl bromide (26.9 ml, 0.25 mole), hydroxylamine hydrochloride (69.5 g, 1 mole) and sodium hydroxide (40 g, 1 mole) in methanol (225 ml) and water (50 ml) was stirred at room temperature for 3.5 days and then refluxed for 1 hr. The resulting solution was treated with 250 ml of water, cooled and made alkaline (pH 10) with saturated aqueous sodium hydroxide. Cooling gave 6.79 g of di-n-butylhydroxylamine which after one recrystallization from methanol and water melted at 50-53° (Lit.[28] 52-3°); IR(nujol) 3.19μ (OH); nmr($DCCl_3$) δ 8.23 (broad s, OH); 2.69 (t, J = 8 cps, NCH_2); 1.48 (m, CH_2CH_2); 0.93 (distorted t, CH_3, J = 6 cps).

The filtrate was acidified with concentrated hydrochloric acid and concentrated to 300 ml. The resulting solution was made alkaline (pH 10) and the salts which precipitated were filtered and washed several times with small amounts of ether. The aqueous solution was extracted with three 200 ml portions of ether and the ether extracts were combined and dried. Removal of the ether gave

n-butylhydroxylamine which after one recrystallization from hexane melted at 51-4° (Lit.[43] 54°); yield, 6.31 g (28%); IR(nujol) 3.1-4.2μ (NH,OH); nmr($DCCl_3$) δ 6.80 (s, 2, NHOH); 2.92 (t, NCH_2, J = 7 cps); 1.46 (m, CH_2CH_2); 0.93 (distorted t, CH_3, J = 6 cps).

The same reaction when carried out at reflux for 6 hrs gave 20% yield of di-n-butylhydroxylamine and 35% yield of n-butylhydroxylamine.

Examples for which yields are reported are listed in Table VII.

Table VII

Alkylation of Hydroxylamines

Alkyl Halide	Hydroxylamine	Product(% Yield)	Ref.
C_2H_5I	NH_2OH	$(C_2H_5)_2NOH$(na)	40
n-C_3H_7I	NH_2OH	(n-$C_3H_7)_2NOH$(na)	40
i-C_3H_7I	NH_2OH	(i-$C_3H_7)_2NOH$(na)	40
n-C_4H_9Br	NH_2OH	(n-$C_4H_9)_2NOH$(37)	1
$PhCH_2Cl$	NH_2OH	$(PhCH_2)_2NOH$(50)	41
$MeOCH_2CH_2Br$	NH_2OH	$(MeOCH_2CH_2)_2NOH$(52.6)	42
$Me_2NCH_2CH_2Cl$	CH_3NHOH	$Me_2NCH_2CH_2$(Me)NOH(18.2)	38

5. REDUCTION OF NITRONES

Nitrones are reduced to disubstituted hydroxylamines in good yields by lithium aluminum hydride, potassium borohydride and hydrogenation over platinum black. Other reducing agents give amines or Schiff bases. Examples are given in Table VIII.

Dimers from tetrahydropyridine N-oxides are not affected by lithium aluminum hydride.[16]

Table VIII

N,N-Dialkylhydroxylamines from Nitrones, $R^1R^2C{=}N(O)R^3$

Nitrone R^1	R^2	R^3	Reducing Agent	% Yield	Ref.
Ph	H	$PhCH_2$	$LiAlH_4$	85	44
Ph	H	CH_3	$LiAlH_4$	94	44
Ph	H	t-C_8H_{15}	$LiAlH_4$	52	44
Ph	H	t-Bu	$LiAlH_4$	77	45,46
Ph	H	Ph	H_2(Pt.)	100	47
4-$MeOC_6H_4$	H	Ph	H_2(Pt.)	100	47
Ph	Ph	CH_3	$LiAlH_4$	91	44
Ph	Ph	$PhCH_2$	$LiAlH_4$	90	44
Ph	Ph	Ph	H_2(Pt.)	100	47
2,4,4-Trimethyl-Δ^1-pyrroline-1-oxide			KBH_4	34	15
4,5,5-Trimethyl-Δ^1-pyrroline-1-oxide			KBH_4	na	15

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