3.42 (s, 3 H), 3.74 (s, 3 H), 4.52 (dd, $J$ = 9, 9 Hz, 1 H), 4.85 (ddd, $J$ = 9, 7, 4 Hz, 1 H), 5.05–5.20 (m, 3 H), 5.66 (ddd, $J$ = 18, 10, 9 Hz, 1 H); IR ($CHCl_3$) superimposable on that of the enriched mixture of **17***l*.

**Acknowledgment.** We are pleased to acknowledge support of this work by the National Science Foundation through Grant CHE-8405527. We are also grateful to Mr. C. B. Green for high field $^1H$ NMR measurements.

**Registry No.** **1a**, 99439-83-5; **1b**, 99439-82-4; **1c**, 76454-94-9; **1d**, 76454-93-8; **2ia**, 93684-44-7; **2b**, 88362-45-2; **3a**, 101030-94-8; **3b**, 101030-96-0; **3c**, 101030-98-2; **3d**, 101031-00-9; **3e**, 101031-02-1; **3f**, 101031-04-3; **5u**, 101031-05-4; **5l**, 101142-46-5; **6u**, 101142-49-8; **6l**, 101142-50-1; **7l**, 101031-06-5; **7u**, 101142-47-6; **8l**, 101142-51-2; **8u**, 101142-52-3; **9l**, 101031-07-6; **9u**, 101142-48-7; **10l**, 101142-53-4; **10u**, 101142-54-5; **11**, 101031-14-5; **12**, 101142-69-2; **13u**, 101031-09-8; **13l**, 101142-56-7; **14u**, 101142-58-9; **14l**, 101142-60-3; **15l**, 101031-11-2; **15u**, 101142-62-5; **16l**, 101143-46-8; **16u**, 101143-48-0; **17l**, 101031-13-4; **17u**, 101142-64-7; **18l**, 101142-66-9; **18u**, 101142-68-1; $C_6H_5CH_2Br$, 101142-68-1; (4*S*,2′*R*)-2-(2,3-dimethyl-3-butenyl)-4,5-dihydro-4-(1-methylethyl)oxazole, 99440-13-8; (4*S*,2′*S*)-2-(2,3-dimethyl-3-butenyl)-4,5-dihydro-4-(1-methylethyl)oxazole, 99440-14-9.

# Preparation of Vicinal *N*-Alkylamino Alcohols via Acylation–Rearrangement of Nitrones Followed by Hydride Reduction

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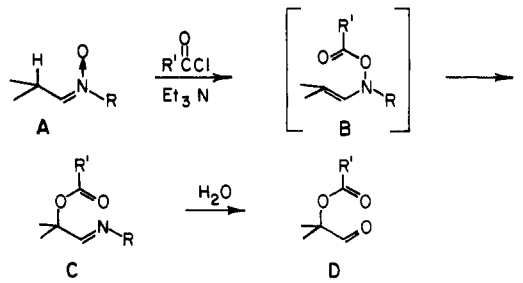
*Received July 23, 1985*

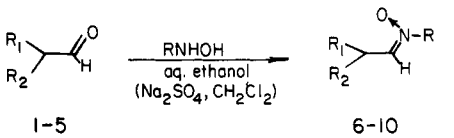
Acylation–rearrangement of *N-tert*-butyl and *N*-cyclohexyl nitrones of cyclohexanecarboxaldehyde (**1**), *n*-butyraldehyde, isobutyraldehyde, 3-cyclohexenecarboxaldehyde, and α-methylpropionaldehyde gave α-pivaloyloxy imines, which underwent reduction with lithium aluminum hydride to *N-tert*-butyl- and *N*-cyclohexylamino alcohols (Table I). Reduction of the α-pivaloyloxy imines derived from **1** with sodium borohydride gave stable *N*-alkylamino pivalates **17a,b**. Acylation–rearrangement of the *N*-methyl nitrone of **1** with pivaloyl chloride afforded a 3:1 mixture of the α-pivaloyloxy imine **11c** and an imide, *N*-pivaloyl-*N*-methylcyclohexanecarboxamide (**18**). It is proposed that the latter arises by elimination of an *O*-acyl nitrone intermediate (**22**) to a nitrilium pivalate ion pair followed by collapse to an *O*-acyl imidate and O → N rearrangement. Carboxylation of the *N-tert*-butyl, *N*-cyclohexyl, and *N*-methyl nitrones with methyl chloroformate gave imino carbonates, reduction of which with sodium borohydride afforded spiro *N*-alkyloxazolidinones **27**. 1-[(*N*-Methyl- and 1-[(*N*,*N*-dimethylamino)-methyl]cyclohexanol (**12c** and **29**) were obtained from the *N*-methyloxazolidinone by hydrolysis and lithium aluminum hydride reduction, respectively.

The reaction of nitrones A of aldehydes and ketones with acid chlorides in the presence of triethylamine at 0–25 °C affords α-acyloxy imines C, which undergo ready hydrolysis to α-acyloxy aldehydes D.[1] This novel method for α-oxygenation presumably proceeds via spontaneous [3,3]sigmatropic rearrangement of an intermediate *N*-vinyl-*O*-acylhydroxylamine (A → B → C). Since the imine double bond in the isolable intermediate C should be reduced readily by hydride reagents,[2] we considered that the acylation–rearrangement of nitrones could be adapted to provide a useful method for synthesis of the medicinally important[3] vicinal *N*-alkylamino alcohols. In fact, reduction of the α-pivaloyloxy imine from the *N-tert*-butyl nitrone of cyclohexanecarboxaldehyde with lithium aluminum hydride gave 1-[(*N-tert*-butylamino)methyl]-cyclohexanol (**12a**).[1] In this paper we report the preparation of a series of *N-tert*-butyl-, *N*-cyclohexyl-, and *N*-methylamino alcohols via acylation–rearrangement of nitrones and subsequent hydride reduction. *N*-Alkyloxazolidinones **27** were obtained by acylation–rearrangement with methyl chloroformate followed by sodium borohydride reduction.




## Results and Discussion

The *N-tert*-butyl nitrones **6a–10a** were prepared as reported previously[1] by condensation of cyclohexanecarboxaldehyde (**1**), *n*-butyraldehyde (**2**), isobutyraldehyde (**3**), 3-cyclohexenecarboxaldehyde (**4**), and α-phenylpropionaldehyde (**5**) with *N-tert*-butylhydroxylamine[4] in dichloromethane containing sodium sulfate at 25 °C.[5] The

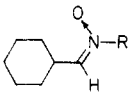
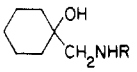
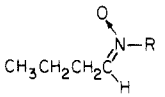
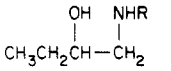
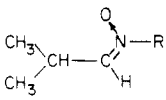
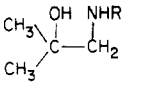
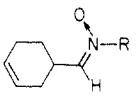
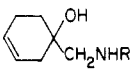
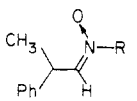
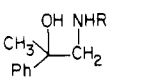



*N*-cyclohexyl nitrones **6b–10b** of the same five aldehydes and the *N*-methyl nitrone **6c** of cyclohexanecarboxaldehyde were formed by reaction of *N*-cyclohexyl- or *N*-methylhydroxylamine hydrochloride with the aldehyde

(1) Cummins, C. H.; Coates, R. M. *J. Org. Chem.* **1983**, *48*, 2070–2076.
(2) Harada, K. In "The Chemistry of the Carbon–Nitrogen Double Bond"; Patai, S., Ed.; Interscience: New York, 1970; pp 276–293.
(3) Lednicer, D.; Mitscher, L. A. "The Organic Chemistry of Drug Synthesis"; Wiley: New York, 1977; pp 62–83.
(4) Calder, A.; Forrester, A. R.; Hepburn, S. P. *Org. Synth.* **1972**, *52*, 77–82.
(5) Torssell, K.; Zeuthen, O. *Acta. Chem. Scand., Ser. B* **1978**, *B32*, 118–124.

0022-3263/86/1951-1383$01.50/0 

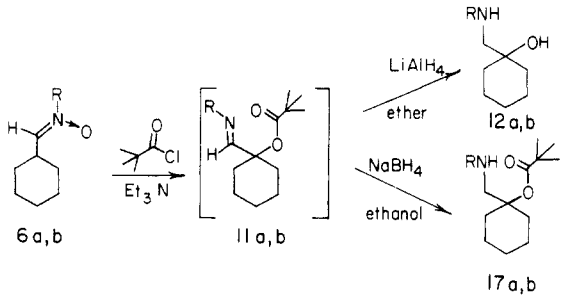
**Table I. *N*-Alkylamino Alcohols Prepared from Nitrones via Acylation–Rearrangement[a] and Subsequent Hydride Reduction[b]**

| nitrone | compd | N-substituent | amino alcohol | compd | yield, %[c] |
|---|---|---|---|---|---|
|  | **6a** | *t*-butyl |  | **12a** | 63 |
| | **6b** | cyclohexyl | | **12b** | 70 |
| | **6c** | methyl | | **12c** | 38[d] |
|  | **7a** | *t*-butyl |  | **13a** | 61 |
| | **7b** | cyclohexyl | | **13b** | 45 |
|  | **8a** | *t*-butyl |  | **14a** | 63 |
| | **8b** | cyclohexyl | | **14b** | 61 |
|  | **9a** | *t*-butyl |  | **15a** | 63 |
| | **9b** | cyclohexyl | | **15b** | 50 |
|  | **10a** | *t*-butyl |  | **16a** | 87 |
| | **10b** | cyclohexyl | | **16b** | 69 |

[a] 1 equiv of pivaloyl chloride and 1 equiv of triethylamine in ether at 0 → 25 °C for 2 h. [b] $LiAlH_4$ in ether at 25 °C. [c] Overall yields based on nitrone. [d] The *N*-methylamino alcohol was prepared in three steps: (1) 20 equiv of methyl chloroformate and 2 equiv of triethylamine in ether at 25 °C for 25 h; (2) 3 equiv of $NaBH_4$ in absolute ethanol at 25 °C for 1 h, which afforded oxazolidine **17c**; (3) hydrolysis with 4 equiv of KOH in absolute ethanol at reflux for 2 h.

in aqueous ethanol containing 1.16 equiv of sodium acetate at room temperature.[6] The latter six nitrones were obtained as crystalline, hygroscopic solids.

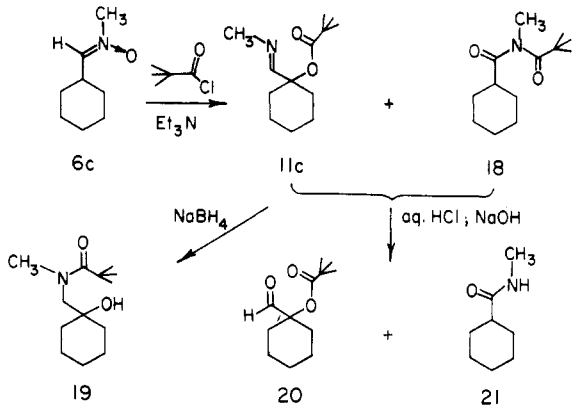
Acylation–rearrangement of the *N*-*tert*-butyl and *N*-cyclohexyl nitrones **6a,b–10a,b** were conducted with 1 equiv of pivaloyl chloride and 1 equiv of triethylamine in ether at 0–25 °C for 2 h. Although some of α-pivaloyloxy imines were previously purified by distillation,[1] in the present work the unpurified imine products were usually reduced directly with about 3 mol equiv of lithium aluminum hydride in ether at 0–25 °C for 3 h. The *N*-alkylamino alcohols **12a,b–16a,b** were obtained in 45–87% overall yield (Table I). The two-step reaction sequence is illustrated with the nitrones of cyclohexanecarboxaldehyde (**6a,b** → **11a,b** → **12a,b**).




Reduction of the α-pivaloyloxy imines **11a** and **11b** with sodium borohydride in ethanol afforded *N*-*tert*-butyl- and *N*-cyclohexylamino pivalates **17a** (62%) and **17b** (85%). The amino esters proved to be stable to Kugelrohr distillation at 110–130 °C, and attempts to effect thermal or base-catalyzed rearrangement of **17a** to the isomeric hydroxy amide were unsuccessful. Evidently O → N migration of the pivaloyl group is inhibited by steric interactions with the *N*-*tert*-butyl or *N*-cyclohexyl substituents. It is not clear whether the usually facile O → N rearrangement is simply kinetically slow or whether the equilibrium actually lies on the side of the amino esters **17a** and **17b** owing to steric hindrance.

(6) Paulsen, H.; Budzis, M. *Chem. Ber.* **1974**, *107*, 1998–2008.

A side reaction was discovered when *N*-methyl nitrone **6c** was subjected to the usual acylation–rearrangement conditions. Thus, reaction of **6c** with pivaloyl chloride in the presence of 1 equiv of triethylamine afforded a 3:1–2 mixture (83%) of the expected α-pivaloyl imine **11c** and *N*-methyl imide **18** after Kugelrohr distillation at 85 °C.[7] Although the imide byproduct was not separated from the mixture, its structure can be assigned on the basis of IR and $^1H$ NMR spectral data, hydrolysis results, and an independent synthesis.




Hydrolysis of a mixture of **11c** and **18** first with hydrochloric acid in aqueous ethanol and then with sodium hydroxide in the same solvent at room temperature gave a mixture of α-pivaloyloxy aldehyde **20** and *N*-methylcyclohexanecarboxamide (**21**).[8] The IR and $^1H$ NMR spectral characteristics of the mixture match those of in-

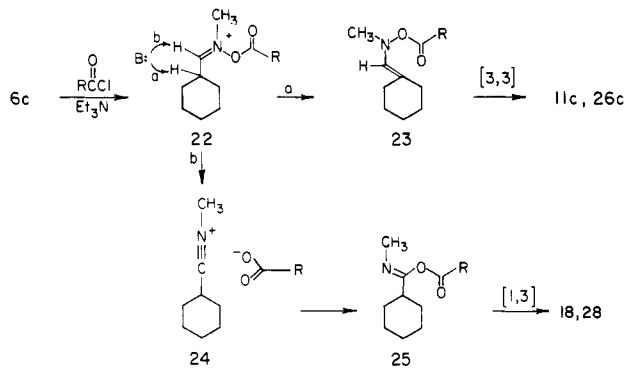
(7) The ratio of **11c** to **18** varied from 3:1 to 0.7:1 in five runs conducted ostensibly in the same manner. The factors responsible for the variability in the product ratio are not clear at this time.

(8) *N*-Methylcyclohexanecarboxamide (**21**) was isolated in good yield (along with **19**) from reduction of the mixture of **11c** and **18** with sodium borohydride in ethanol (see following paragraph in the text) and from hydrolysis of **18** (synthesized from **21**) with aqueous acid. The predominant hydrolysis of this unsymmetrical imide at the more hindered carbonyl group is surprising. A plausible explanation might be that the hydrolysis is slower than reversible N ⇄ O acyl rearrangement to the *O*-acyl imidate **25** (R = *t*-Bu), which then undergoes rapid regioselective hydrolysis to **21**.

dependently prepared samples of **20**[1] and **21**. Reaction of **21** with pivaloyl chloride and triethylamine in ether provided an authentic sample of imide **18** (contaminated with 14% of unreacted **21**). The possibility that the byproduct might be the isomeric *O*-acyl imidate **25** is excluded by consideration of IR data. The C=O and C=N stretching frequencies of *O*-acyl imidates appear in the ranges of 1740–1755 and 1675–1690 $cm^{-1}$, respectively, whereas imides display two carbonyl absorptions at 1685–1710 and 1655–1690 $cm^{-1}$.[9a] Imide **18** exhibits a carbonyl peak at 1680 $cm^{-1}$, a shoulder at 1695 $cm^{-1}$, and no absorption in the 1740–1755-$cm^{-1}$ region.

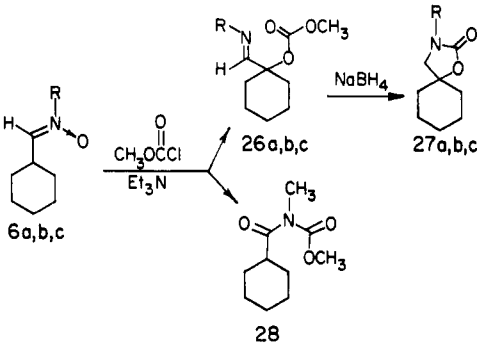
Reduction of the mixture of **11c** and **18** with lithium aluminum hydride gave a chromatographically inseparable mixture of amino alcohols presumed to be the [(*N*-methylamino)- and [(*N*-methyl-*N*-neopentylamino)-methyl]cyclohexanols. Reduction of the mixture with sodium borohydride afforded pivalamido alcohol **19**, which was separated from **21** by chromatography. Evidently O → N migration of the pivaloyl group occurred spontaneously under the reduction conditions. The facility of this acyl transfer reaction contrasts sharply with the stability of amino pivalates **17a** and **17b**.

It seems reasonable to suppose that the mixture of **11c** and **18** arises by partioning of the O-acyl nitrone **22** between *N*-vinyl-*O*-acylhydroxylamine **23** and a nitrilium carboxylate ion pair (**24**). Collapse of the ion pair to *O*-acyl imidate **25** followed by a well-precedented O → N acyl rearrangement[9] gives rise to *N*-methyl imide **18**. The

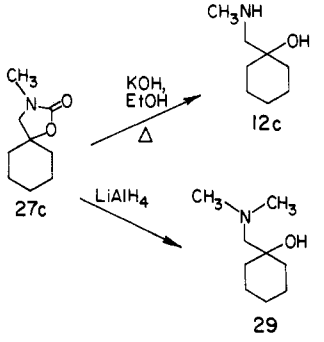



rearrangement of aldonitrones to amides in the presence of various acids and electrophilic reagents including acetic anhydride, acetyl chloride, and benzoyl chloride is well-known.[10,11] Although several different mechanisms have been postulated for this transformation,[11a,c,12] those involving acylating agents as catalyst have in common an N → C acyloxy rearrangement analogous to **22** → **25**. The apparent absence of imide byproducts in the acylation–rearrangements of *N*-*tert*-butyl and *N*-cyclohexyl nitrones is attributable to steric hindrance by the bulky substituents on nitrogen, impeding attack of triethylamine at the imine carbon of intermediate **22**.

The acylation–rearrangement of nitrones **6a–c** with methyl chloroformate proved to be much slower than those performed with acid chlorides. However, good yields of the unpurified imino carbonates **26a** (86%) and **26b** (82%) were obtained when the reaction was conducted with 20 equiv of methyl chloroformate for 24 h. The *N*-methyl nitrone **6c** afforded a 3:1 mixture (77%) of the imino carbonate **26c** and a compound presumed to be *N*-methyl imide **28**.




Reduction of imino carbonates **26a**, **26b**, and **26c** with sodium borohydride in ethanol afforded spiro *N*-alkyloxazolidinones **27a** (66%), **27b** (51%), and **27c** (66%) after purification by crystallization or chromatography. Hydrolysis of **27c** with potassium hydroxide in ethanol at reflux for 2 h gave *N*-methylamino alcohol **12c**, which was not accessible by reduction of **11c** with lithium aluminum hydride owing to facile O → N migration of the pivaloyl group. Reduction of **27c** with lithium aluminum hydride provided *N*,*N*-dimethylamino alcohol **29** in 72% yield.




Vicinal amino alcohols have previously been prepared by reduction of α-amino carbonyl compounds,[13] cyanohydrins, azido alcohols, and nitro alcohols, by aminolysis of epoxides, by oxyamination of olefins with osmium imines,[14] by oxidative cyclization of allylic carbamates,[15] and by hydrolysis of 2-oxazolidinones.[16] 2-Oxazolidinones have been prepared by reaction of 1,2-amino alcohols with phosgene or phosgene equivalents.[17] The two-step sequence of acylation–rearrangement of nitrones followed by hydride reduction (e.g., **6a,b** → **11a,b** → **12a,b**) or the three-step alternative involving carboxylation–rearrangement with methyl chloroformate, sodium borohydride reduction, and hydrolysis (**6c** → **26c** → **27c** → **12c**) should provide a useful complement to these known methods.

(9) (a) Curtin, D. Y.; Miller, L. A. *Tetrahedron Lett.* **1965**, 1869–1876. (b) McCarty, C. G.; Garner, L. A. In "The Chemistry of Functional Groups: The Chemistry of Amidines and Imidates"; Patai, S., Ed.; Interscience: New York, 1975; pp 220–229.

(10) (a) Beckmann, E. *Chem. Ber.* **1890**, *23*, 3331–3341. (b) Beckmann, E. *Chem. Ber.* **1893**, *26*, 2272–2285. (c) Beckmann, E. *Ann. Chem.* **1909**, *365*, 201–214.

(11) (a) Krohnke, F. *Ann. Chem.* **1957**, *604*, 203–206. (b) "The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives": Breuer, E. In "The Chemistry of Functional Groups"; Patai, S., Ed.; Interscience: New York, 1982; pp 484–486. (c) Lamchen, M. In "Mechanisms of Molecular Migrations"; Thyagarajan, B. S., Ed.; Interscience: New York, 1968; Vol. 1, pp 36–43.

(12) (a) Umesawa, B. *Chem. Pharm. Bull.* **1960**, *8*, 698–705. (b) Umesawa, B. *Chem. Pharm. Bull.* **1960**, *8*, 967–975. (c) Tamagaki, S.; Kozuka, S.; Oae, S. *Tetrahedron* **1970**, *26*, 1795–1804. (d) Tamagaki, S.; Oae, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2851–2852.

(13) Tramontini, M. *Synthesis* **1982**, 605–644.

(14) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628–2638 and references cited therein.

(15) (a) Minami, N.; Ko, S. S.; Kishi, Y. *J. Am. Chem. Soc.* **1982**, *104*, 1109–1111. (b) Cardillo, G.; Orena, M.; Porzi, G.; Sandri, S. *J. Chem. Soc., Chem. Commun.* **1982**, *1308*–1309. (c) Pauls, H. W.; Fraser-Reid, B. *J. Org. Chem.* **1983**, *48*, 1392–1393. (d) Knapp, S.; Patel, D. V. *J. Am. Chem. Soc.* **1983**, *105*, 6985–6986.

(16) Adams, R.; Segur, J. B. *J. Am. Chem. Soc.* **1923**, *45*, 785–790.

(17) Dyen, M. E.; Swern, D. *Chem. Rev.* **1967**, *67*, 197–246.

## Experimental Section

**General Aspects.** Melting points were determined on a Buchi melting point apparatus and are uncorrected. IR spectra were determined with either a Perkin-Elmer Model 137 spectrophotometer or a Nicolet Model 7199 Fourier transform (FT) IR spectrophotometer. $^1$H NMR spectra were recorded on a Varian Associates EM-390 (90 Mz, continuous wave mode) spectrometer, with an internal lock on tetramethylsilane. Elemental analyses were performed at the University of Illinois Microanalytical Laboratory by J. Nemeth and Associates. Analytical gas chromatography was carried out with a Varian Model 3700 gas chromatograph using 3% OV-17 on 100/200 mesh Chromosorb Q, packed in a 1.8 m × 6.4 mm column.

Silica gel chromatographic purifications were conducted by flash chromatography[18] with Woelm 32–63-$\mu$m silica packed in glass columns. The weight of the silica was approximately 100 times the weight of the material. Thin-layer chromatography was performed on Sybron/Brinkman precoated, plastic-backed plates, coated with a 0.25-mm layer of silica gel impregnated with $UV_{254}$ fluorescent indicator. Thin-layer chromatography was used to determine the appropriate solvent system for flash chromatographic separations, which was 10–30% ethyl acetate in hexane unless otherwise specified. Chromatography solvents were distilled before use.

All air- or water-sensitive reactions were carried out in a nitrogen atmosphere using standard techniques for the exclusion of air and moisture. Glassware used for water-sensitive reactions was dried in a circulating oven at 130 °C for at least 1 h. Tetrahydrofuran was purified by distillation from sodium–benzophenone ketyl. All other solvents were reagent grade unless described otherwise.

***N*-*tert*-Butylhydroxylamine** was prepared according to the method of Calder, Forrester, and Hepburn[15] in similar yields, with one modification. The solution of 2-methyl-2-nitropropane in 250 mL of diethyl ether obtained in the first step of the procedure was not fractionally distilled to remove the solvent but was used directly in the aluminum–amalgam reduction. The volume of ether which was initially placed in the reaction vessel prior to the reduction was correspondingly decreased from 1.5 to 1.25 L, to maintain a constant total reaction volume. The hydroxylamine was dried under reduced pressure and stored in a desiccator or under nitrogen in a freezer for up to 3 months without appreciable decomposition.

***N*-*tert*-Butyl nitrones 6a–10a** of cyclohexanecarboxaldehyde (**1**), *n*-butyraldehyde (**2**), isobutyraldehyde (**3**), 3-cyclohexenecarboxaldehyde (**4**), and 2-phenylpropionaldehyde (**5**) were prepared according to the procedure of Torsell and Zuethen[5] as previously reported.[1] Solutions of *N*-*tert*-butylhydroxylamine (56.3 mmol) and the aldehydes (71.0 mmol) in 20 mL of dichloromethane in which anhydrous sodium sulfate was suspended were allowed to stir at room temperature for 19 h. The physical and spectral properties of the five nitrones agree with those reported previously.[1,5]

***N*-Cyclohexyl and *N*-Methyl Nitrones 6b–10b and 6c.** The nitrones were prepared by a modification of the procedure of Paulsen and Budzis.[6] A solution of the appropriate aldehyde (12.8 mmol), *N*-cyclohexylhydroxylamine hydrochloride or *N*-methylhydroxylamine hydrochloride (12.0 mmol), and anhydrous sodium acetate (14.8 mmol) in 10 mL of water and 15 mL of ethyl alcohol was stirred at room temperature for 24 h. The solution was extracted with five 20-mL portions of chloroform. The chloroform extracts were combined, washed with two 15-mL portions of saturated aqueous sodium bicarbonate, and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by purification of the residue by distillation or recrystallization, afforded the nitrones **6b–10b** and **6c**.

***N*-(Cyclohexylmethylidene)cyclohexanamine *N*-oxide (6b)** was obtained as a white solid after purification by recrystallization from hexane: yield, 1.69 g (67%); mp 117–118 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.87–2.20 (m, 20 H, $(CH_2)_5$, $(CH_2)_5$), 2.97 (m, 1 H, HCC=N), 3.58 (m, 1 H, CHN=C), 6.46 (d, 1 H, $J$ = 7.5 Hz, HC=N). Anal. Calcd for $C_{13}H_{23}NO$: C, 74.59; H, 11.07; N, 6.69. Found: C, 74.79; H, 11.05; N, 6.73.

***N*-Butylidenecyclohexanamine *N*-oxide (7b)** was obtained as a white, low-melting solid after purification by Kugelrohr distillation at 106 °C (0.6 mm): yield, 1.55 g (76%); mp 101–103 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.93 (t, 3 H, $J$ = 6.5 Hz, $CH_3$), 1.07–2.17 (m, 12 H, $(CH_2)_5$, $CH_2CH_2CH_3$), 2.47 (m, 2 H, $CH_2CH_2CH_3$), 3.63 (m, 1 H, CHN=C), 6.70 (t, 1 H, $J$ = 6 Hz, HC=N). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 70.82; H, 11.56; N, 8.20.

***N*-(2-Methylpropylidene)cyclohexanamine *N*-oxide (8b)** was obtained as a white solid after purification by Kugelrohr distillation at 110 °C (0.55 mm): Yield, 1.51 g (74%); mp 95.5–98.0 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.76–2.10 (m, 10 H, $(CH_2)_5$), 1.07 (d, 6 H, $J$ = 7 Hz, $CN(CH_3)_2$), 3.17 (octet, 1 H, $J$ = 7 Hz, CHN=C), 3.57 (m, 1 H, CHN=) 6.48 (d, 1 H, $J$ = 7 H, HC=N). Anal. Calcd for $C_{10}H_{19}NO$: C, 70.96; H, 11.31; N, 8.27. Found: C, 70.88; H, 11.20; N, 8.08.

***N*-(Cyclohex-3-enylmethylidene)cyclohexanamine *N*-oxide (9b)** was obtained as a white solid after recrystalization from 6% dichloromethane in hexane: yield, 1.48 g (59%); mp 104–106 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.83–2.97 (m, 16 H, $(CH_2)_5$, $(CH_2)_2$, $CH_2$) 3.30 (m, 1 H, CHC=N), 3.63 (m, 1 H, CHN=C), 5.62–5.90 (m, 2 H, CH=CH), 6.62 (d, 1 H, $J$ = 7.5 Hz, HC=N). Anal. Calcd for $C_{13}H_{21}NO$: C, 75.32; H, 10.21; N, 6.76. Found: C, 75.70; H, 10.19; N, 6.62.

***N*-(2-Phenylpropylidene)cyclohexanamine *N*-oxide (10b)** was obtained as a white solid after purification by recrystallization from hexane: yield, 2.04 g (73%); mp 91–92 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.90–2.27 (m, 10 H, $(CH_2)_5$), 1.45 (d, 3 H, $J$ = 7 Hz, $CH_3$), 3.63 (m, 1 H, CHN=C), 4.40 (quintet, 1 H, $J$ = 7 Hz, CHC=N), 6.78 (d, 1 H, $J$ = 7 Hz, HC=N), 7.03–7.57 (m, 5 H, Ar H). Anal. Calcd for $C_{15}H_{21}NO$: C, 77.88; H, 9.15; N, 6.05. Found: C, 78.19; H, 9.03; N, 5.89.

***N*-(Cyclohexylmethylidene)methanamine *N*-oxide (6c)** was prepared from 3.00 g (35.9 mmol) of *N*-methylhydroxylamine hydrochloride, 4.32 g (38.5 mmol) of cyclohexanecarboxaldehyde, and 3.72 g (45.3 mmol) of anhydrous sodium acetate as described in the preceding general procedure for the preparation of *N*-methyl and *N*-cyclohexyl nitrones and was purified by recrystallization from hexane: yield, 4.20 g (83%); mp 47.5–49.5 °C; $^1$H NMR ($CDCl_3$) $\delta$ 0.80–2.10 (m, 10 H, $(CH_2)_5$), 2.70–3.23 (m, 1 H, CHC=N), 3.67 (s, 3 H, $CH_3$), 6.49 (d, 1 H, $J$ = 6.75 Hz, HC=N).

**General Procedure for Acylation–Rearrangement of *N*-*tert*-Butyl and *N*-Cyclohexyl Nitrones 6a–10a and 6b–10b with Pivaloyl Chloride.**[1] A solution of pivaloyl chloride (3.5 nmol) in 25 mL of anhydrous diethyl ether was stirred and cooled at 0 °C under nitrogen as 0.48 mL (3.5 mmol) of triethylamine was introduced via syringe. A solution of the *N*-*tert*-butyl or *N*-cyclohexyl nitrone (3.5 mmol) in 3.3 mL of anhydrous ether was then added dropwise. The resulting suspension of precipitated triethylamine hydrochloride was allowed to warm to room temperature and stirred for an additional 2 h. Filtration of the precipitate and evaporation of the solvent at reduced pressure on a rotary evaporator afforded the crude $\alpha$-acyloxy imines, which were reduced directly to the amino alcohols in most cases. The preparation and characterization of $\alpha$-pivaloyloxy imines **6a–8a** have been reported previously.[1]

***N*-[(1-((2,2-Dimethylpropanoyl)oxy)cyclohexyl)-methylidene]cyclohexanamine (11b)** was prepared from 0.500 g (2.4 mmol) of nitrone **6b** according to the preceding general procedure for the preparation of $\alpha$-acyloxy imines. Kugelrohr distillation at 115 °C (0.45 mm) removed nonvolatile impurities and afforded imine **11b** as a colorless liquid: yield, 0.653 g (93%); $^1$H NMR ($CDCl_3$) $\delta$ 1.00–2.40 (m, 20 H, $(CH_2)_5$, $(CH_2)_5$), 1.20 (s, 9 H, $C(CH_3)_3$), 2.77–3.13 (m, 1 H, CHN=C), 7.68 (s, 1 H, HC=N).

**General Procedure for Reduction of $\alpha$-Pivaloyloxy Imines to *N*-*tert*-Butyl- and *N*-Cyclohexylamino Alcohols 12a–16a and 12b–16b with Lithium Aluminum Hydride.** A suspension of lithium aluminum hydride (11 mmol, 95% dispersion in mineral oil) in 10 mL of anhydrous diethyl ether was stirred under nitrogen at 0 °C. A solution of the $\alpha$-acyloxy imine (unpurified unless otherwise stated) obtained from the nitrone (3.5 mmol) in 10 mL of diethyl ether was added dropwise. After the addition was complete, the suspension was allowed to warm to room temperature and was stirred for an additional 3 h. The suspension was

(18) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923–2925.

cooled to 0 °C, and 3 mL of isopropyl alcohol was added. After sequential addition of 0.42 mL of water, 0.42 mL of 15% aqueous sodium hydroxide, and 1.26 mL of water, the suspension was filtered, the solids were washed well with diethyl ether, and the ether portions were combined. The ether solution was extracted with four 20-mL portions of 10% aqueous hydrochloric acid, and the aqueous extracts were combined and made basic to pH paper with 15% aqueous sodium hydroxide. The aqueous solution was extracted with four 40-mL portions of dichloromethane, and the dichloromethane extracts were combined and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by purification of the residue by Kugelrohr distillation afforded amino alcohols **12a–16a** and **12b–16b**.

**1-[((1,1-Dimethylethyl)amino)methyl]-1-cyclohexanol (12a)** was prepared from 0.50 g (2.7 mmol) of nitrone **6a**. Purification by Kugelrohr distillation at 95 °C (0.75 mm) gave 0.32 g (63%). The IR and $^1H$ NMR spectra are coincident with those obtained earlier.[1]

**1-[(1,1-Dimethylethyl)amino]-2-butanol (13a)** was prepared from 0.50 g (3.5 mmol) of nitrone **7a** and purified by Kugelrohr distillation at 90 °C (0.6 mm): yield, 0.31 g (61%); IR (neat) 3300 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.80–1.03 (t, 3 H, $J$ = 6 Hz, $CH_2CH_3$), 1.10 (s, 9 H, $C(CH_3)_3$), 1.27–1.60 (m, 2 H, $CH_2CH_3$), 2.23–2.77 (m, 2 H, $CH_2N$), 3.23–3.53 (m, 1 H, CHOH).

**1-[(1,1-Dimethylethyl)amino]-2-methyl-2-propanol (14a)** was prepared from 0.50 g (3.5 mmol) of nitrone **8a** and purified by Kugelrohr distillation at 75 °C (0.3 mm); yield, 0.32 g (63%); IR (neat) 3300 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 1.10 (s, 9 H, $C(CH_3)_3$), 1.15 (s, 6 H, $C(CH_3)_2$), 1.30–2.3 (m, 2 H, NH, OH), 2.47 (s, 2 H, $CH_2N$). Anal. Calcd for $C_8H_{19}NO$: C, 66.16; H, 13.19; N, 9.64. Found: C, 66.42; H, 12.91; N, 9.87.

**1-[((1,1-Dimethylethyl)amino)methyl]-1-cyclohex-3-enol (15a)** was prepared from 0.50 g (2.8 mmol) of nitrone **9a** and purified by Kugelrohr distillation at 90 °C (0.3 mm): yield, 0.32 g (63%); IR (neat) 3400 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.97–2.32 (m, 6 H, ring $CH_2$), 1.02 (s, 9 H, $C(CH_3)_3$), 2.42 (s, 2 H, $CH_2N$), 5.38–5.77 (m, 2 H, CH=CH).

**α-[((1,1-Dimethylethyl)amino)methyl]-α-methylbenzenemethanol (16a)** was prepared from 0.34 g (1.7 mmol) of nitrone **10a** and purified by Kugelrohr distillation at 130 °C (0.2 mm): yield, 0.30 g (87%). The spectral data obtained for this compound are in agreement with the values reported in the literature.[13]

**1-[(Cyclohexylamino)methyl]cyclohexanol (12b)** was prepared from 0.50 g (2.4 mmol) of nitrone **7b**. In this case the intermediate imine was purified by Kugelrohr distillation at 110 °C (0.4 mm). Kugelrohr distillation at 120 °C (0.2 mm) afforded amino alcohol **12b**: yield, 0.35 g (70%); IR (neat) 3350 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.50–2.30 (m, 20 H, $(CH_2)_5$, $(CH_2)_5$), 2.30–2.70 (m, 2 H, CHN, NH), 2.53 (s, 2 H, $CH_2N$).

**1-(Cyclohexylamino)-2-butanol (13b)** was prepared from 0.50 g (3.0 mmol) of nitrone **7b** and purified by Kugelrohr distillation at 100 °C (0.8 mm): yield, 0.23 g (45%); IR (neat) 3375 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.90–2.10 (m, 10 H, $(CH_2)_5$), 0.93 (t, 3 H, $J$ = 6 Hz, $CH_2CH_3$), 2.23–2.60 (m, 2 H, $CH_2CH_3$), 2.60–2.83 (m, 2 H, $CH_2N$), 2.87–3.30 (m, 1 H, CHN), 3.33–3.67 (m, 1 H, CHOH).

**1-(Cyclohexylamino)-2-methyl-2-propanol (14b)** was prepared from 0.50 g (3.0 mmol) of nitrone **8b** and was purified by Kugelrohr distillation at 100 °C (0.25 mm): yield, 0.31 g (61%); IR (neat) 3350 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.80–2.07 (m, 10 H, $(CH_2)_5$), 2.67–2.85 (m, 2 H, CHN, NH), 2.53 (s, 2 H, $CH_2N$). Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.36; N, 8.18. Found: C, 70.26; H, 12.59; N, 8.19.

**1-[(Cyclohexylamino)methyl]-1-cyclohex-3-enol (15b)** was prepared from 0.50 g (2.4 mmol) of nitrone **9b** and purified by Kugelrohr distillation at 110 °C (0.55 mm): yield, 0.25 g (50%); IR (neat) 3010 (vinyl H), 3300 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.73–2.65 (m, 17 H, ring $CH_2$, CHN), 2.57 (s, 2 H, $CH_2N$), 5.40–5.83 (m, 2 H, CH=CH).

**α-[(Cyclohexylamino)methyl]-α-methylbenzenemethanol (16b)** was prepared from 0.500 g (2.16 mmol) of nitrone **10b** and purified by Kugelrohr distillation at 120 °C (0.4 mm): yield, 0.347 g (69%); IR (neat) 3050 (Ar H), 3400 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.75–2.07 (m, 10 H, $(CH_2)_5$), 1.43 (s, 3 H, $CH_3$), 2.15–2.50 (m, 1 H, CHN), 2.67 (d, 1 H, $J$ = 12 Hz, CHHN), 3.07 (d, 1 H, $J$ = 12 Hz, CHHN), 7.03–7.53 (m, 5 H, Ar H). Anal. Calcd for $C_{15}H_{23}NO$: C, 77.21; H, 9.93; N, 6.00. Found: C, 77.16; H, 10.12; N, 6.10.

**General Procedure for the Reduction of α-Pivaloyloxy and α-(Methoxycarbonyl)oxy Imines with Sodium Borohydride.** A suspension of 0.120 g (3.11 mmol) of 98% sodium borohydride in 10 mL of absolute ethyl alcohol was stirred under nitrogen at 0 °C. A solution of 0.250 g (1.04 mmol) of the α-pivaloyloxy or α-(methoxycarbonyl)oxy imine (**11a–c** or **26a–c**) in 5 mL of absolute ethyl alcohol was added dropwise. After the addition was complete, the suspension was allowed to warm to room temperature and stirred for ca. 1 h, at which time the imine was completely consumed, as determined by thin-layer chromatography on silica gel using 30% ethyl acetate in hexane as eluant. The suspension was cooled to 0 °C, and 5 mL of 10 aqueous hydrochloric acid was added carefully. The resulting solution was allowed to warm to room temperature and stirred for an additional 30 min. The solution was made basic to pH paper with 15% aqueous sodium hydroxide and diluted with 25 mL of water. The basic solution was extracted with one 50-mL portion of dichloromethane and two 35-mL portions of dichloromethane. The dichloromethane extracts were then combined and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator followed by purification of the residue by flash chromatography, Kugelrohr distillation, or recrystallization afforded the amino pivalates **17a, b**, hydroxy pivalamide **19**, and oxazolidones **27a–c**.

**1-[((1,1-Dimethylethyl)amino)methyl]cyclohexyl 2,2-dimethylpropanoate (17a)** was prepared by sodium borohydride reduction of 0.250 g (0.935 mmol) of imine **11a** and purified by Kugelrohr distillation at 110 °C (0.4 mm): yield, 0.157 g (62%); mp 36–38 °C; IR (neat) 1715 ($CO_2R$), 3325 $cm^{-1}$ (NH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.70–2.60 (m, 11 H, $(CH_2)_5$, NH), 1.03 (s, 9 H, $C(CH_3)_3$), 1.20 (s, 9 H, $C(CH_3)_3$), 2.90 (s, 2 H, $CH_2N$). Anal. Calcd for $C_{16}H_{31}NO_2$: C, 71.33; H, 11.60; N, 5.20. Found: C, 71.01; H, 11.51; N, 5.05.

**1-[(Cyclohexylamino)methyl]cyclohexyl 2,2-dimethylpropanoate (17b)** was prepared by sodium borohydride reduction of 0.250 g (0.852 mmol) of imine **11b** and purified by Kugelrohr distillation at 130 °C (0.35 mm). The yield was 0.214 g (85%): mp 40–44 °C; IR (neat) 1715 ($CO_2R$), 3380 $cm^{-1}$ (NH, OH); $^1H$ NMR ($CDCl_3$) $\delta$ 0.73–2.70 (m, 22 H, $(CH_2)_5$, $(CH_2)_5$, CHN, NH), 2.95 (s, 2 H, $CH_2N$). Anal. Calcd for $C_{18}H_{33}NO_2$; C, 73.17; H, 11.36; N, 4.74. Found: C, 73.14; H, 11.47; N, 4.75.

***N*-[1-(1-Hydroxycyclohexyl)methyl]-*N*-methyl-1,1-dimethylpropanamide (19)** was prepared by sodium borohydride reduction of 0.300 g (1.33 mmol) of a mixture containing 0.162 g (0.719 mmol) of imine **11c** and 0.138 g (0.613 mmol) of imide **18** (see following procedure). Purification by flash chromatography gave 0.090 g (30%, 55% based on starting imine) of hydroxy amide **19**: mp 71.5–73.5 °C; $^1H$ NMR ($CDCl_3$) $\delta$ 1.00–1.90 (m, 11 H, $(CH_2)_5$, OH), 1.30 (s, 9 H, $C(CH_3)_3$), 3.22 (s, 3 H, $CH_3N$), 3.37 (s, 3 H, $CH_2N$). Anal. Calcd for $C_{13}H_{25}NO_2$: C, 68.68; H, 11.08; N, 6.16. Found: C, 68.77; H, 11.10; N, 5.96. The more polar *N*-methyl amide **21** (80 mg, 92% based on imide **18**) was also isolated from later chromatography fractions. Anal. Calcd for $C_8H_{15}NO$: C, 68.04; H, 10.71; N, 9.92. Found, C, 67.78; H, 10.43; N, 9.68.

***N*-[((1-(2,2-Dimethylpropanoyl)oxy)cyclohexyl)methylidene]methanamide (11c) and *N*-(2,2-Dimethylpropanoyl)-*N*-cyclohexanoylmethanamine (18).** A solution of 0.43 g (3.5 mmol) of pivaloyl chloride in 25 mL of anhydrous diethyl ether was stirred and cooled at 0 °C under nitrogen as 0.49 mL (0.36 g, 3.6 mmol) of triethylamine was introduced via syringe. A solution of 0.50 g (3.5 mmol) of *N*-methyl nitrone **6c** in 10 mL of diethyl ether was then added dropwise. The resulting suspension of precipitated triethylamine hydrochloride was allowed to warm to room temperature and stirred for an additional 12 h. Filtration of the precipitate and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by purification of the residue by Kugelrohr distillation at 85 °C (0.35 mm), afforded 0.660 g (83%) of an approximately 3:1 mixture of imine **11c** and imide **18** as judged from the $^1H$ NMR spectrum of the mixture in chloroform-*d*.[7] The resonances assigned to imine **11c** are as follows: $^1H$ NMR ($CDCl_3$) $\delta$ 1.03–2.30 (m, 10 H, $(CH_2)_5$), 1.27 (s, 9 H, $C(CH_3)_3$), 3.30 (d, 3 H, $J$ = 1.8 Hz, $CH_3$), 7.70 (q, 1 H, $J$ = 1.8 Hz, HC=N). These NMR data are consistent with

those observed for other α-acyloxy imines.[1]

The $^1$H NMR spectrum of the mixture also showed the following peaks attributable to imide **18**: δ 1.32 (s, $C(CH_3)_3$), 3.11 (s, $NCH_3$). These data are in reasonable agreement with those of authentic imide **18** prepared from *N*-methylcyclohexanecarboxamide (**21**) and pivaloyl chloride (see following procedure). The identity of the imide component was confirmed by GC analysis of the mixture obtained from a different run using the following temperature program: 120 °C for 3 min and then increasing at 20 °C/min to 200 °C. The retention times of **11c** and **18** were 2.5 and 6.2 min, respectively. Coinjection with an authentic sample of the imide increased the height of the peak at 6.2 min.

***N*-(2,2-Dimethylpropanoyl)-*N*-methylcyclohexanecarboxamide (18).** A solution of 1.65 g (11.7 mmol) of amide **21** (see following procedure) in 50 mL of anhydrous diethyl ether was stirred under nitrogen at 0 °C as 2.44 mL (1.77 g, 17.5 mmol) of triethylamine was introduced via syringe. A solution of 2.11 g (17.5 mmol) of pivaloyl chloride in 10 mL of diethyl ether was then added dropwise. After the addition was complete, the cooling bath was removed, and stirring was continued for an additional 48 h. The solvent was removed at reduced pressure on a rotary evaporator, and the residue was treated with anhydrous diethyl ether. Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator followed by purification of the residue by fractional distillation afforded, after collection of approximately 0.4 g of a lower boiling forerun, imide **18** as a colorless liquid, contaminated with approximately 14% of amide **21**, as judged by the $^1$H NMR spectrum. The yield was 1.78 g (68%): bp 96–98 °C (0.6 mm); IR (neat) 1680 (C=O), 1695 cm$^{-1}$ (s, C=O); $^1$H NMR ($CDCl_3$) δ 1.03–1.97 (m, 10 H, $(CH_2)_5$), 1.32 (s, 9 H, $C(CH_3)_3$), 2.40–2.73 (m, 1 H, CHC=O), 3.08 (s, 3 H, $CH_3N$).

***N*-Methylcyclohexanecarboxamide (21). A. From Cyclohexanecarbonyl Chloride.** A heterogeneous mixture of 7.94 g of 40% aqueous methylamine (3.18 g, 102 mmol) and 3.61 g (34.1 mmol) of sodium carbonate in 30 mL of water and 30 mL of diethyl ether was stirred under nitrogen at 0 °C. A solution of 5.00 g (34.1 mmol) of cyclohexanecarbonyl chloride in 50 mL of diethyl ether was added dropwise. After the addition was complete, the cooling bath was removed, and stirring was continued for an additional 29 h. The mixture was diluted with 50 mL of water, 50 mL of 15% aqueous sodium hydroxide, and 150 mL of dichloromethane and was shaken. The organic layer was separated, the aqueous layer was extracted with 100 mL of dichloromethane, and the dichloromethane extract was combined with the organic layer and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by recrystallization of the residue from diethyl ether afforded, in two crops, 3.32 g (69%) of amide **21** as a white needle-like solid: mp 112–113 °C; $^1$H NMR ($CDCl_3$) δ 0.98–2.40 (m, 11 H, $(CH_2)_5CH$), 2.75 (d, 3 H, $J$ = 4.5 Hz, $CH_3$), 5.82–6.28 (m, 1 H, NH).

**B. From Hydrolysis of a Mixture of Imine 11c and Imide 18.** A solution of 0.10 g (0.44 mmol) of a 2:3 mixture of imine **11c** and imide **18** in 3 mL of ethyl alcohol was stirred at room temperature under nitrogen as 2 mL of 10% aqueous hydrochloric acid was added. The solution was stirred for 1 h and then made basic to pH paper with 15% aqueous sodium hydroxide, and stirring was continued for an additional 30 min. The solution was extracted with three 15-mL portions of dichloromethane, and the dichloromethane extracts were combined and dried. Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator afforded a colorless oil. The $^1$H NMR spectrum of the product in $CDCl_3$ exhibited the following peaks: δ 1.19 (s, $(CH_3)_3C$), 2.76 (d, $J$ = 5 Hz, $NHCH_3$), 5.80 (br s, NH), 9.54 (s, CHO). Irradiation of the broad singlet at δ 5.80 caused the doublet to collapse to a singlet. These NMR properties indicate that the product was a mixture of the known[1] α-pivaloyloxy aldehyde **20** and *N*-methyl amide **21**.

**C. From Hydrolysis of Imide 18.** A solution of 0.124 g (0.55 mmol) of imide **18** in 3 mL of ethyl alcohol and 2 mL of 10% aqueous hydrochloric acid was stirred at room temperature for 1 h. The solution was then made basic to pH paper with 10% aqueous sodium hydroxide and extracted with three 15-mL portions of dichloromethane. The dichloromethane extracts were combined, dried, and evaporated at reduced pressure. Recrystallization of the residue from diethyl ether afforded 0.053 g (69%) of amide **21** as a white solid. The melting point determined from a mixture of the product and authentic **21** showed no depression from the value reported in part A. The $^1$H NMR spectrum of the product was identical with that of authentic **21**.

The $^1$H NMR spectrum of the residue obtained from evaporation of the mother liquors indicated the presence of additional amide **21** and some starting imide **18**. A small *tert*-butyl peak in the spectrum at δ 1.12 could be taken to indicate the presence of at most a minor amount of *N*-methylpivalamide.

**D. From Sodium Borohydride Reduction of a Mixture of 11c and 18.** See preparation of **19** above.

**Procedures for Acylation–Rearrangement of Cyclohexanecarboxaldehyde Nitrones 6a–c with Methyl Chloroformate.** A solution of methyl chloroformate (54.6 mmol) in 25 mL of anhydrous diethyl ether was stirred and cooled at 0 °C under nitrogen as 0.759 mL (5.46 mmol) of triethylamine was introduced via syringe. A solution of *N*-*tert*-butyl nitrone **6a** (2.73 mmol) in 10 mL of anhydrous diethyl ether was then added dropwise. The resulting suspension of precipitated triethylamine hydrochloride was allowed to warm to room temperature and stirred for an additional 25 h. Filtration of the precipitate and evaporation of the filtrate at reduced pressure on a rotary evaporator afforded the crude α-(methoxycarbonyl)oxy imine **26a**, which was not rigorously purified but was simply evacuated in a Kugelrohr apparatus to remove nonvolatile impurities. The product is assigned the structure of imine **26a** on the basis of the $^1$H NMR spectrum.

Imine **26b** was prepared as described above from nitrone **6b**. Imine **26c** was prepared as described above, with the exception that fewer equivalents of methyl chloroformate and triethylamine were employed. A solution of methyl chloroformate (10.6 mmol) in 25 mL of anhydrous diethyl ether was used, and a solution of *N*-methyl nitrone **6a** (3.5 mmol) in 10 mL of anhydrous diethyl ether was added after injection of 0.59 mL (4.2 mmol) of triethylamine.

***N*-[(1-((Methoxycarbonyl)oxy)cyclohexyl)methylidene]-1,1-dimethylethanamine (26a)**: yield of unpurified product, 0.564 g (86%); $^1$H NMR ($CDCl_3$) δ 0.77–2.33 (m, 10 H, $(CH_2)_5$), 1.15 (s, 9 H, $C(CH_3)_3$), 3.68 (s, 3 H, $OCH_3$), 7.63 (s, 1 H, HC=N).

***N*-[(1-((Methoxycarbonyl)oxy)cyclohexyl)methylidene]-cyclohexanamine (26b)**: yield of unpurified product, 0.263 g (82%): $^1$H NMR ($CDCl_3$) δ 0.90–2.70 (m, 20 H, $(CH_2)_5$, $(CH_2)_5$), 2.83–3.33 (m, 1 H, CHN=C), 3.70 (s, 3 H, $OCH_3$), 7.73 (s, 1 H, HC=N).

***N*-[(1-((Methoxycarbonyl)oxy)cyclohexyl)methylidene]-methanamine (26c)**: yield of unpurified product, 0.546 g (77%); $^1$H NMR ($CDCl_3$) δ 0.83–2.50 (m, 10 H, $(CH_2)_5$), 3.32 (d, 3 H, $J$ = 1.5 Hz, $CH_3N$=C), 3.73 (s, 3 H, $OCH_3$) 7.73 (q, 1 H, $J$ = 1.5 Hz, HC=N).

The product of this reaction was contaminated by approximately 25% of another compound, which is assigned the structure of isomeric imide **28** on the basis of the following absorptions in the $^1$H NMR spectrum of the mixture: $^1$H NMR ($CDCl_3$) δ 0.83–2.50 (m, 11 H, $(CH_2)_5$, CH), 3.13 (s, 3 H, $CH_3N$), 3.80 (s, 3 H, $OCH_3$).

**3-(1,1-Dimethylethyl)-1-oxa-3-azaspiro[4.5]decan-2-one (27a)** was prepared from 0.250 g (1.04 mmol) of imine **26a** by the general procedure given above for sodium borohydride reductions. Recrystallization from hexane afforded 0.145 g (66%) of the oxazolidinone: mp 75–79 °C; $^1$H NMR ($CDCl_3$) δ 1.03–2.33 (m, 10 H, $(CH_2)_5$), 1.37 (s, 9 H, $C(CH_3)_3$), 3.25 (s, 2 H, $CH_2N$). Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.21; H, 10.02; N, 6.63. Found: C, 68.43; H, 10.24; N, 6.52.

**3-Cyclohexyl-1-oxa-3-azaspiro[4.5]decan-2-one (27b)** was prepared by sodium borohydride reduction of 0.263 g (0.982 mmol) of imine **26b**. Recrystallization from hexane gave 0.118 g (51%) of oxazolidinone **27b** as a white solid: mp 96.0–98.5 °C; $^1$H NMR ($CDCl_3$) δ 0.80–2.67 (m, 20 H, $(CH_2)_5$, $(CH_2)_5$), 3.13 (s, 2 H, $CH_2N$), 3.40–3.97 (m, 1 H, CHN). Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.75; H, 9.85; N, 5.78.

**3-Methyl-1-oxa-3-azaspiro[4.5]decan-2-one (27c)** was prepared by sodium borohydride reduction of 0.250 g of a mixture containing 0.19 g (0.95 mmol) of imine **26c** and 0.06 g (0.30 mmol) of imide **28**. Purification by flash chromatography using 30% ethyl acetate in hexane as eluant gave 0.140 g (66%, 88% based

on starting imine) of the oxazolidinone **27c**: $^1$H NMR ($CDCl_3$) $\delta$ 1.07–2.27 (m, 10 H, $(CH_2)_5$), 2.87 (s, 3 H, $CH_3N$), 3.25 (s, 2 H, $CH_2N$). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 63.77; H, 8.82; N, 8.01.

**1-[(Methylamino)methyl]cyclohexanol (12c)** was prepared by hydrolysis of oxazolidone **27c** by the method of Adams and Segur.[14] A solution of 0.19 g (3.4 mmol) of potassium hydroxide and 0.143 g (0.844) of **27c** in 0.7 mL of absolute ethanol was heated at reflux under nitrogen for 2 h. After being cooled to room temperature, the suspension was diluted with enough water to dissolve the precipitated inorganic salts. The resulting solution was extracted with four 3-mL portions of dichloromethane, and the dichloromethane extracts were combined and dried. Filtration and evaporation of the solvent at reduced pressure of a rotary evaporator followed by purification of the residue by Kugelrohr distillation at 85 °C (0.6 mm) afforded amino alcohol **12c** as a colorless liquid: yield, 0.091 g (75%); IR (neat) 3300 cm$^{-1}$ (NH, OH); $^1$H NMR ($CDCl_3$) $\delta$ 0.80–2.33 (m, 10 H, $(CH_2)_5$), 2.45 (s, 3 H, $CH_3N$), 2.48 (s, 2 H, $CH_2N$).

**1-[(Dimethylamino)methyl]cyclohexanol (29).** A suspension of 0.060 g (1.50 mmol) of 95% lithium aluminum hydride in 2 mL of anhydrous diethyl ether was stirred under nitrogen at 0 °C. A solution of 0.085 g (0.510 mmol) of oxazolidone **27c** in 1 mL of anhydrous diethyl ether was added dropwise. After the addition was complete, the suspension was allowed to warm to room temperature and stirred for an additional 20 h. The suspension was cooled to 0 °C, and 1 mL of isopropyl alcohol was added. After sequential addition of 0.05 mL of water, 0.05 mL of 15% aqueous sodium hydroxide, and 0.15 mL of water, the suspension was filtered, the solids were washed well with diethyl ether, and the ether portions were combined. The ether solution was extracted with three 10-mL portions of 10% aqueous hydrochloric acid, and the aqueous extracts were combined and made basic to pH paper with 15% aqueous sodium hydroxide. The aqueous solution was extracted with three 20-mL portions of dichloromethane, and the dichloromethane extracts were combined and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by purification of the residue by Kugelrohr distillation at 90 °C (0.7 mm), afforded dimethylamino alcohol **29** as a colorless liquid: yield, 0.0571 g (72%); IR (neat) 3390 cm$^{-1}$ (OH); $^1$H NMR ($CDCl_3$) $\delta$ 0.97–1.90 (m, 10 H, $(CH_2)_5$), 2.28 (s, 2 H, $CH_2N$), 2.37 (s, 6 H, $N(CH_3)_2$), 3.18 (br s, 1 H, OH).

A small portion of amino alcohol **29** was converted to the hydrochloride salt by bubbling anhydrous hydrogen chloride through a diethyl ether solution. The melting point of the hydrochloride was 171–175 °C (lit.[19] mp 172–174 °C).

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# Metal–Ammonia Reduction of Naphthalene at −33 °C: Formation of Oligomeric Compounds

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Naphthalene (**1**) has been reductively protonated in a dry ammonia/cosolvent mixture at −33 °C using Li, Na, K, and Mg. In addition to 1,4-dihydro-, 1,2-dihydro-, and 1,2,3,4-tetrahydronaphthalene (**2–4**, respectively) substantial amounts (20–70%) of oligomeric compounds were formed in the case of Li and Na. The reactions have been followed in time in order to obtain insight into the influence of the metal on the reaction course. The results indicate that the oligomerization proceeds via an anionic reaction mechanism by attack of the naphthalene monoanion onto the olefinic bond of 1,2-dihydronaphthalene.

Recently the formation of dimeric species of tetralin (**4**) was reported when this compound was used as a hydrogen-donating solvent in coal liquefaction.[1,2] This bitetralyl formation is thought to occur via intermediately formed dihydronaphthalene species. In order to get a better mechanistic insight into such dimerization reactions we have now studied the metal–ammonia reduction of naphthalene (**1**) to **4** since dihydronaphthalene species are accepted to play an important role in this reaction (Scheme I).

In the course of the reaction of **1** with alkali metals in ammonia the mono- and dianion of **1** were proved to be formed.[3] The dianion formation proceeds through an

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