fractometer. X-ray powder photographs were taken with a Philips powder X-ray diffractometer. All melting points were recorded with a hot plate device attached to a thermometer and are uncorrected.

Materials. Coumarin and 4-hydroxycoumarin from Aldrich were used after recrystallizing from hot water several times. With the exception of 4-acetoxycoumarin the other four acetoxycoumarins were prepared from the corresponding hydroxycoumarins by refluxing a mixture of the hydroxycoumarin and acetic anhydride for about 4 h and then adding the mixture to crushed ice. Extraction with ether gave the acetoxycoumarins. The rest of the coumarins including 4-acetoxycoumarin listed in Table I were prepared by following the literature methods.[30] These samples were recrystallized from the solvents indicated in Table II several times and were used for photolysis and X-ray work.

Irradiation Techniques. Powdered single crystals of coumarins kept in a petri dish were irradiated with a Hanovia 450-W medium-pressure mercury arc lamp from a distance of about 2 ft. Samples were turned around periodically to provide uniform exposure. Progress of the irradiation was monitored by the variation in melting point and ^{1}H NMR and IR spectra. After complete conversion, the time of which was dependent on the nature of the coumarin, the dimer was separated from the monomer by TLC (silica gel, hexane/benzene). Dimers were identified by their spectral properties (Table IV). The method of identification is discussed in detail in the Discussion.

No change was observed in some of the coumarins (Table I) even after 200 h of irradiation. In the reactive coumarins the yield reached a saturation limit after a particular duration of irradiation. Yield of the dimer with respect to the time of irradiation was measured by taking the ^{1}H NMR of about 10-mg quantities (out of 500-mg) from the irradiated material at various time intervals. As illustrated in Figure 1 in some of the coumarins the induction period was noticed and in the others the dimerization initiated immediately after UV exposure.

Crystal Structure Analyses. Crystallization conditions, analytical results, and salient crystallographic data are provided in Tables II and V. Intensity measurements were carried out with an ENRAF-Nonius CAD-4 diffractometer. Crystals of 4-methoxycoumarin and 4-methyl-6-chlorocoumarin were not of good quality for accurate work. However interests in the work being mainly in the packing of the molecules rather than details of molecular geometry, these crystals were used in their structure determinations. All the structures were solved (7-methoxycoumarin not without difficulty) with the help of direct methods (Multan Program) and refined[31] by full-matrix least-squares analysis by using the program SHELX-76.[32] The positional and anisotropic thermal parameters of all non-hydrogen atoms were refined. Hydrogen atoms were refined with their positional and isotropic parameters only.

Acknowledgment. The University Grants Commission, Government of India, is thanked for financial support. We thank Prof. J. R. Scheffer and Drs. M. Bhadbhade and T. N. Guru Row for useful discussions.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, bond length, and bond angles for the structures discussed in the paper (54 pages). Ordering information is given on any current masthead page.

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Stereospecific Synthesis of Difunctionalized 2,5-Disubstituted *cis*-2,5-Dimethylpyrrolidine (Azethoxyl) Nitroxides by Oxidative Cleavage of Protected 8-Azabicyclo[3.2.1]octane Precursors

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Received October 18, 1984

Dimethylnortropinone nitroxide **6** was converted into bicyclic ketones **8–10**. Rearrangement of the corresponding oxime derivatives **14** and **16** led, respectively, to lactams **18** and **19**. Hydrolysis of **19** with concomitant oxidation gave the *cis*-azethoxyl nitroxide amino acid **20**. Alternatively, reaction of **8** and **10** with BuLi followed by dehydration and ozonolysis of the resulting alkene mixture gave, respectively, cis-substituted pyrrolidines **26** and **29**. From **29** the (somewhat unstable) *cis*-azethoxyl nitroxide diols **32** were prepared. A third method of cleavage of the bicyclic ring system was established by the route **10** → **35** → **36** → **37**. From **37** difunctionalized *cis*-azethoxyl nitroxides **40** and **41** were prepared.

Stereochemically homogeneous difunctionalized azethoxyl nitroxide spin labels[1] are of interest as potential cross-linking agents, as spin labels for saturation transfer electron paramagnetic resonance (STEPR) studies of macromolecular motion,[2] and as possible contrast enhancing agents for whole-body nuclear magnetic resonance imaging applications.[3] We have recently described the stereoselective synthesis of a series of trans 2,5-difunctionalized pyrrolidine (azethoxyl) nitroxides.[4] The key reaction was the addition of a Grignard reagent to a 2,5,5-trisubstituted pyrroline nitrone followed by oxidation (**1** → **2**). We now report a novel synthetic entry into the cis series of azethoxyl nitroxides through oxidative cleavage of N-oxygenated 8-azabicyclo[3.2.1]octane precursors, as shown systematically by **3** → **4**.

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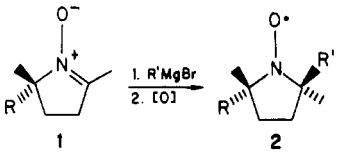


1 2

3 4

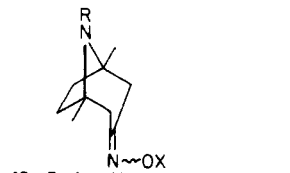
Results and Discussion

Dimethylnortropinone nitroxide **6**, prepared by Rassat and Ronzaud,[5] served as the starting point. We were able to improve on the synthesis of **6** by isolation of the bicyclic

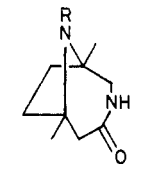
5, R = H
6, R = O•
7, R = OH
8, R = OAc
9, R = $OCOC(CH_3)_3$
10, R = $OSi(CH_3)_2C(CH_3)_3$
11, R = Ac

amine precursor **5** as the oxalate salt and the use of sodium tungstate as catalyst for the hydrogen peroxide oxidation of **5**, leading to **6**. Nitroxide **6** underwent smooth reduction to hydroxy amine **7** upon catalytic hydrogenation over Pd/C. The hydroxy group of **7** was protected by reaction with either acetyl chloride, pivaloyl chloride, or *tert*-butyldimethylsilyl chloride to give, respectively, bicyclic ketones **8**, **9**, and **10**.

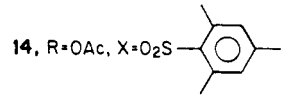
Our first objective was a bicyclic lactam that could afford *cis*-azethoxyl nitroxide amino acid **20** by hydrolysis followed by oxidation. Model experiments with the *N*-acetyl ketone **11** proceeded well. Thus, **11** was converted into its oxime **12**, the *O*-tosyl derivative **13** of which readily gave



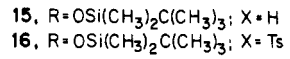
12, R = Ac; X = H
13, R = Ac; X = Ts



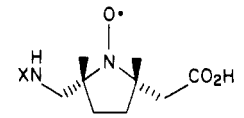
17, R = Ac
18, R = OAc
19, R = $OSi(CH_3)_2C(CH_3)_3$



14, R = OAc, X = O_2S—



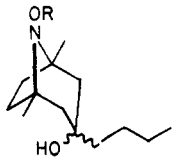
15, R = $OSi(CH_3)_2C(CH_3)_3$; X = H
16, R = $OSi(CH_3)_2C(CH_3)_3$; X = Ts



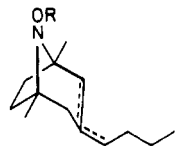
20, X = H
21, X = PhCO

lactam **17** by a Beckmann rearrangement. Efforts to duplicate this pathway starting with *N*-acetoxy ketone **8** failed when complex mixtures were obtained by reaction of **8** with hydroxylamine, undoubtedly due to a competing reaction of the *N*-acetoxy group. However, reaction of **8** with *O*-(mesitylsulfonyl)hydroxylamine[6] afforded (mesitylsulfonyl)oxime **14**, and this substance underwent rearrangement[7] to *N*-acetoxy lactam **18**. The most convenient route to a bicyclic lactam, however, was by conversion of bicyclic silyloxy derivative **10** into oxime **15**, tosylation to give **16**, and rearrangement of the latter intermediate to give lactam **19**. Removal of the silyl protecting group, ring cleavage to the amino acid, and oxidation of the hydroxylamine to the nitroxide were all achieved on heating lactam **19** in methanolic potassium hydroxide under air, producing crystalline nitroxide amino acid **20**. Alternatively, the hydrolysis reaction could be quenched with excess benzoyl chloride, leading to benzamide nitroxide carboxylic acid **21**.

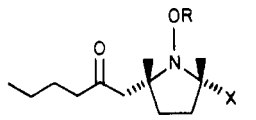
Our next objective was to explore possible routes to longer chain *cis*-azethoxyl nitroxides beginning with one or the other of the bicyclic intermediates. Thus, acetoxy derivative **8** reacted selectively at the ketone group with butyllithium, affording alcohol **22**. Dehydration of **22** was



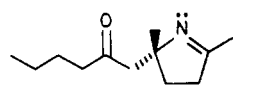
22, R = Ac
23, R = $Si(CH_3)_2C(CH_3)_3$



24, R = Ac
25, R = $Si(CH_3)_2C(CH_3)_3$



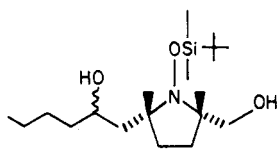
26, R = Ac; X = CHO
27, R = Ac; X = CO_2H
28, R = Ac; X = CO_2Me
29, R = $Si(CH_3)_2C(CH_3)_3$; X = CHO



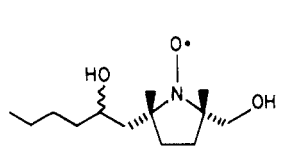
30

effected in good yield by treatment with thionyl chloride in pyridine. A mixture of alkenes **24** was obtained, which was immediately ozonized to give aldehyde **26**. Jones oxidation gave acid **27**, an unstable substance which appeared to suffer decarboxylation with concomitant elimination of acetic acid to give a material tentatively identified as imine **30**. However, immediate esterification of **27** with diazomethane afforded the stable ester **28**.

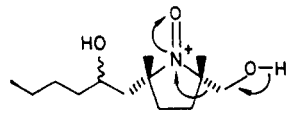
Owing to difficulties in preparing nitroxides derived from **28** by selective hydrolysis approaches, we examined a partially parallel series of reactions beginning with silyl-protected ketone **10**. Thus, alcohol **23**, alkene mixture **25**, and aldehyde **29** were prepared in good yield. With the aim of avoiding the decarboxylation problems associated with **27**, aldehyde **29** was reduced with excess sodium borohydride, affording a separable mixture of diastereomeric alcohols **31**. Cleavage of the silyl group fol-



31a, b



32a, b



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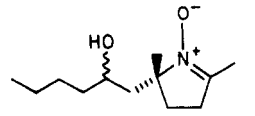


34

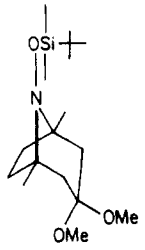
(5) Rassat, A.; Ronzaud, J. *Tetrahedron* **1976**, 239–244.

(6) Krause, J. G. *Synthesis* **1972**, 140.

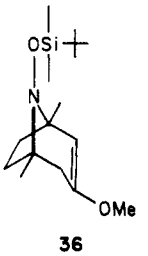
(7) Tamura, Y.; Fujiwara, H.; Sumoto, K.; Ikeda, M.; Kita, Y. *Synthesis* **1973**, 215–216.

lowed by air oxidation gave nitroxides **32**. Interestingly, these nitroxides were not stable, undergoing conversion to a mixture of diamagnetic products in which nitrone **34** appeared to predominate (by NMR). Possibly, **32** underwent oxidation in air to oxoammonium ion **33**, which subsequently lost formaldehyde to give **34**.

A third method was developed for the cleavage of the bicyclic ring system of silyl ketone **10**, leading to difunctionalized pyrrolidine nitroxides. Thus, reaction of **10** with trimethyl orthoformate gave ketal **35**, which readily lost



35



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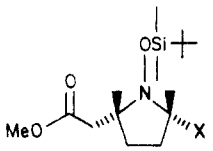
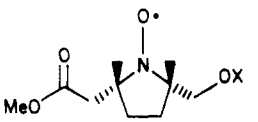


37, X = CHO
38, X = CH_2OH
39, X = CH_2OAc



40, X = Ac
41, X = H

methanol under acid catalysis to give enol ether **36**. Ozonolysis of **36** followed by a reductive workup afforded the ring-cleaved ester aldehyde **37**. Reduction with sodium borohydride gave alcohol **38**, which was acetylated to give diester **39**. Selective cleavage of the siloxy group of both **38** and **39** was accomplished with aqueous HF in acetonitrile to give the corresponding *N*-hydroxy intermediates, which were subsequently oxidized to give, respectively, nitroxide diester **40** and nitroxide ester alcohol **41**. Nitroxide **41**, like the alcohols **32**, underwent decomposition to diamagnetic products upon storage for a few days at 25 °C under air. By contrast, nitroxide diester **40** could be stored indefinitely without decomposition. Apparently, acetylation of the hydroxy group prevented the oxidative fragmentation reaction (**33** → **34**) leading to the corresponding nitrone.

The *cis*-azethoxyl nitroxides herein described possess uniquely positioned polar substituents proximal to the NO· group. Nitroxide **20** has already been used in one study pertaining to NMR imaging[3a] and the potential of others as contrast enhacing agents is being pursued.

Experimental Section[8]

1,5-Dimethyl-8-azabicyclo[3.2.1]octan-3-one Oxalate Salt (5). The procedure of Rassat[5] was modified as follows. To an ice-cold solution of 2,5-hexanedione (7.01 g, 61.6 mmol, distilled) and acetonedicarboxylic acid (17.1 g, 117 mmol, Aldrich) dissolved in water (50 mL) was added 15.4 g of KOH in 10 mL of water, followed by a solution of 10 g of NH_4Cl and 10 g of $NaOAc·3H_2O$ in 95 mL of water. The pH was adjusted to 9.0 with ca. 6 mL of aqueous KOH (1 g/mL). Water (40 mL) was added and the pH was readjusted to 9.0. This solution was allowed to stir at 25 °C for 3 days, during which time the mixture darkened and a brown oil separated. The mixture was cooled to 0 °C and acidified with cold 50% H_2SO_4, causing vigorous gas evolution and the separation of a tan solid. The mixture was decanted and the solid was washed with water. The wash was combined with the supernate, which was then washed with CH_2Cl_2. The aqueous phase was basified with KOH, saturated with K_2CO_3; and extracted 7 times with ether. The combined etheral extracts were dried (anhydrous K_2CO_3), filtered, and then treated with a saturated solution of oxalic acid in ether. The amine salt was collected and washed with ethanol. The pale yellow solid was dissolved in the minimum amount of warm water and then precipitated with acetone, affording pure salt **5** (2.60 g, 21%). The analytical specimen was obtained as a powder from 95% ethanol: mp 197–200 °C; NMR (D_2O) δ 1.37 (s, 6), 1.89 (s, 4), 2.57 (m, 4). Anal. Calcd for $C_{20}H_{32}N_2O_6$: C, 60.58; H, 8.14; N, 7.07. Found: C, 60.42; H, 8.22; N, 7.08.

1,5-Dimethyl-8-hydroxy-8-azabicyclo[3.2.1]octan-3-one (7). To an ice-cold solution of salt **5** (6.10 g), K_2CO_3 (12.0 g), and $Na_2WO_4·2H_2O$ (1.80 g) in water (50 mL) was added dropwise 30% H_2O_2 (10 mL). The ice bath was removed and the mixture was stirred at 25 °C for 2 h, when another 2.0 mL of 30% H_2O_2 was added. After 4.5 h the orange mixture was saturated with NaCl and extracted with ether until the extract was colorless. The combined extracts containing nitroxide **6** (may be obtained in pure form, mp 44.5 °C[5]) was immediately reduced by the addition of 30% Pd on carbon (0.5 g) followed by placing under a H_2 atmosphere (balloon) for 0.5 h at 23 °C. Normally, this ether solution of crude **7** was used directly for the preparation of **8**–**10**. In one experiment, a portion of the ether solution was evaporated to dryness and the residue was sublimed, affording pure hydroxy amine **7** as a white solid: mp 118–120 °C; NMR δ 1.24 (s, 6), 1.57 (s, 4), 1.91 (d, 2), 2.82 (d, 2), 6.04 (s, 1); IR ($CDCl_3$) 3580, 3250, 1700 cm^{-1}. Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.27. Found: C, 63.91; H, 9.15; N, 8.12.

1,5-Dimethyl-8-(*tert*-butyldimethylsiloxy)-8-azabicyclo-[3.2.1]octan-3-one (10). The entire ether solution of crude **7** from the previous experiment was evaporated to dryness, and the residue was dissolved in dry DMF (25 mL) and treated with imidazole (7.8 g) and *tert*-butyldimethylchlorosilane (8.46 g). After a 38-h stir at 23 °C the mixture was diluted with 35 mL of hexanes and 10 mL of water. The usual workup gave a thick oil, which was flash chromatographed (ether–hexanes, 5:95) to give crude **10** (7.58 g, 87%). Crystallization from hexanes afforded the analytical specimen: mp 60–61 °C; NMR δ 0.18 (s, 6), 0.94 (s, 9), 1.15 (s, 6), 1.55 (br s, 4), 2.32 (AB, 4); IR ($CDCl_3$) 1705 cm^{-1}. Anal. Calcd for $C_{15}H_{29}NO_2Si$: C, 63.56; H, 10.31; N, 4.94. Found: C, 63.49; H, 10.08; N, 4.92.

1,5-Dimethyl-8-acetoxy-8-azabicyclo[3.2.1]octan-3-one (8). The ether solution containing crude **7** (see above) derived from 811 mg of oxalate salt **5** was treated with Et_3N (0.65 mL) and AcCl (0.35 mL) and stirred for 2.5 h. The solution was washed with water, and the organic phase was dried ($MgSO_4$) and filtered through silica gel. The ether was removed by careful fractional distillation, leaving a colorless oil which was taken up in hexanes and seeded. There was obtained 584 mg (68%) of **8** as colorless crystals: mp 71.5–72.5 °C; NMR δ 1.16 (s, 6), 1.50–1.84 (m, 4), 1.98 (d, 2), 2.10 (s, 3), 2.62 (d, 2); IR ($CDCl_3$) 1770, 1715 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63. Found: C, 62.49; H, 7.97; N, 6.61.

1,5-Dimethyl-8-(pivaloyloxy)-8-azabicyclo[3.2.1]octan-3-one (9). This substance was prepared by the procedure given for **8** above, substituting pivaloyl chloride for AcCl. Yields are somewhat higher, with **9** obtained by repeated recrystallization from ether as massive prisms: mp 71–72 °C; NMR δ 1.18 (s, 6), 1.24 (s, 9), 1.54–1.95 (m, 4), 2.06 (d, 2), 2.63 (d, 2). Anal. Calcd for $C_{14}H_{23}NO_3$: C, 66.37; H, 9.15; N, 5.53. Found: C, 66.46; H, 9.44; N, 5.37.

1,5-Dimethyl-8-acetyl-8-azabicyclo[3.2.1]octan-3-one (11). To a stirred solution of oxalate salt **5** (396 mg) in dry pyridine (8 mL) was added Ac_2O (1 mL). After 12 h at 60 °C the solvent was removed, and the resulting yellow oil was taken up in ether and filtered through silica gel. Removal of the solvent gave an oil which crystallized (384 mg, 98%). Recrystallization from pentane gave the analytical specimen as massive prisms: mp 54–55 °C; NMR δ 1.58 (s, 6), 1.71 (d, 4), 2.14 (s, 3), 2.41 (AB, 4); IR ($CDCl_3$) 1715, 1640 cm^{-1}. Anal. Calcd for $C_{11}H_{17}NO_2$: C, 67.66; H, 8.77; N, 7.17. Found: C, 67.96; H, 8.76; N, 7.07.

1,5-Dimethyl-8-acetyl-8-azabicyclo[3.2.1]octan-3-one Oxime (12). A mixture of ketone **11** (681 mg), $NH_2OH·HCl$ (375 mg), and $NaOAc·3H_2O$ (733 mg) in ethanol (3 mL) was heated at 70 °C for 6 h and then filtered and evaporated to dryness. The residue was dissolved in EtOAc–ethanol and filtered through silica

(8) Footnote 20 of ref 4 applies here.

gel. Removal of the solvent gave an oil which crystallized. This was powdered and then sublimed [120 °C (0.05 mmHg)] to give pure oxime **12** (685 mg, 93%): mp 142.5–143 °C; NMR δ 1.58 (s, 6), 1.66 (m, 4), 2.04–2.36 (m, 2), 2.12 (s, 3), 2.60 (d, 1), 3.06 (d, 1). Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.97; H, 8.70; N, 13.27.

1,5-Dimethyl-8-acetyl-8-azabicyclo[3.2.1]octan-3-one *O*-(Tolylsulfonyl)oxime (13). To a 0 °C solution of oxime **12** (609 mg) in pyridine (5 mL) was added TsCl (1.10 g). After 1.5 h at 25 °C, the yellow mixture was concentrated, diluted with CH_2Cl_2, washed with water and brine, and dried ($MgSO_4$). The solvent was removed, and the residue was chromatographed over silica gel. Elution with EtOAc gave **13** as colorless crystals (1.01 g, 96%). Recrystallization from toluene–hexane gave the analytical specimen: mp 125 °C dec; NMR δ 1.20–1.80 (m, 4), 1.58 (s, 6), 2.10 (s, 3), 2.14–2.70 (m, 4), 2.42 (s, 3), 3.20 (d, 1), 7.20–7.40 (m, 2), 7.70–7.90 (m, 2); IR ($CDCl_3$) 1640 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_2O_4S$: C, 59.32; H, 6.64; N, 7.69. Found: C, 59.39; H, 6.44; N, 7.58.

1,6-Dimethyl-9-acetyl-3,9-diazabicyclo[4.2.1]nonan-4-one (17). A solution of tosylate **13** (21.8 mg) in water–THF (2:3, 1.3 mL) was heated at 50 °C for 6 h and the solvent was removed. The residue was dissolved in CH_2Cl_2, washed with chilled $NaHCO_3$, dried ($MgSO_4$), and concentrated to dryness. Crystallization of the resulting white solid from EtOAc–hexane gave lactam **17** (10 mg, 78%): mp 120.5–121.5 °C; NMR δ 1.56 (s, 3), 1.59 (s, 3), 1.66–2.06 (m, 4), 2.16 (s, 3), 2.46 (d, 1), 2.64–2.90 (m, 1), 3.20 (d, 1), 3.85 (d, 1), 6.74 (br s, 1); IR ($CDCl_3$) 3400, 1640 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.83; H, 8.63; N, 13.32. Found: C, 62.67; H, 8.70; N, 13.74.

1,5-Dimethyl-8-acetoxy-8-azabicyclo[3.2.1]octan-3-one *O*-(Mesitylsulfonyl)oxime (14). The general procedure of Tamura et al.[7] was followed. To an ice-cooled stirred solution of *N*-acetoxy ketone **8** (219 mg, 1.03 mmol) in CH_2Cl_2 (2 mL) was added *O*-(mesitylsulfonyl)hydroxylamine[8] (215 mg, 1.00 mmol). The resulting solution was allowed to warm to 25 °C over 25 min and then the solvent was removed, affording crystalline **14** suitable for the next reaction. Recrystallization from CH_2Cl_2–pentane afforded the analytical specimen: NMR δ 1.14 (s, 3), 1.17 (s, 3), 1.30–1.90 (m, 4), 1.98–2.96 (m, 4), 2.08 (s, 3), 2.27 (s, 3), 2.61 (s, 6), 6.93 (s, 2); IR ($CDCl_3$) 1720 cm^{-1}. Anal. Calcd for $C_{20}H_{28}N_2O_5S$: C, 58.80; H, 6.91; N, 6.86. Found: C, 58.89; H, 6.53; N, 6.82.

1,6-Dimethyl-9-acetoxy-3,9-diazabicyclo[4.2.1]nonan-4-one (18). Crude **14**, obtained as described above from the reaction of 224 mg of **8**, was dissolved in 1:1 CH_3CN–water (6 mL) containing Et_3N (3 drops) and then heated at 47 °C for 3 h. The solution was concentrated, diluted with aqueous $NaHCO_3$, and extracted with $CHCl_3$. The usual workup afforded 226 mg (94%) of crystalline **18**. Recrystallization from EtOAc–hexane (avoid excessive heating) afforded the analytical specimen: mp 172 °C dec; NMR δ 1.11 (s, 3), 1.16 (s, 3), 1.60–2.06 (m, 4), 2.12 (s, 3), 2.30–2.62 (m, 1), 3.32 (d, 1), 3.84 (d, 1), 6.72 (br s, 1); IR ($CDCl_3$) 3420, 3220, 1770, 1660 cm^{-1}. Anal. Calcd for $C_{11}H_{18}N_2O_3$: C, 58.39; H, 8.02; N, 12.38. Found: C, 58.49; H, 8.17; N, 12.02.

1,5-Dimethyl-8-(*tert*-butyldimethylsiloxy)-8-azabicyclo-[3.2.1]octan-3-one Oxime (15). A mixture of ketone **10** (1.60 g, 5.64 mmol), $NH_2OH·HCl$ (818 mg, 11.8 mmol), and NaOAc (9.66 mg, 12 mmol) in absolute ethanol (15 mL) was stirred at 23 °C for 12 h. The mixture was diluted with EtOAc (10 mL), filtered, and concentrated. The residue was triturated with xylene. The xylene extract was concentrated to dryness, affording **15** (1.68 g, 100%) as a colorless powder. Recrystallization from EtOAc gave the analytical specimen: mp 159–160 °C; NMR δ 0.15 (s, 6), 0.94 (s, 9), 1.13 (2 s, 6), 1.38–1.62 (m, 4), 1.72 (d, 1), 2.32 (d, 1), 2.70 (d, 2), 8.87 (br s, 1); IR ($CDCl_3$) 3250, 1630 cm^{-1}. Anal. Calcd for $C_{15}H_{30}N_2O_2Si$: C, 60.36; H, 10.13; N, 9.38. Found: C, 60.25; H, 10.02; N, 9.14.

1,5-Dimethyl-8-(*tert*-butyldimethylsiloxy)-8-azabicyclo-[3.2.1]octan-3-one *O*-(Tolylsulfonyl)oxime (16). A 0 °C solution of oxime **15** (1.681 g) and TsCl (2.152 g) in pyridine (21 mL) was allowed to warm to 15 °C over 2 h. The mixture was diluted with hexane and then quenched by addition of cold aqueous $NaHCO_3$. The usual workup afforded **16** (2.5 g, 98%) as a pale yellow solid. Recrystallization from hexane afforded the analytical specimen: mp 101–102 °C; NMR δ 0.12 (s, 6), 0.89 (s, 9), 1.10 (s, 6), 1.24–1.56 (m, 4), 1.60–1.94 (m, 2), 2.44 (s, 3), 2.52–2.80 (m, 2), 7.34 (d, 2), 7.86 (d, 2). Anal. Calcd for $C_{22}H_{36}N_2O_4SSi$: C, 58.37; H, 8.02; N, 6.19. Found: C, 58.31; H, 8.31; N, 6.37.

1,6-Dimethyl-9-(*tert*-butyldimethylsiloxy)-3,9-diazabicyclo[4.2.1]nonan-4-one (19). A solution of tosylate **16** (613 mg) in 6:2:1 CH_3CN–pyridine–water (10 mL) was heated at 50 °C for 35 min. The solution was cooled, diluted with ether–hexane (25 mL), and washed with water. The usual workup gave **19** (314 mg, 78%) as colorless crystals. Recrystallization from hexane gave the analytical specimen: mp 120–130 °C; NMR δ 0.14 (s, 6), 0.97 (s, 9), 1.08 (s, 3), 1.14 (s, 3), 1.50–2.06 (m, 5), 2.06–2.40 (m, 1), 3.91 (AB, 2), 6.00 (br s, 1); IR 1660 cm^{-1}; MS 299 (24), 298.208 (100) (calcd for $C_{15}H_{30}N_2O_2Si$, 298.208), 272 (10), 270 (10), 242 (19), 241 (93). Anal. Calcd for $C_{15}H_{30}N_2O_2Si·^1/_2H_2O$: C, 58.56; H, 10.17; N, 9.12. Found: C, 58.61; H, 10.40; N, 9.06.

***cis*-2,5-Dimethyl-2-(aminomethyl)-5-(2-carboxyethyl)-tetrahydropyrrole-1-oxyl (20).** A solution of lactam **19** (346 mg) in a 2 N ethanolic solution of KOH (4 mL) was heated at 75 °C under air for 12 h. The resulting yellow solution was concentrated to 1 mL, diluted with water (1 mL), and stirred 12 h at 25 °C. The solution was concentrated to 1 mL and extracted with ether, and the aqueous phase was passed through an ion-exchange column (Amberlite IRC-50, ammonium form). The eluate was evaporated to dryness. Preparative TLC (silica gel, $CHCl_3$–MeOH–EtOH–water, 7:3:1:0.5) gave **20** (24 mg, 10%) as a yellow solid. Although initially soluble in $CHCl_3$, over a 2-day period the compound is converted into a less soluble (zwitterionic?) form. Recrystallization from MeOH–EtOH gave the analytical specimen: mp 173–174 °C; IR (KBr) 3300–2400, 1550 cm^{-1}; ESR (water) a_N = 15.3 G. Anal. Calcd for $C_9H_{17}N_2O_3$: C, 53.72; H, 8.51; N, 13.92. Found: C, 53.41; H, 8.84; N, 13.69.

***cis*-2,5-Dimethyl-2-[(benzoylamino)methyl]-5-(carboxymethyl)tetrahydropyrrole-1-oxyl (21).** A mixture of **19** (52 mg), KOH (85 mg), and MeOH–water (7:3, 3 mL) was refluxed for 20 h under air and then stirred under air at 25 °C for 3.5 h. The resulting yellow solution was concentrated to 0.3 mL, diluted with water (0.7 mL), cooled to 0 °C, neutralized with concentrated HCl, and evaporated to dryness in vacuo. The yellow residue was triturated with MeOH (3 × 4 mL). To the combined MeOH extract was added Na_2CO_3 (30 mg), followed by enough water to effect solution. Benzoyl chloride (0.1 mL) was added at 0 °C with stirring. The pH was kept above 8 by addition of Na_2CO_3 (30 mg) and water (0.5 mL). More benzoyl chloride (0.1 mL) was added. After a 30-min stir at 0 °C, the pH was adjusted to 10, water (15 mL) was added, and the solution was washed with ether. Then $CHCl_3$ (5 mL) was added, and the mixture was brought to pH 2 by addition of concentrated HCl. The mixture was extracted well with $CHCl_3$. The extract was dried ($MgSO_4$), concentrated, and subjected to preparative TLC (silica gel, MeOH–$CHCl_3$, 1:9). The yellow band was nitroxide **21** (23 mg, 43%), isolated as a yellow oil. The analytical specimen was obtained by crystallization from ether–hexane–benzene: mp 111–112 °C; IR ($CDCl_3$) 3500–2300, 1660–1550 cm^{-1}; ESR ($CHCl_3$) three lines, a_N = 14.5 G. Anal. Calcd for $C_{16}H_{21}N_2O_4$: C, 62.93; H, 6.93; N, 9.18. Found: C, 62.91; H, 6.92; N, 9.12.

1,5-Dimethyl-8-acetoxy-3-butyl-8-azabicyclo[3.2.1]octan-3-ol (22). A stirred solution of ketone **8** (103 mg) in dry ether (5 mL) was cooled to −78 °C and treated dropwise with 1.6 M butyllithium in hexane (0.34 mL). After 1 h, the reaction was quenched by addition of saturated aqueous NH_4Cl (0.02 mL) and allowed to warm to 25 °C. Water was added and the crystalline alcohol (99 mg) was isolated by ether extraction. Recrystallization from hexane afforded **22** (90 mg, 69%) as fine colorless needles (mixture of α and β isomers): mp 107–109 °C; NMR δ 1.08 and 1.14 (s, 3), 2.04 and 2.07 (s, 3); IR 3600, 3500, 1750 cm^{-1}. Anal. Calcd for $C_{15}H_{27}NO_3$: C, 66.88; H, 10.10; N, 5.20. Found: C, 67.00; H, 10.46; N, 5.01.

1,5-Dimethyl-8-acetoxy-3-butyl-8-azabicyclo[3.2.1]oct-2-ene (24). To a 0 °C stirred solution of recrystallized **22** (353 mg, 1.31 mmol) in dry pyridine (10 mL) was added thionyl chloride (0.113 mL, 1.57 mmol, distilled from quinoline). The ice bath was removed and after 2 h most of the solvent was removed under vacuum. The residue was dissolved in ether, washed with chilled 1% HCl, chilled water, and brine, and dried ($MgSO_4$). Evaporation of the solvent gave an essentially pure mixture of isomeric alkenes **24** (283 mg, 86%) as a colorless oil. A portion was

chromatographed over silica gel (1:1 ether–hexane) and then subjected to preparative TLC (R_f 0.6) over silica gel using the same solvent, affording the analytical specimen as a colorless oil. Anal. Calcd for $C_{15}H_{25}N$: C, 71.67; H, 10.03; N, 5.41. Found: C, 71.72; H, 5.41; N, 10.03.

***cis*-2,5-Dimethyl-1-acetoxy-2-formyl-5-(2-oxohexyl)tetrahydropyrrole (26).** Ozone was bubbled through a −78 °C solution of alkene mixture **24** (670 mg) dissolved in CH_2Cl_2 for 15 min (persistent blue color). The solution was purged with N_2, treated with Me_2S (0.5 mL), and allowed to warm to 25 °C. The resulting yellow solution was filtered through silica gel and then evaporated to dryness, leaving a yellow oil. The oil was flash chromatographed (4:1 hexane–EtOAc) over silica gel, affording 182 mg (24%) of **26** as a colorless oil: NMR δ 0.82 (t, 3), 1.00–2.12 (m, 8), 1.14 (s, 3), 1.26 (s, 3), 2.00 (s, 3), 2.22–2.52 (m, 2), 2.62 (s, 2), 9.52 (s, 1); IR 1775, 1710 cm^{-1}; MS 254.175 (calcd for $C_{15}H_{25}NO_4$ − CHO, 254.176). Also recovered from the chromatography was ketone **8** (133 mg, 24%).

***cis*-2,5-Dimethyl-1-acetoxy-2-carbomethoxy-5-(2-oxohexyl)tetrahydropyrrole (28).** To a stirred solution of aldehyde **26** (92 mg) in acetone (1 mL) at 23 °C was added dropwise 2.67 M Jones reagent until a yellow color persisted for 1 min. A small drop of 2-propanol was added followed by CH_2Cl_2 and filtration. The filtrate was washed with water. The usual workup gave 77 mg of crude acid **27**. In earlier experiments **27** was observed to decompose on standing 2 h at 23 °C, probably by loss of CO_2 and AcOH to give imine **30**: NMR δ 1.82 (t, 3), 1.00–2.16 (m, 6), 1.22 (s, 3), 1.99 (s, 3), 2.34 (t, 2), 2.56 (t, 2), 2.72 (s, 2); IR 1755, 1650 cm^{-1}. Therefore, crude **27** was immediately treated with excess diazomethane in ether (9 mL), affording after workup 79 mg (77%) of crude ester **28**. This was purified by preparative TLC over silica gel (1:3 EtOAc–hexane), affording 41 mg of pure **28** as a colorless oil: NMR δ (diagnostic peaks only) 0.92 (t, 3), 1.22 (s, 3), 1.34 (s, 3), 2.03 (s, 3), 2.66 (AB, J = 16 Hz, 2), 3.64 (s, 3); IR 1770, 1735, 1710 cm^{-1}; MS 313.189 (3) (calcd for $C_{16}H_{27}NO_5$, 313.189), 271 (10), 254 (20), 212 (100).

1,5-Dimethyl-8-(*tert*-butyldimethylsiloxy)-3-butyl-8-azabicyclo[3.2.1]octan-3-ol (23). To a stirred solution of ketone **10** (1.17 g) in dry ether (100 mL) at −78 °C was added 2.0 M BuLi in hexane (2.3 mL). After 1 h the reaction was quenched by addition of saturated aqueous NH_4Cl (5 mL) and then allowed to warm to 25 °C. The usual workup gave alcohol **23** (1.38 g, 98%) as a white pasty solid. Preparative TLC gave a purified sample of **23** as a colorless oil, which was analyzed by MS: MS 341.276 (1) (calcd for $C_{19}H_{39}N_4OSi$, 341.275), 283 (20), 268 (5), 226 (100); NMR δ 0.13 (m, 6), 0.92 (m, 14), 1.02 (s, 6), 1.10 (m, 2), 1.16–1.56 (m, 7), 1.58–1.72 (m, 1), 1.80–2.12 (m, 3); IR 3500, 3200 cm^{-1}.

1,5-Dimethyl-8-(*tert*-butyldimethylsiloxy)-3-butyl-8-azabicyclo[3.2.1]oct-2-ene (25). To a 0 °C solution of **23** (740 mg) in pyridine (5 mL) was added $SOCl_2$ (0.425 mL, freshly distilled from quinoline). The mixture was allowed to warm to 10 °C over 1.5 h and then it was diluted with hexane (10 mL) and washed with water. The usual workup followed by filtration through silica gel gave the alkene mixture (608 mg, 87%) as a pale yellow oil in which **25** predominated: NMR δ 0.09 (s, 6), 0.88 (m, 12), 1.10 (s, 6), 1.1–2.40 (m, 12), 5.08 and 5.22 (br s, 1); IR 1650 cm^{-1}. Anal. Calcd for $C_{19}H_{37}NOSi$: C, 70.52; H, 11.53; N, 4.33. Found: C, 70.34; H, 11.78; N, 4.51.

***cis*-2,5-Dimethyl-1-(*tert*-butyldimethylsiloxy)-2-formyl-5-(2-oxohexyl)tetrahydropyrrole (29).** Through a solution of **25** (265 mg), CH_2Cl_2 (8 mL), and propionaldehyde (4 mL) at −78 °C a stream of ozone in oxygen was bubbled for 10 min. The cold solution was purged with nitrogen for 5 min, and then Me_2S (1.5 mL) was added. After a 30-min stir at −78 °C the solution was warmed to 25 °C and then concentrated to dryness. The residue was dissolved in hexane and then washed with water, dried ($MgSO_4$), and evaporated to dryness, affording 249 mg of a light yellow oil. This was flash chromatographed over silica gel (1:9 ether–hexane) to give ketone **10** (16 mg, 7%) and aldehyde **29** (119 mg, 41%) as a colorless oil: NMR δ −0.04 (s, 3), 0.16 (s, 3), 0.90 (m, 12), 1.21 (s, 6), 1.20–2.91 (m, 12), 9.45 (s, 1); IR ($CDCl_3$) 1725 cm^{-1}. Anal. Calcd for $C_{19}H_{37}NO_3Si$: C, 64.18; H, 10.49; N, 3.94. Found: C, 64.41; H, 10.56; N, 3.86.

***cis*-2,5-Dimethyl-1-(*tert*-butyldimethylsiloxy)-2-(hydroxymethyl)-5-(2-hydroxyhexyl)tetrahydropyrrole (31).** To a stirred solution of **29** (68 mg) in MeOH (0.7 mL) at 0 °C was added $NaBH_4$ (30 mg). After a 30-min stir the reaction was quenched by addition of aqueous formic acid (4 drops) and then evaporated to dryness at 5 °C. The white residue was treated with cold aqueous $NaHCO_3$ and extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and concentrated to dryness. The residue was flash chromatographed over silica gel. Elution with 1:1 ether–hexane gave first diastereomer A (45 mg) and then diastereomer B (17 mg) as colorless oils (91%). Isomer A: NMR δ 0.16 (s, 3), 0.19 (s, 3), 0.95 (s, 12), 1.10 (s, 3), 1.26 (s, 3), 1.20–2.14 (m, 13), 2.80 (br s, 1), 3.32 (AB, 2), 3.80 (br s, 1). Isomer B: NMR δ 0.18 (s, 3), 0.27 (s, 3), 0.95 (s, 12), 1.12 (s, 3), 1.19 (s, 3), 1.26–2.10 (m, 13), 3.38 (AB, 2), 3.86 (br s, 1), 5.30 (br s, 1). Anal. (mixture) Calcd for $C_{19}H_{41}NO_3Si$: C, 63.45; H, 11.49; N, 3.90. Found: C, 63.26; H, 11.49; N, 3.67.

***cis*-2,5-Dimethyl-2-(hydroxymethyl)-5-(2-hydroxyhexyl)tetrahydropyrrole-1-oxyl (32).** To a solution of **31** (135 mg) in CH_3CN (2 mL) was added 48% HF (5 drops). After a 2-h stir at 25 °C the solution was neutralized with aqueous $NaHCO_3$, concentrated to 1 mL, and saturated with NaCl. Extraction with $CHCl_3$ afforded a light yellow oil (99 mg) which was flash chromatographed over silica gel, giving the crude hydroxylamine (69 mg) as a colorless oil. This was dissolved in MeOH (3 mL) and stirred for 2 days under air. The solvent was replaced with $CHCl_3$, which was the dried and evaporated to give a yellow oil (67 mg). Flash chromatography gave the hydroxylamine (23 mg) and nitroxide **32** (35 mg, 38%) as a yellow oil: ESR ($CHCl_3$) three lines, a_N = 14.9 G. Anal. Calcd for $C_{13}H_{26}NO_3 \cdot {}^1/_4H_2O$: C, 62.74; H, 10.73; N, 5.63. Found: C, 62.88; H, 10.77; N, 5.73.

1,5-Dimethyl-3,3-dimethoxy-8-(*tert*-butyldimethylsiloxy)-8-azabicyclo[3.2.1]octane (35). A solution of ketone **10** (1.835 g) and $TsOH \cdot H_2O$ (162 mg) in $HC(OMe)_3$ (15 mL) and MeOH (12 mL) was heated at 50 °C for 11 h. The solution was cooled, diluted with hexane (25 mL), and washed with $NaHCO_3$. The organic layer was dried and then evaporated, giving essentially pure **35** (1.723 g, 81%) as a white pasty solid. Low-temperature crystallization from hexane gave the analytical specimen: mp 65–66 °C; NMR δ 0.09 (s, 6), 0.90 (s, 9), 1.00 (s, 6), 1.20–1.58 (m, 4), 1.60–2.04 (m, 4), 3.12 (s, 6). Anal. Calcd for $C_{17}H_{35}NO_3Si$: C, 61.96; H, 10.70; N, 4.25. Found: C, 62.06; H, 11.01; N, 4.07.

1,5-Dimethyl-3-methoxy-8-(*tert*-butyldimethylsiloxy)-8-azabicyclo[3.2.1]oct-2-ene (36). $TsOH \cdot H_2O$ was dissolved in dry benzene (50 mL). About 10 mL of benzene was distilled off, and the remaining solution was added to ketal **35** (898 mg) dissolved in benzene (10 mL). The solution was reduced to about 5 mL by distillation and then cooled. After addition of hexane (25 mL) the organic phase was washed with aqueous $NaHCO_3$, dried, and filtered through silica gel, affording 663 mg of a mixture of **36** and ketone **10**. This was dissolved in hexane and passed over silica gel, effectively removing **10** and affording the pure enol ether **36** (453 mg, 56%) as a colorless oil. Preparative TLC (1:1 ether–hexane) separated **36** into two isomers (invertomers at N), readily distinguished by NMR. Isomer A: R_f 0.67; NMR δ 0.10 (s, 6), 0.96 (s, 9), 1.11 (s, 3), 1.13 (s, 3), 1.32 (d, 1), 1.57 (m, 4), 2.48 (d, 1), 3.48 (s, 3), 4.28 (, 1); IR 1665 cm^{-1}. Isomer B: R_f 0.34; NMR δ 0.14 (s, 6), 0.92 (s, 9), 1.24 (s, 6), 1.52–2.10 (m, 5), 2.52 (d, 1), 3.44 (s, 3), 4.48 (m, 1); IR 1665 cm^{-1}. An equilibrium mixture (2:1 A–B) was obtained from the pure isomers on standing at 23 °C for 36 h. The mass spectra of both isomers are identical: 297.504 (55) (calcd for $C_{16}H_{31}NO_2Si$, 297.504), 282 (20), 240 (100).

***cis*-2,5-Dimethyl-1-(*tert*-butyldimethylsiloxy)-2-formyl-5-[(methoxycarbonyl)methyl]tetrahydropyrrole (37).** Through a solution of **36** (204 mg) in MeOH (12 mL) at −78 °C a stream of ozone was bubbled for 15 min followed by nitrogen for 5 min. Then Me_2S (0.6 mL) was added and the solution was stirred for 30 min and then allowed to warm to 23 °C. The solvent was evaporated, the residue was dissolved in hexane, and this was washed with water, dried ($MgSO_4$), evaporated, and flash chromatographed. Elution with 1:9 ether–hexane gave **37** (105 mg, 47%) as a colorless oil: IR ($CDCl_3$) 1725 cm^{-1}; NMR δ −0.05 (s, 3), 0.13 (s, 3), 0.93 (s, 9), 1.23 (s, 6), 1.50–2.10 (m, 4), 2.50 (AB, 2), 3.64 (s, 3), 9.42 (s, 1). Anal. Calcd for $C_{16}H_{31}NO_4Si$: C, 58.32; H, 9.48; N, 4.25. Found: C, 58.63; H, 9.50; N, 4.28.

***cis*-2,5-Dimethyl-1-(*tert*-butyldimethylsiloxy)-2-(hydroxymethyl)-5-[(methoxycarbonyl)methyl]tetrahydropyrrole (38).** To a 0 °C solution of aldehyde **37** (308 mg) in MeOH (2 mL) was added $NaBH_4$ (40 mg). After 30 min formic

acid (0.1 mL) was added, and the volatiles were removed under vacuum at 5 °C. The solid was triturated with cold aqueous $NaHCO_3$, and $CHCl_3$ was added. The organic phase was dried and filtered through silica gel, affording pure **38** (299 mg, 96%) as a colorless oil: NMR δ 0.13 (br s, 6), 0.92 (br s, 9), 1.04 (s, 3), 1.99 (s, 3), 1.6–2.1 (m, 4), 2.26 (br s, 2), 2.95–3.40 (m, 2), 3.62 (s, 3 H); IR 3500–3000, 1720 cm^{-1}. Anal. Calcd for $C_{16}H_{33}NO_4Si$: C, 57.97; H, 10.03; N, 4.22. Found: C, 58.63; H, 9.50; N, 4.28.

***cis*-2,5-Dimethyl-1-(*tert*-butyldimethylsiloxy)-2-(acetoxymethyl)-5-[(methoxycarbonyl)methyl]tetrahydropyrrole (39).** To a 0 °C solution of **42** (25 mg) in hexane (0.2 mL) containing Et_3N (0.1 mL) was added AcCl (1.5 equiv). After 30 min cold aqueous $NaHCO_3$ was added followed by more hexane. The organic phase was dried and evaporated, affording **39** (24 mg, 87%). Preparative TLC over silica gel (1:1 ether–hexane) afforded the analytical specimen as a colorless oil: NMR δ 0.12 (s, 6), 0.92 (s, 9), 1.12 (s, 3), 1.99 (s, 3), 1.5–2.0 (m, 4), 2.03 (s, 3), 2.45 (AB, J = 14 Hz, 2), 3.62 (s, 3), 3.84 (s, 2); IR 1735 cm^{-1}; MS 373 (13), 359 (10), 316.159 (15) (M – $C(CH_3)_3$; calcd for $C_{14}H_{26}NO_5Si$, 316.158), 301 (24), 300 (100). Anal. Calcd for $C_{18}H_{35}NO_5Si$: C, 57.87; H, 9.44; N, 3.75. Found: C, 58.29; H, 9.74; N, 3.57.

***cis*-2,5-Dimethyl-2-(acetoxymethyl)-5-[(methoxycarbonyl)methyl]tetrahydropyrrole-1-oxyl (40).** To a solution of **39** (11 mg) in CH_3CN (0.5 mL) at 23 °C was added 48% HF (2 drops). After a 2-h stir water (0.5 mL) was added and the solution was extracted with $CHCl_3$. The extract was washed with water, dried ($MgSO_4$), and concentrated to dryness to give the crude hydroxylamine (7.4 mg) as a colorless oil: NMR δ 1.43 (s, 3), 1.46 (s, 3), 2.00–2.16 (m, 4), 2.18 (s, 3), 2.85 (AB, 2), 3.77 (s, 3), 4.14 (AB, 2); IR ($CDCl_3$) 3200, 1735 cm^{-1}. This was dissolved in MeOH (1 mL) containing $Cu(OAc)_2 \cdot H_2O$ (1 mg) and stirred for 16 h under air at 0 °C. The solvent was evaporated, and the residue was dissolved in a mixture of water (0.5 mL) and $CHCl_3$ (0.5 mL). The mixture was extracted with $CHCl_3$, and the extract was dried ($MgSO_4$) and concentrated to dryness to give **40** (5.3 mg, 71%) as a yellow oil: IR 1740 cm^{-1}; ESR ($CHCl_3$) three lines, a_N = 14.5 G. Anal. Calcd for $C_{12}H_{20}NO_5$: C, 55.80; H, 7.81; N, 5.42. Found: C, 56.04; H, 7.82; N, 5.45.

***cis*-2,5-Dimethyl-2-(hydroxymethyl)-5-[(methoxycarbonyl)methyl]tetrahydropyrrole-1-oxyl (41).** To a solution of **38** (50 mg) in CH_3CN (1.5 mL) at 25 °C was added 48% HF (1 drop). After a 1-h stir the solution was neutralized with saturated $NaHCO_3$ and evaporated to dryness. Water (0.2 mL) and $CHCl_3$ (1.5 mL) were added, the aqueous phase was saturated with NaCl, and the mixture was extracted with $CHCl_3$. The extract was dried ($MgSO_4$) and evaporated to give the crude hydroxylamine (34 mg) as a colorless oil: NMR δ 1.36 (s, 3), 1.50 (s, 3), 1.85–2.60 (br s, 4), 2.64–3.32 (m, 2), 3.48 (d, 1), 3.75 (s, 3), 4.01 (d, 1), 7.80 (br s, 2). The oil was dissolved in $CHCl_3$ (1 mL), stirred for 1 day under air, and evaporated to give a yellow oil (33 mg). Flash chromatography over silica gel gave the hydroxylamine (28 mg) and nitroxide **41** (5 mg, 15%) as a yellow oil: ESR ($CHCl_3$) three lines, a_N = 14.7 G. Anal. Calcd for $C_{10}H_{18}NO_4$: C, 55.54; H, 8.39; N, 6.48. Found: C, 55.70; H, 8.47; N, 6.75.

Acknowledgment. This research was supported by Public Health Service Research Grant 27137 from the National Institute of General Medical Sciences.

Registry No. **5**, 38390-77-1; **6**, 34061-60-4; **7**, 96454-06-7; **8**, 96453-76-8; **9**, 96453-77-9; **10**, 96453-78-0; **11**, 96453-79-1; **12**, 96453-80-4; **13**, 96453-81-5; **14**, 96453-83-7; **15**, 96453-84-8; **16**, 96453-85-9; **17**, 96453-82-6; **18**, 96453-86-0; **19**, 96453-87-1; **20**, 96453-88-2; **21**, 96453-89-3; *endo*-**22**, 96453-90-6; *exo*-**22**, 96454-10-3; **23**, 96453-94-0; **24** (isomer 1), 96453-91-7; **24** (isomer 2), 96454-08-9; **25** (isomer 1), 96453-95-1; **25** (isomer 2), 96454-09-0; **26**, 96453-92-8; **27**, 96481-28-6; **28**, 96453-93-9; **29**, 96453-96-2; **30**, 96454-07-8; **31** (isomer a), 96453-97-3; **31** (isomer b), 96553-55-8; **32** (isomer a), 96453-98-4; **32** (isomer b), 96553-56-9; **35**, 96453-99-5; **36**, 96454-00-1; **37**, 96454-01-2; **38**, 96454-02-3; **39**, 96454-03-4; **40**, 96454-04-5; **41**, 96454-05-6; $CH_3CO(CH_2)_2COCH_3$, 110-13-4; HO_2CCOCO_2H, 542-05-2; Me_3CCOCl, 3282-30-2; *t*-$Bu(Me)_2SiCl$, 18162-48-6; PhCOCl, 98-88-4; *O*-(mesitylsulfonyl)hydroxylamine, 36016-40-7.