distilled in a Kugelrohr apparatus at 140–145 °C (0.02 torr) to afford GLC-pure product (6.85 g) as a yellow liquid: 38% yield as **7**; ^{1}H NMR ($CDCl_3$) δ 0.87 (t, CH_3, 3 H), 1.12–1.69 (m, CH_2, 8 H), 3.13–3.99 (m, NCH_2, $OCHCH_2O$, OCH_2CH_2O, 23 H), 8.08 (s, CHO, 1 H); mass spectrum, *m/e* (relative intensity) 361 (M^+, 9.7), 219 (19.5), 131 (18.6), 87 (100); IR (neat) 2930, 2860, 1680, 1470, 1360, 1130 cm^{-1}. Anal. Calcd for $C_{18}H_{35}NO_6$: C, 59.81; H, 9.76; N, 3.87. Found: C, 59.51; H, 9.74; N, 4.00.

Chloromethyl Oligoethylene Glycols. Ethylene oxide, which was purified by passage through a 40% NaOH aqueous solution and dried over NaOH pellets and soda lime, was introduced to 3-chloro-1,2-propanediol (111 g, 1.0 mol) in the presence of 1.5 g of boron trifluoride etherate at 80 °C. After a 66-g (1.5 mol) increase in weight was attained, the reaction was stopped, and the product was purged with nitrogen gas to remove unreacted ethylene oxide. (Chloromethyl)diethylene glycol (**11**, 27.4 g) and (chloromethyl)triethylene glycol (**12**, 19.4 g) were separated by fractional distillation under reduced pressure. **11**: bp 90–93 °C (0.015 torr); colorless liquid; ^{1}H NMR ($CDCl_3$) δ 3.56 (s, OH, 2 H), 3.50–3.85 (m, OCH_2, $ClCH_2$, 8 H), 3.85–4.12 (m, OCH, 1 H); IR (neat) 3340, 2960, 2870, 1300, 1120, 1060, 750 cm^{-1}. **12**: bp 121–123 °C (0.01 torr); pale yellow liquid; ^{1}H NMR ($CDCl_3$) δ 3.46 (s, OH, 2 H), 3.52–3.87 (m, OCH_2, $ClCH_2$, 12 H), 3.87–4.16 (m, OCH, 1 H).

[(Hexylamino)methyl]diethylene Glycol (13). The procedure for **1a** was followed by using **11** and hexylamine: bp 120–125 °C (0.005 torr; Kugelrohr distillation); pale yellow liquid; 58% yield; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, CH_3, 3 H), 1.12–1.68 (m, CH_2, 8 H), 2.45–2.84 (m, NCH_2, 4 H), 3.26 (s, OH, NH, 3 H), 3.40–4.02 (m, $OCHCH_2O$, OCH_2CH_2O, 7 H). Anal. Calcd for $C_{11}H_{25}NO_3$: C, 60.24; H, 11.49; N, 6.39. Found: C, 60.45; 11.67; N, 6.46.

[(Hexylamino)methyl]triethylene Glycol (14): bp 130–135 °C (0.005 torr, Kugelrohr distillation); pale yellow liquid; 58% yield; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3 H), 1.10–1.67 (m, 8 H), 2.45–2.83 (m, 4 H), 3.25 (s, 3 H), 3.44–4.02 (m, 11 H). Anal. Calcd for $C_{13}H_{29}NO_4$: C, 59.29; H, 11.10; N, 5.32. Found: C, 59.34; H, 11.31; N, 5.40.

(Aminomethyl)triethylene Glycol (16). Although this compound could be prepared from **12** by using the Gabriel method, the workup was difficult, because the intermediary phthalimide derivative could not be isolated by recrystallization in a pure state. The following procedure was employed. Into 26% aqueous ammonia solution (262 g, 4.0 mol) containing potassium carbonate (4.1 g, 0.03 mol) was added **12** (8.0 g, 0.04 mol) dropwise. After the mixture was stirred at room temperature for 55 h, water and ammonia were removed, and the residue was taken up in methanol, filtered, and distilled in a Kugelrohr apparatus to give **16** (3.1 g, 43% yield) as a pale yellow liquid: bp 145–148 °C (0.06 torr); ^{1}H NMR ($CDCl_3$) δ 2.50–2.99 (m, 2 H), 3.31 (s, 4 H), 3.43–3.92 (m, 11 H); IR (neat) 3350, 3280, 2940, 2870, 1460, 1360, 1120, 1070 cm^{-1}. Anal. Calcd for $C_7H_{17}NO_4$: C, 46.91; H, 9.56; N, 7.82. Found: C, 47.15; H, 9.61; N, 7.69.

(Aminomethyl)diethylene Glycol (15). The above procedure was adopted: bp 127–129 °C (0.15 torr); mp 47–52 °C; pale yellow solid; 53% yield; ^{1}H NMR ($CDCl_3$) δ 2.55–2.91 (m, 2 H), 3.52 (s, 4 H), 3.40–3.92 (m, 7 H); IR (neat) 3350, 3280, 2930, 2870, 1470, 1360, 1120, 1080 cm^{-1}. Anal. Calcd for $C_5H_{13}NO_3$: C, 44.43; H, 9.69; N, 10.36. Found: C, 44.03; H, 9.67; N, 10.14.

(Aminomethyl)-15-crown-5 (5h) from 15. By a procedure similar to that for **5a**, the reaction between **15** (6.8 g, 0.05 mol) and triethylene glycol ditosylate (22.8 g, 0.05 mol) was done in the presence of sodium metal (2.3 g, 0.1 mol) dissolved in *tert*-butyl alcohol: bp 113–117 °C (0.005 torr; Kugelrohr distillation); yellow liquid; 53% yield; ^{1}H NMR ($CDCl_3$) δ 2.58–2.91 (m, NCH_2, 2 H), 3.13 (s, NH_2, 2 H), 3.32–3.99 (m, $OCHCH_2O$, OCH_2CH_2O, 19 H); mass spectrum, *m/e* (relative intensity) 249 (M^+, 0.6), 219 (4.3), 177 (9.3), 133 (25.6), 89 (49.1), 46 (100); IR (neat) 3350, 3290, 2930, 2870, 1460, 1360, 1120 cm^{-1}. Anal. Calcd for $C_{11}H_{23}NO_5$: C, 53.00; H, 9.30; N, 5.62. Found: C, 53.22; H, 9.45; N, 5.48.

(Aminomethyl)-18-crown-6 (6h) from 15. The procedure for **5a** was followed by using sodium metal, **15**, and tetraethylene glycol ditosylate as reactants: bp 119–122 °C (0.005 torr; Kugelrohr distillation); yellow liquid; 43% yield; ^{1}H NMR ($CDCl_3$) δ 2.53–2.88 (s + m, NCH_2, NH_2, 4 H), 3.42–3.91 (m, $OCHCH_2O$, OCH_2CH_2O, 23 H); mass spectrum, *m/e* (relative intensity) 293 (M^+, 0.3), 263 (1.4), 177 (5.3), 133 (15.8), 89 (51.4), 45 (100); IR (neat) 3360, 3300, 2940, 2870, 1460, 1350, 1100 cm^{-1}. Anal. Calcd for $C_{13}H_{27}NO_6$: C, 53.23; H, 9.28; N, 4.77. Found: C, 52.73; H, 9.58; N, 4.65.

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Registry No. **1a**, 83585-48-2; **1b**, 19737-19-0; **1c**, 5840-15-3; **1d**, 54127-58-1; **1e**, 1191-45-3; **1f**, 60095-23-0; **1g**, 22741-52-2; **1h**, 616-30-8; **2**, 37860-51-8; **3**, 41024-91-3; **4**, 638-56-2; **5a**, 83585-49-3; **5b**, 83585-50-6; **5c**, 83585-51-7; **5d**, 83585-52-8; **5e**, 83585-53-9; **5f**, 83585-54-0; **5g**, 83585-55-1; **5h**, 83585-56-2; **6a**, 83585-57-3; **6b**, 83585-58-4; **6c**, 83585-59-5; **6g**, 83585-60-8; **6h**, 83585-61-9; **7**, 83585-62-0; **8**, 83585-63-1; **11**, 83585-64-2; **12**, 83585-65-3; **13**, 83585-66-4; **14**, 83585-67-5; **15**, 83585-68-6; **16**, 83585-69-7; hexylamine, 111-26-2; ethylamine, 75-04-7; aniline, 62-53-3; benzylamine, 100-46-9; decylamine, 2016-57-1; 1,2-ethanediamine, 107-15-3; ethylene oxide, 75-21-8; triethylene glycol ditosylate, 19249-03-7; 15-crown-5, 33100-27-5; monaza-15-crown-5, 66943-05-3; tetraethylene glycol, 112-60-7; 3-chloro-1,2-propanediol, 96-24-2.

Reactions of Lithio Trimethylsilyl Compounds with Nitrones

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The reactions of lithio compounds, generated in situ from 2-[(trimethylsilyl)methyl]pyridine (**1**), *N,N*-dimethyl(trimethylsilyl)acetamide (**2**), and ethyl (trimethylsilyl)acetate (**3**) and LDA in THF, with various nitrones have been investigated. The lithio compounds of **1**–**3** reacted with α,*N*-diarylnitrones to give the corresponding (*E*)-alkenes together with azoxybenzene and/or azobenzene. On the other hand, the reaction of lithio derivative of **1** with α-aryl-*N*-alkylnitrones, α,*N*-dialkylnitrones, and cyclic nitrones afforded the aziridine compounds as the major products, accompanied by hydroxylamine derivatives in some cases. The lithio derivative of **2** or **3** reacted with α,*N*-dialkylnitrones and cyclic nitrones to give the aziridine and/or isoxazolidinone derivatives. The pathways for the formation of the above products are also described.

Several kinds of reactions using metalated α-silyl derivatives have recently been developed. In particular, an important application of these derivatives is in the conversion of carbonyl compounds to the corresponding al-

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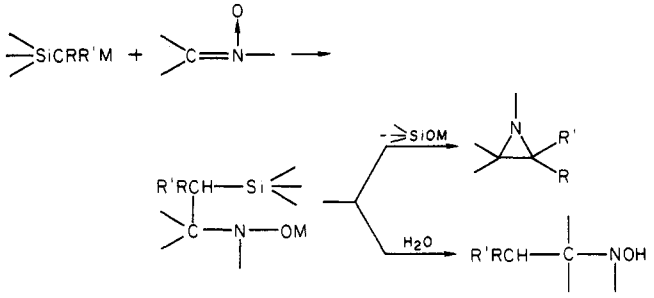
Table I. Reactions of Lithio Derivatives of 1–3 with Nitrones 4

silyl compd	nitrone	(E)-alkene no.	R	Ar	% yield	% yield PhN=N-(→O)Ph	% yield PhN=NPh	recovery of 4, %
1	4a	5a	2-pyridyl	Ph	72	20	30	
1	4b	5b	2-pyridyl	p-$MeOC_6H_4$	80	47	19	
1	4c	5c	2-pyridyl	p-$NO_2C_6H_4$	22.5	12.5	18.5	52
2	4a	6a	$CONMe_2$	Ph	39	31		7
2	4b	6b	$CONMe_2$	p-$MeOC_6H_4$	60.5	57	11	8
2	4c	6c	$CONMe_2$	p-$NO_2C_6H_4$	20	15	10	10
3	4a	7a	CO_2Et	Ph	49	38		8
3	4c	7c	CO_2Et	p-$NO_2C_6H_4$	26	30	7	38
3	4d	7d	CO_2Et	p-MeC_6H_4	41	36		

kenes (the Peterson reaction).[1-7] It has also been found that lithium-2-[(trimethylsilyl)methyl]pyridine reacted with Schiff bases to give 2-alkenylpyridines.[8] Upon consideration of the above olefination reactions, it seemed that the conversion of nitrones to aziridines and/or hydroxylamines could be effected by using metalated α-silyl derivatives as illustrated below:



M = metal

However, the reaction of metalated α-silyl derivatives with nitrones has not so far been investigated. In this paper we report the reactions of lithio derivatives generated in situ from 2-[(trimethylsilyl)methyl]pyridine (1), *N,N*-dimethyl(trimethylsilyl)acetamide (2), and ethyl (trimethylsilyl)acetate (3) and lithium diisopropylamide (LDA) with various nitrones.[9]

Results and Discussion

Reactions with α,*N*-Diarylnitrones. Treatment of 1 with LDA in tetrahydrofuran (THF) at −78 °C afforded a solution of the corresponding lithio derivative, which was allowed to react with an equimolar amount of α,*N*-diphenyl- (**4a**), α-(*p*-methoxyphenyl)-*N*-phenyl- (**4b**), or α-(*p*-nitrophenyl)-*N*-phenylnitrone (**4c**) at −78 °C for 1 h and then at room temperature for 2 h. After the reaction mixture was quenched with water, the products were purified by recrystallization and/or chromatography. Contrary to expectation, a mixture of the corresponding (*E*)-1-aryl-2-(2-pyridyl)ethene (**5**), azoxybenzene, and/or azobenzene was obtained in each case.

Similarly, the reactions of lithio compounds derived from 2 and 3 with **4a–c** and/or α-*p*-tolyl-*N*-phenylnitrone (**4d**) gave the corresponding (*E*)-alkenes **6** and **7**, together with azoxybenzene and/or azobenzene (Scheme I). Structural elucidation of alkenes **5–7** was accomplished on the basis of spectral data. The results are summarized in Table I.

Scheme I

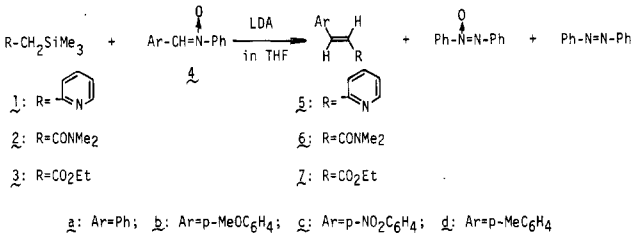


Table II. Reaction of the Lithio Derivative of 2-[(Trimethylsilyl)methyl]pyridine (1) with α-Aryl-*N*-alkylnitrones (8)

compd	Ar	R	product yield,[a] % 9	10
a	Ph	Me	48	14
b	p-$MeOC_6H_4$	Me	55.5[b]	
c	p-MeC_6H_4	Me	30	
d	Ph	$PhCH_2$	35	2

[a] In the reaction with **8b**, (*E*)-alkene **7b** was obtained in a trace amount. [b] Estimated from the ^1H NMR spectrum.

As shown in Table I, the yields of products in the reactions with **4b** and **4d**, which have an electron-donating methoxy or methyl group, are higher than those in the case of **4c**, which has an electron-withdrawing nitro group. In addition, the yield of alkene is nearly equal to the total yield of azoxybenzene and azobenzene in each case. On the basis of the above facts and the following evidence, the pathway for the reaction can be explained as depicted in Scheme II.

An initial nucleophilic attack of the lithio derivative of 1, 2, or 3 on the α-carbon atom in 4 yields adduct A. This is followed by dissociation of A into alkene 5, 6, or 7 and lithium *N*-(trimethylsiloxy)aniline B. It can be concluded that azoxybenzene and azobenzene arise from B, because the treatment of *N*-(trimethylsiloxy)aniline, prepared from phenylhydroxylamine and trimethylchlorosilane in the presence of triethylamine, with LDA in THF afforded a mixture of azoxybenzene and azobenzene. However, the mechanism for the formation of these compounds from B is not clear.

Since it is known that the Peterson reaction usually gives a mixture of (*E*)- and (*Z*)-alkenes, the reaction using 4 provides a selective synthetic means of obtaining (*E*)-alkenes. The driving force for the formation of alkene from A seems to be attributable to favorable elimination of relatively stable anion B. However, the mechanism for the selective formation of (*E*)-alkene is not evident.[10]

(1) Peterson, D. J. *J. Org. Chem.* **1968**, 33, 780.
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(3) Hartzell, S. L.; Sullivan, D. F.; Rathke, M. W. *Tetrahedron Lett.* **1974**, 1403.
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(5) Chan, T. H.; Moreland, M. *Tetrahedron Lett.* **1978**, 515.
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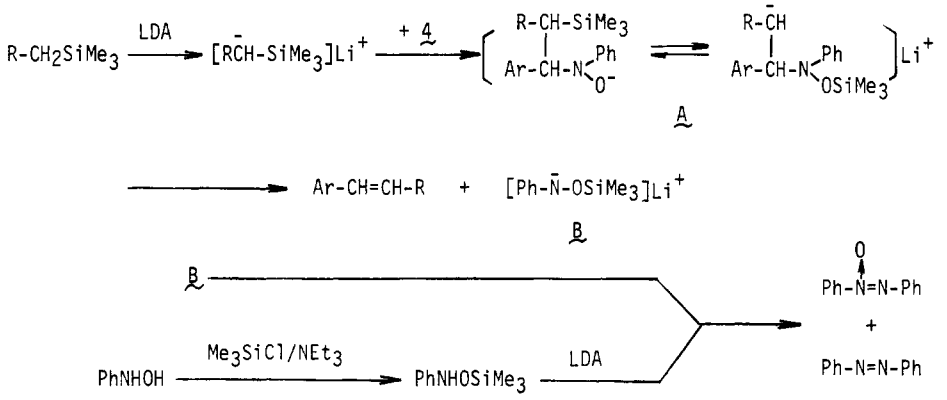
(7) Konakahara, T.; Takagi, Y. *Synthesis* **1979**, 192.
(8) Konakahara, T.; Takagi, Y. *Tetrahedron Lett.* **1980**, *21*, 2073.
(9) Part of this work has been reported as a preliminary communication: Tsuge, O.; Sone, K.; Urano, S. *Chem. Lett.* **1980**, 977.

Scheme II

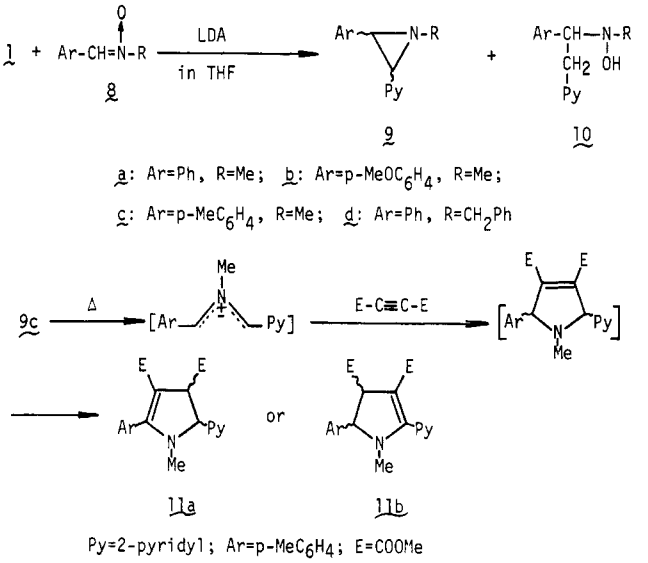


Reactions with α-Aryl-*N*-alkyl- and α,*N*-Dialkylnitrones. If an acyclic *N*-alkylnitrone is employed in place of *N*-arylnitrones **4**, the elimination of an anion like B from an initial adduct must be suppressed because of its lower stability. Under such circumstances, an aziridine and/or hydroxylamine derivative must be formed via the pathway described in the begining of the text.

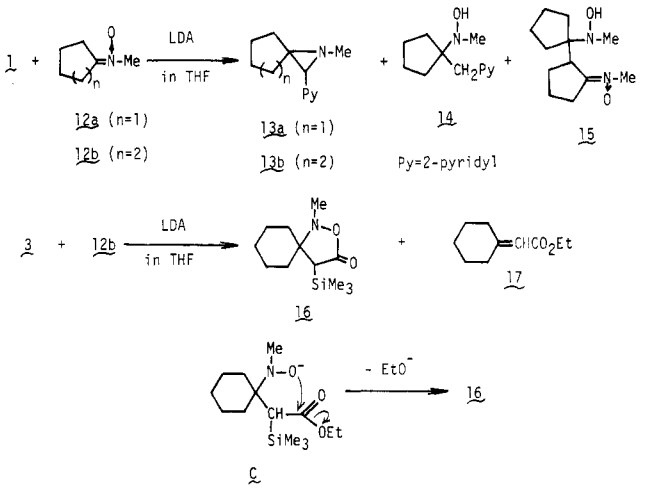
When the lithio derivative of **1** was allowed to react with α-phenyl-*N*-methyl- (**8a**), α-(*p*-methoxyphenyl)-*N*-methyl- (**8b**), α-*p*-tolyl-*N*-methyl- (**8c**), and α-phenyl-*N*-benzylnitrone (**8d**) under conditions similar to those in the reaction with **4**, the expected aziridines **9** were obtained as the major products, accompanied by hydroxylamine derivatives **10** in some cases. The yields of products are listed in Table II. However, the ^{1}H NMR spectra showed that all of the aziridines **9** were mixtures of cis and trans isomers. Treatment of **9a** (a mixture of cis and trans isomers) with picric acid readily afforded a mixture of picrates (mp 135–139 °C dec) from which a single picrate (mp 83–85 °C dec), crystallizing in a 1:2:2:1 ratio of aziridine, picric acid, ethanol, and water, was isolated by recrystallization from aqueous ethanol. The stereochemistry of aziridine in the picrate has not been clarified,[11] however. Further evidence of the aziridine structure for **9** was provided. The reaction of **9c** with dimethyl acetylenedicarboxylate (DMAD) in refluxing xylene afforded a 2-pyrroline compound whose structure was assumed as either **11a** or **11b**, which arose from a 1,3-dipolar cycloaddition of an azomethine ylide generated from ring opening of **9c**, followed by a hydrogen shift (Scheme III).

The lithio derivative of **1** reacted with cyclopentylidenemethylamine *N*-oxide (**12a**) under similar conditions to give the expected aziridine **13a** and hydroxylamine derivative **14** in low yields, together with a dimer (**15**) of **12a**. The same reaction with cyclohexylidenemethylamine *N*-oxide (**12b**) gave aziridine **13b** in 18% yield as the sole isolated product. In the reaction of the lithio derivative of **3** with **12b**, however, the expected aziridine and/or hydroxylamine derivatives were not formed, but instead, trimethylsilyl-substituted isoxazolidine compound **16** and alkene **17** were obtained. The formation of **16** can be readily explained as shown in Scheme IV. Thus a cyclization of the initial adduct C with concurrent elimination of ethoxide ion gives **16**.

Scheme III



Scheme IV

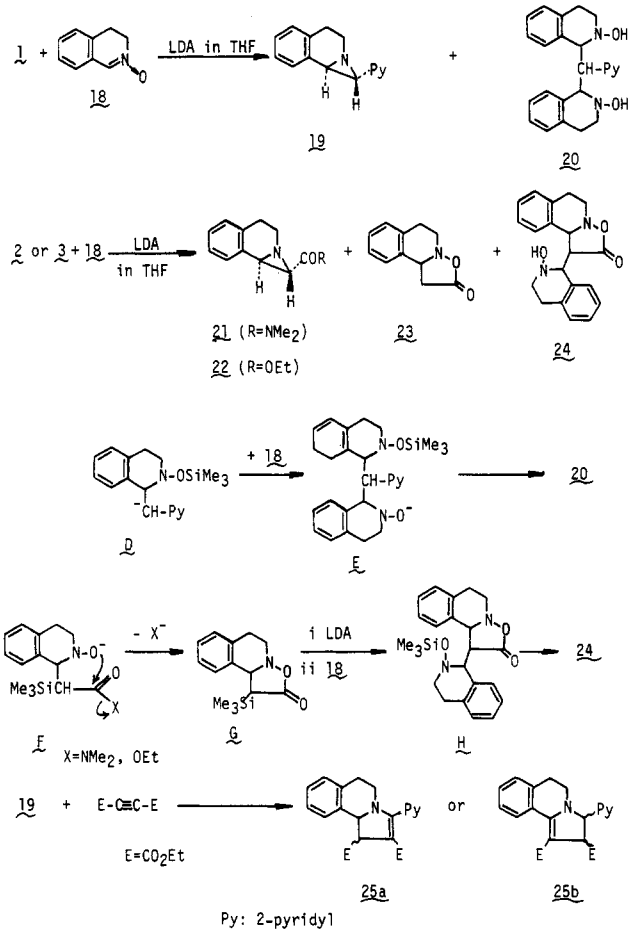


Reactions with Cyclic Nitrones. The reaction with a cyclic nitrone seemed to be particularly favorable for the aziridine formation, because the elimination of an anion like B is not possible in an adduct derived from the nitrone. We have thus investigated the reaction with cyclic nitrones. The lithio derivative of **1** reacted with 3,4-dihydroisoquinoline *N*-oxide (**18**) to give the expected aziridine **19** and bis[1-(2-hydroxy-1,2,3,4-tetrahydroisoquinolyl)](2-pyridyl)methane (**20**)[12] in 36% and 20% yields. In the

(10) Two pathways have been proposed for the formation of (*E*)-alkenes from (β-hydroxyalkyl)trimethylsilanes under basic conditions. One is the path via syn elimination of trimethylsilanol[24] and the other via a 1,3-migration of trimethylsilyl group, followed by anti elimination of trimethylsilanol.[25] The formation of (*E*)-alkenes in the present work might be explained by syn elimination of B from an initial threo adduct and/or by a 1,4-migration of trimethylsilyl group in an initial erythro adduct, followed by anti elimination of B.

(11) It is known that in 1,2,3-trisubstituted aziridines, the values of trans coupling constants (2–2.7 Hz) are smaller than those of cis coupling constants (5–6 Hz).[13] However, the value of the coupling constant between two methine hydrogens of aziridine in the picrate was 4.0 Hz.

Scheme V



reaction of lithio derivatives of **2** and **3** with **18**, the corresponding aziridines **21** and **22** were also formed as the major products together with two isoxazolidinone derivatives, **23** and **24**, respectively.

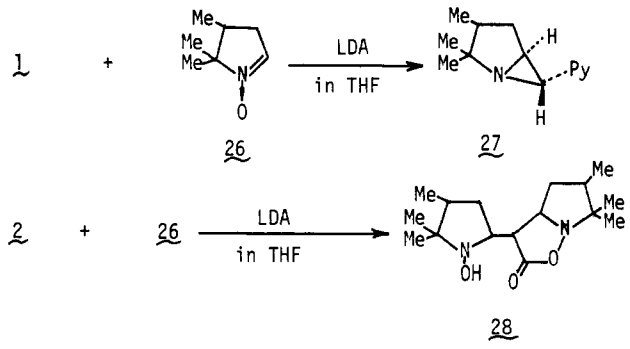
Structural elucidation of all products was accomplished on the basis of spectral data. It is known that in 1,2,3-trisubstituted aziridines the values of trans coupling constants (2–2.7 Hz) are smaller than those of cis coupling constants (5–6 Hz).[13] The coupling constants between two hydrogens in aziridine rings are 2.3, 2.5, and 2.2 Hz in **19**, **21**, and **22**, respectively. Thus, it can be concluded that the hydrogens in aziridine rings of **19**, **21**, and **22** are located trans.

The pathways for the formation of **20**, **23**, and **24** can be explained as shown in Scheme V. The initial adduct D derived from **1** and **18** reacts further with **18** to yield 1:2 adduct E, which on treatment with water gives stable compound **20**. In a manner similar to that mentioned for the formation of **16**, the initial adduct F derived from **2** or **3** and **18** undergoes a cyclization with concurrent elimination of dimethylamide or ethoxide ion to yield silylated isoxazolidinone G, similar to **16**. Silylated isoxazolidinone G partially undergoes metalation with LDA, and subsequent reaction of metalated G with **18** yields H, which on treatment with water gives **24**. It is evident that **23** is derived from G.

The structure of **19** was also supported by the formation of a 2-pyrroline, whose structure was assumed as either **25a** or **25b** from the reaction with DMAD.

(12) We wish to correct the structure proposed previously[9] for the hydroxylamine derivative to **20**.
(13) Deyrup, J. A.; Greenwald, R. B. *J. Am. Chem. Soc.* **1965**, *87*, 4538.

Scheme VI



In the reaction with 4,5,5-trimethyl-1-pyrroline *N*-oxide (**26**), the lithio derivative of **1** gave the expected *trans*-aziridine derivative **27** in 30% yield. On the other hand, the reaction of the lithio derivative of **2** with **26** did not give an aziridine, but instead isoxazolidinone compound **27** was obtained as the sole isolated product (Scheme VI). The formation of **27** can be interpreted by the same pathway as that for **24**.

However, the reaction of the lithio derivative of **1** with 2,5,5-trimethyl-1-pyrroline *N*-oxide did not take place. This is presumably attributable to the fact that a nucleophilic attack on the α-carbon atom of the nitrone is difficult, owing to a steric hindrance.

Experimental Section

Melting points were determined on a Yanagimoto micro melting point apparatus and were uncorrected. IR spectra were obtained on a JASCO IRA-1 spectrometer and mass spectra on a JEOL JMS-01SG-2 spectrometer (70 eV). NMR spectra were obtained (using tetramethylsilane as an internal reference) on Hitachi R-40 and JEOL SX-100 spectrometers.

Materials. 2-[(Trimethylsilyl)methyl]pyridine (**1**),[14] *N*,*N*-dimethyl(trimethylsilyl)acetamide (**2**),[15] and ethyl (trimethylsilyl)acetate (**3**)[15] were prepared by the reported methods.

α-Aryl-*N*-phenylnitrones **4a–d**,[16] α-phenyl-*N*-benzylnitrone (**8d**),[17] cyclopentylidene- (**12a**)[18] and cyclohexylidenemethylamine *N*-oxide (**12b**),[18] 3,4-dihydroisoquinoline *N*-oxide (**18**),[19] 4,5,5-trimethyl-1-pyrroline *N*-oxide (**26**),[20] and 2,5,5-trimethyl-1-pyrroline *N*-oxide[21] were prepared according to the reported methods. α-Aryl-*N*-methylnitrones **8a–c** were prepared from the reaction of the corresponding benzaldehyde with *N*-methylhydroxylamine hydrochloride in the presence of sodium acetate in ethanol at room temperature. **8a**: mp 83.5–85.5 °C; ^{1}H NMR ($CDCl_3$) δ 3.60 (3 H, s), 7.10–7.33 (4 H, m), 7.98–8.18 (2 H, m). Anal. Calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 71.21; H, 6.75; N, 10.33. **8b**: mp 69–70 °C; ^{1}H NMR ($CDCl_3$) δ 3.73 (6 H, s), 6.84 (2 H, d, J = 9.0 Hz), 7.14 (1 H, s), 8.16 (2 H, d, J = 9.0 Hz). Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.37; H, 6.79; N, 8.53. **8c**: mp 122–124.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.36, 3.81 (each 3 H, s), 7.18 (2 H, d, J = 9.0 Hz), 7.28 (1 H, s), 8.08 (2 H, d, J = 9.0 Hz). Anal. Calcd for $C_9H_{11}NO$: C, 72.45; H, 7.43; N, 9.39. Found: C, 72.31; H, 7.48; N, 9.53.

Reactions of Trimethylsilyl Compounds 1–3 with α,*N*-Diarylnitrones 4. A 15% solution of butyllithium (6.25 mL, 10 mmol) in hexane was added to a solution of diisopropylamine (1.01 g, 10 mmol) in THF (20 mL) at −78 °C with stirring under oxy-

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gen-free dry nitrogen. To the solution was added a solution of the appropriate trimethylsilyl compound (10 mmol) in THF (3 mL) dropwise over 5 min. After an additional 10 min at this temperature, a solution of the nitrone **4** (10 mmol) in THF (12–20 mL) was added dropwise to the mixture over 20 min. The resultant mixture was stirred for 1 h at −78 °C and then allowed to warm to room temperature with stirring during 1 h. After the mixture was stirred for an additional 2 h at room temperature, it was quenched with ice–water (100 mL) and completely extracted with ether. The extract was dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed on silica gel with hexane, benzene, and chloroform as the eluents to give the products. The yields of products are listed in Table I.

5a: colorless prisms; mp 90–90.5 °C (lit.[22] mp 90.5–91 °C); IR (KBr) 1630, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19, 7.70 (each d, 1 H, J = 17.0 Hz), 7.03–7.90 (m, 8 H), 8.58–8.75 (m, 1 H); mass spectrum, m/e 181 (M^+).

5b: pale yellow prisms; mp 75.5–77 °C; IR (KBr) 1630, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.77 (s, 3 H), 6.80–7.90 (m, 7 H), 7.06, 7.63 (each d, 1 H, J = 16.0 Hz), 8.56–8.70 (m, 1 H); mass spectrum, m/e 211 (M^+). Anal. Calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.50; H, 6.18; N, 6.64.

5c: yellow prisms; mp 125–127.5 °C; IR (KBr) 1595, 965 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26, 7.69 (each d, 1 H, J = 17.0 Hz), 7.10–8.70 (m, 8 H); mass spectrum, m/e 226 (M^+). Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.46; N, 12.38. Found: C, 68.96; H, 4.55; N, 12.31.

6a: colorless leaflets; mp 96–98 °C; IR (KBr) 1645, 1600, 995 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.95–3.25 (br, 6 H), 6.91, 7.71 (each d, 1 H, J = 16.0 Hz), 7.25–7.70 (m, 5 H); mass spectrum, m/e 175 (M^+). Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.49; H, 7.45; N, 7.93.

6b: colorless needles; mp 101–102 °C; IR (KBr) 1640, 1595, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.00–3.20 (br, 6 H), 3.81 (s, 3 H), 6.79, 7.68 (each d, 1 H, J = 16.0 Hz), 6.98–7.05, 7.40–7.70 (each m, 2 H); ^{13}C NMR ($CDCl_3$) δ 35.8, 37.2 (each q, NCH_3), 55.3 (q, OCH_3), 114.1, 114.9 (each d, =CH), 169.9 (s, C=O); mass spectrum, m/e 205 (M^+). Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.30; H, 7.36; N, 6.86.

6c: orange needles; mp 176–178 °C; IR (KBr) 1645, 1610, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.11, 3.24 (each s, 3 H), 7.09, 7.73 (each d, 1 H, J = 17.0 Hz), 7.50–8.00, 8.10–8.50 (each m, 2 H); mass spectrum, m/e 220 (M^+). Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 60.29; H, 5.40; N, 12.59.

7a: yellow oil; IR (neat) 1710, 1635, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.34 (t, 3 H), 4.31 (q, 2 H), 6.52, 7.81 (each d, 1 H, J = 16.0 Hz), 7.20–7.70 (m, 5 H); mass spectrum, m/e 176 (M^+). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.07; H, 6.73.

7c: colorless needles; mp 136–137 °C; IR (KBr) 1705, 1595, 980 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.36 (t, 3 H), 4.33 (q, 2 H), 6.61, 7.77 (each d, 1 H, J = 16.0 Hz), 7.74, 8.32 (each d, 2 H); mass spectrum, m/e 221 (M^+). Anal. Calcd for $C_{11}H_{11}NO_4$: C, 59.72; H, 5.01; N, 6.33. Found: C, 59.81; H, 4.93; N, 6.21.

7d: yellow oil; IR (neat) 1710, 1640, 985 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.18 (t, 3 H), 2.19 (s, 3 H), 4.14 (q, 2 H), 6.27, 7.58 (each d, 1 H, J = 16.0 Hz), 6.90–7.40 (m, 4 H); mass spectrum, m/e 190 (M^+). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.40. Found: C, 75.83; H, 7.45.

Reaction of *N*-(Trimethylsiloxy)aniline with LDA. A solution of trimethylchlorosilane (5.43 g, 50 mmol) in THF (25 mL) was added to a solution of phenylhydroxylamine (5.45 g, 50 mmol) and triethylamine (5.05 g, 50 mmol) in THF (30 mL) at room temperature. After the reaction mixture was stirred for 10 min, it was filtered to remove the precipitated triethylammonium chloride. To the filtrate was added at −78 °C a solution of LDA, prepared from diisopropylamine (5.05 g, 50 mmol) and a 15% hexane solution of butyllithium (31.25 mL, 50 mmol) in THF (100 mL). The resultant mixture was stirred for 1 h at this temperature and then allowed to warm to room temperature during 1 h. After the mixture was stirred for an additional 2 h at room temperature, it was quenched with ice–water (200 mL) and well extracted with ether. The extract was dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed on silica gel with hexane as an eluent to give 1.15 g (33%) of azobenzene and 1.34 g (27%) of azoxybenzene.

Reaction of 1 with α-Phenyl-*N*-methylnitrone (8a). A solution of **8a** (1.35 g, 10 mmol) in THF (12 mL) was added to a solution of the lithio derivative, generated in situ from **1** (1.65 g, 10 mmol) and LDA in THF in a similar manner as above, at −78 °C. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm to room temperature with stirring during 1 h. After the mixture was stirred for an additional 2 h at room temperature, it was worked up as described in the reaction with **4**. The dried and evaporated extract was chromatographed on silica gel. From the chloroform elution was obtained aziridine **9a** (999 mg, 48%) together with recovered **1** (57 mg, 3.5%) and **8a** (106 mg, 8%), and from the ethyl acetate elution the hydroxylamine **10a** (323 mg, 14%) was obtained. **9a**: colorless oil; ^1H NMR ($CDCl_3$) δ 2.25 (br, 1.6 H, NCH_3), 2.44 (br, 1.4 H, NCH_3), 3.16, 3.50 (each br, 1 H, >CH), 6.92–7.65 (m, 8 H), 8.50 (d, 1 H, J = 4.0 Hz); mass spectrum, m/e 210 (M^+). Picrate (from aqueous ethanol): mp 83–85 °C dec; ^1H NMR ($CDCl_3$) δ 1.05, 1.24 (each t, 3 H, J = 7.0 Hz), 2.80 (s, 3 H, NCH_3), 3.22–3.44 (m, 2 H, $>CH_2$), 3.71 (q, 2 H, J = 7.0 Hz), 4.70, 5.30 (each d, 1 H, >CH, J = 4.0 Hz), 5.44–6.28 (br, 6 H, OH), 6.63–7.78 (m, 8 H), 8.67 (d, 1 H, J = 5.0 Hz), 8.98 (s, 4 H). Anal. Calcd for $C_{30}H_{34}N_8O_{17}(C_{14}H_{14}N_2{\cdot}2C_6H_3N_3O_7{\cdot}2C_2H_6O{\cdot}H_2O)$: C, 46.27; H, 4.37; N, 14.39. Found: C, 46.43; H, 4.32; N, 14.60. **10a**: colorless oil; IR (neat) 3200 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.52 (s, 3 H, NCH_3), 3.44 (ddd, 2 H, CH_2, J = 14.0, 7.0, 5.0 Hz), 6.73–7.70 (m, 8 H), 8.49 (dd, 1 H, J = 5.0, 1.5 Hz); mass spectrum, m/e 228 (M^+). Anal. Calcd for $C_{14}H_{16}N_2O$: C, 73.65; H, 7.06; N, 12.27. Found: C, 73.76; H, 7.14; N, 12.48.

The reactions of **1** with other α-aryl-*N*-alkylnitrones **8b–d** were carried out under similar conditions, and the yields of products are listed in Table II.

9b: colorless oil; ^1H NMR ($CDCl_3$) δ 2.27 (br, 2 H, NCH_3), 2.45 (br, 1 H, NCH_3), 3.10, 3.40 (each br, 1 H, >CH), 3.75 (s, 3 H, OCH_3), 6.75–7.70 (m, 7 H), 8.50 (br d, 1 H); ^{13}C NMR ($CDCl_3$) δ 39.1, 49.9 (each d), 47.9, 55.2 (each q), 159.2 (s); mass spectrum, m/e 240 (M^+). **9c**: colorless oil; ^1H NMR ($CDCl_3$) δ 2.30 (s, 3 H), 2.30 (br, 2.1 H, NCH_3), 2.45 (br, 0.9 H, NCH_3), 3.15, 3.44 (each br, 1 H, >CH), 7.00–7.72 (m, 7 H), 8.50 (br d, 1 H, J = 5 Hz); ^{13}C NMR ($CDCl_3$) δ 20.8, 21.1 (each q, $C_6H_4CH_3$), 38.0, 39.1 (each q, NCH_3), 46.9, 47.7 (each d), 50.2, 50.5 (each d), 159.5 (s); mass spectrum, m/e 224 (M^+). **9d**: colorless oil; ^1H NMR ($CDCl_3$) δ 3.16–3.94 (br m, 4 H), 6.92–7.69 (m, 13 H), 8.50 (br, 1 H); mass spectrum, m/e 286 (M^+). **10d**: colorless needles; mp 149–151 °C; IR (KBr) 3180 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.36 (dd, 2 H, CH_2, J = 3.5, 6.0 Hz, changed to a doublet when treated with D_2O), 2.20, 2.62 (each d, 1 H, CH_2, J = 14.0 Hz), 4.15 (t, 1 H, >CH, J = 6.0 Hz, changed to a singlet when irradiated at δ 3.36), 6.64–7.53 (m, 15 H, Ar H + OH, changed to 14 H when treated with D_2O), 8.41 (br d, 1 H, J = 5 Hz); mass spectrum, m/e 304 (M^+). Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20. Found: C, 78.65; H, 6.70; N, 9.10.

Reaction of 9c with DMAD. A solution of **9c** (540 mg, 2.41 mmol) and DMAD (342 mg, 2.41 mmol) in xylene (20 mL) was refluxed under nitrogen for 5 h. The reaction mixture was evaporated in vacuo, and the residue was chromatographed on alumina with benzene–chloroform (1:1) as an eluent to give 122 mg (14%) of 2-pyrroline **11**: mp 151–152.5 °C; colorless needles; IR (KBr) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H), 2.45 (s, 3 H, NCH_3), 3.19, 3.44 (each s, 3 H, OCH_3), 4.33 (d, 1 H, >CH, J = 12.0 Hz), 4.95 (d, 1 H, N–CH<, J = 12.0 Hz), 6.92–7.94 (m, 7 H), 8.70 (br, 1 H); mass spectrum, m/e 366 (M^+). Anal. Calcd for $C_{21}H_{22}N_2O_4$: C, 68.83; H, 6.05; N, 7.65. Found: C, 68.90; H, 6.00; N, 7.58.

Reaction of 1 with Cyclopentylidenemethylamine *N*-Oxide (12a). A solution of **12a** (1.13 g, 10 mmol) in THF (10 mL) was added to a solution of the lithio derivative, generated in situ at −78 °C from **1** (1.65 g, 10 mmol) and LDA in THF as described above. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm to room temperature with stirring during 1 h. After the mixture was stirred for an additional 4 h at room temperature, it was worked up as described in the reaction with **4**. The dried and evaporated extract was chromatographed on silica gel to give 382 mg (34%) of dimer **15** and 257 mg (14%) of aziridine **13a** from the chloroform elution and

(22) Piechucki, C. *Synthesis* **1974**, 869.

162 mg (8%) of hydroxylamine compound **14** and 190 mg (17%) of unchanged **12a** from the ethanol elution, respectively.

13a: pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.08–2.04 (br m, 8 H), 2.50 (s, 3 H), 2.71 (s, 1 H), 6.97–7.25 (m, 2 H), 7.44–7.67 (m, 1 H), 8.47 (dd, 1 H, J = 5.0, 1.2 Hz); ^{13}C NMR ($CDCl_3$) δ 24.8, 25.8, 27.0, 30.9 (each t), 40.9 (q), 55.3 (d), 55.4 (s), 159.3 (s); mass spectrum, m/e 188 (M^+). Picrate of **13a**: mp 131.5–133 °C. Anal. Calcd for $C_{12}H_{16}N_2 \cdot 2C_6H_3N_3O_7$: C, 44.59; H, 3.43; N, 17.33. Found: C, 44.60; H, 3.56; N, 17.21. **14**: pale yellow oil; IR (neat) 3300 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.24–2.04 (m, 8 H), 2.67 (s, 3 H), 3.10 (s, 2 H), 6.70–7.30 (br, 1 H, OH, exchanged with D_2O), 7.06–7.37 (m, 2 H), 7.55–7.80 (m, 1 H), 8.55 (dd, 1 H, J = 5.0, 1.2 Hz); mass spectrum, m/e 206 (M^+); picrate of **14**, mp 159–160.5 °C. Anal. Calcd for $C_{12}H_{18}N_2O \cdot 2C_6H_3N_3O_7$: C, 43.38; H, 3.64; N, 16.86. Found: C, 43.38; H, 3.75; N, 16.56. **15**: colorless prisms; mp 101–102.5 °C; IR (KBr) 3120 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.28–1.92 (br, 15 H), 2.53, 2.65 (each s, 3 H), 3.12–3.37 (br, 1 H, OH, exchanged with D_2O); ^{13}C NMR ($CDCl_3$) δ 23.9, 25.3, 26.1, 28.6, 34.3 (each t), 36.4, 41.2 (each q), 60.2 (d), 77.6 (s), 108.3 (s); mass spectrum, m/e 226 (M^+). Anal. Calcd for $C_{12}H_{22}N_2O_2$: C, 63.68; H, 9.80; N, 12.39. Found: C, 63.74; H, 9.94; N, 12.41.

The reaction of the lithio derivative, generated in situ from **1** (1.65 g, 10 mmol) and LDA, with cyclohexylidenemethylamine *N*-oxide (**12b**; 1.27 g, 10 mmol) under the same conditions as above afforded 368 mg (18%) of aziridine **13b**, together with recovery of 660 mg (52%) of **12b**. **13b**: pale yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.12–1.80 (br, 10 H), 2.55 (s, 1 H), 2.60 (s, 3 H), 6.92–7.62 (m, 3 H), 8.40–8.46 (br d, 1 H); ^{13}C NMR ($CDCl_3$) δ 24.8, 25.9, 26.0, 28.8, 31.5 (each t), 38.6 (q), 49.2 (s), 55.1 (d), 158.6 (s); mass spectrum, m/e 202 (M^+); picrate, mp 155–157 °C. Anal. Calcd for $C_{13}H_{18}N_2 \cdot 2C_6H_3N_3O_7$: C, 45.46; H, 3.66; N, 16.97. Found: C, 45.50; H, 3.82; N, 16.78.

Reaction of 3 with 12b. The lithio derivative, generated in situ from **3** (1.60 g, 10 mmol) and LDA in THF, was allowed to react with **12b** (1.27 g, 10 mmol) in THF under the same conditions as above. After the reaction mixture was worked up as described in the reaction with **4**, chromatography of the extract on silica gel gave 52 mg (2%) of alkene **17** (from the hexane–benzene (1:1) elution), 379 mg (16%) of trimethylsilylated isoxazolidinone **16** (from the benzene elution), and 690 mg (54%) of unchanged **12b** (from the chloroform elution), respectively.

16: yellow oil; IR (neat) 1745, 1245, 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.16 (s, 9 H), 1.10–1.90 (m, 10 H), 2.23 (s, 1 H), 2.26 (s, 3 H); mass spectrum, m/e 241 (M^+). Anal. Calcd for $C_{12}H_{23}NO_2Si$: C, 59.75; H, 9.54; N, 5.81. Found: C, 59.61; H, 9.33; N, 5.65. **17**: yellow oil; IR (neat) 1710, 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.18 (t, 3 H), 1.53 (m, 6 H), 2.03–2.90 (m, 4 H), 4.05 (q, 2 H), 5.48 (s, 1 H); mass spectrum, m/e 168 (M^+). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.61; H, 9.65.

Reaction of 1 with 3,4-Dihydroisoquinoline *N*-Oxide (18). A solution of **18** (1.47 g, 10 mmol) in THF (20 mL) was added to a solution of the lithio derivative, generated in situ at −78 °C from **1** (1.65 g, 10 mmol) and LDA in THF as described above. The reaction mixture was stirred for 1 h at this temperature and then allowed to warm to room temperature during 1 h. After the mixture was stirred for an additional 2 h at room temperature, it was worked up as described in the reaction with **4**. Chromatography of the extract on silica gel gave 0.8 g (36%) of aziridine **19** from the chloroform elution and 374 mg (20%) of bis[1-(2-hydroxy-1,2,3,4-tetrahydroisoquinolyl)](2-pyridyl)methane (**20**) from the ethyl acetate elution, respectively.

19: colorless prisms; mp 85–86 °C; ^{1}H NMR ($CDCl_3$) δ 2.48–3.16 (m, 3 H), 3.22, 3.35 (each d, 1 H, J = 2.3 Hz), 3.40–3.74 (m, 1 H), 6.92–7.37 (m, 6 H), 7.48–7.72, 8.40–8.56 (each m, 1 H); ^{13}C NMR ($CDCl_3$) δ 23.6 (t), 41.2 (d), 42.5 (t), 44.7 (d); mass spectrum, m/e 222 (M^+). Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.29; H, 6.40; N, 12.67. **20**: colorless prisms; mp 190–192 °C; IR (KBr) 3250 cm^{-1}; ^{1}H NMR (Me_2SO-d_6) δ 2.60–3.02 (m, 8 H), 3.47 (t, 1 H, CH, J = 7.0 Hz), 4.60 (d, 2 H, >CH, J = 7.0 Hz), 6.88–7.61 (m, 11 H), 8.15–8.35 (br d, 1 H, J = 5 Hz), 8.27 (s, 2 H, OH, exchanged with D_2O); ^{13}C NMR (Me_2SO-d_6) δ 23.6, 49.1 (each t), 58.6, 65.6 (each d); mass spectrum, m/e 387 (M^+). Anal. Calcd for $C_{24}H_{25}N_3O_2$: C, 74.39; H, 6.50; N, 10.85. Found: C, 74.40; H, 6.56; N, 10.74.

Reaction of 2 with 18. A solution of **18** (1.47 g, 10 mmol) in THF (15 mL) was added to a solution of the lithio derivative, generated in situ at −78 °C from **2** (1.59 g, 10 mmol) and LDA in THF as described above. The reaction conditions and workup of the reaction mixture were same as those described in the reaction with **4**. The extract was chromatographed on silica gel to give isoxazolidinones **23** (180 mg, 9.5%) and **24** (10 mg) from the chloroform elution and 235 mg (11%) of aziridine **21** from the methanol elution, respectively.

21: colorless needles: mp 93–94 °C; IR (KBr) 1635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.48–2.68, 2.88–3.04 (each m, 2 H), 2.98, 3.08 (each s, 3 H), 3.31 (d, 1 H, J = 2.5 Hz), 3.38–3.64 (m, 1 H), 6.96–7.44 (m, 4 H); mass spectrum, m/e 216 (M^+). Anal. Calcd for $C_{13}H_{16}N_2O$: C, 72.19; H, 7.46; N, 12.95. Found: C, 72.02; H, 7.45; N, 12.79. **23**: colorless oil; IR (neat) 1775 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.60–3.76 (m, 4 H), 3.15 (d, 2 H, J = 7.0 Hz, changed to a singlet when irradiated at δ 5.04), 5.04 (t, 1 H, J = 7.0 Hz), 6.88–7.32 (m, 4 H); mass spectrum, m/e 189 (M^+). Anal. Calcd for $C_{11}H_{11}NO_2$: C, 69.84; H, 5.82; N, 7.40. Found: C, 69.73; H, 5.78; N, 7.45. **24**: colorless prisms; mp 148–150 °C dec; IR (KBr) 3310, 1770 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.48–4.02 (m, 8 H), 3.67 (t, 1 H, J = 2.0 Hz), 4.65, 5.21 (each d, 1 H, J = 2.0 Hz), 6.96–7.34 (m, 8 H), 7.67 (s, 1 H, OH, exchanged with D_2O); mass spectrum, m/e 336 (M^+). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.33. Found: C, 71.19; H, 5.86; N, 8.30.

Reaction of 3 with 18. A solution of **3** (3.2 g, 20 mmol) in THF (6 mL) was added dropwise to a solution of LDA, prepared from diisopropylamine (2.02 g, 20 mmol) and a 15% hexane solution of butyllithium (12.5 mL, 20 mmol) in THF (30 mL) at −78 °C. A solution of **18** (2.94 g, 20 mmol) in THF (40 mL) was added dropwise to the above solution at −78 °C. The resultant mixture was stirred at this temperature for 1 h and then allowed to warm to room temperature during 1 h. After the mixture was stirred at room temperature for an additional 1 h, it was worked up as described in the reaction with **4**. The extract was triturated with hexane to give 1.52 g of aziridine **22**. The hexane solution was evaporated in vacuo, and the residue was chromatographed on silica gel to give trace of **23** from the benzene–chloroform (1:1) elution and 85 mg of **22** and a trace of **24** from the chloroform elution, respectively.

22: colorless prisms; mp 114–116 °C (lit.[23] mp 115–117 °C); IR (KBr) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.31 (t, 3 H, changed to a singlet when irradiated at δ 4.21), 2.47–3.18 (m, 3 H), 2.87, 3.34 (each d, 1 H, J = 2.2 Hz), 3.40–3.72 (m, 1 H), 4.21 (dq, 2 H, J = 7.0, 1.2 Hz, changed to a singlet when irradiated at δ 1.31), 6.97–7.40 (m, 4 H); mass spectrum, m/e 217 (M^+). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.65; H, 7.05; N, 6.61.

Reaction of 19 with DMAD. A solution of **19** (380 mg, 1.71 mmol) and DMAD (243 mg, 1.71 mmol) in xylene (20 mL) was refluxed under nitrogen for 4 h. The reaction mixture was evaporated in vacuo, and the residue was chromatographed on alumina with chloroform-petroleum ether (7:3) as an eluent to give 164 mg (26%) of 2-pyrroline derivative **25**: pale yellow crystals; mp 139–142 °C; IR (KBr) 1735, 1685 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.85–3.10 (m, 4 H), 3.16, 3.60 (each s, 3 H), 4.45, 5.13 (each d, 1 H, J = 12.0 Hz), 7.06–7.75 (m, 4 H), 8.54, 8.80–8.95 (each m, 1 H); mass spectrum, m/e 364 (M^+). Anal. Calcd for $C_{23}H_{24}N_2O_4$: C, 69.21; H, 5.53; N, 7.69. Found: C, 69.02; H, 5.56; N, 7.58.

Reaction of 1 with 4,5,5-Trimethyl-1-pyrroline *N*-Oxide (26). A solution of **26** (1.27 g, 10 mmol) in THF (15 mL) was added to a solution of the lithio derivative, generated in situ at −78 °C from **1** (1.65 g, 10 mmol) and LDA in THF. The reaction conditions and workup of the reaction mixture were same as in the reaction with **4**. The extract was chromatographed on silica gel to give 609 mg (30%) of aziridine **27** from the chloroform elution and 352 mg (28%) of unchanged **26** from the methanol elution, respectively.

27: pale yellow crystals; mp 50–53 °C; ^{1}H NMR ($CDCl_3$) δ 0.90 (d, 3 H, J = 6.0 Hz), 1.08, 1.20 (each s, 3 H), 1.56–1.82 (m, 2 H), 2.20–2.37 (m, 1 H), 2.49 (dd, 1 H, J = 4.0, 2.5 Hz), 2.84 (d, 1 H,

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J = 2.5 Hz), 6.96-7.24 (m, 2 H), 7.44-7.67, 8.36-8.52 (each m, 1 H); mass spectrum, m/e 202 (M^+). Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.27; H, 8.98; N, 13.57.

Reaction of 2 with 26. A solution of **26** (1.27 g, 10 mmol) in THF (15 mL) was added to a solution of the lithio derivative, generated in situ from **2** (1.59 g, 10 mmol) and LDA in THF at -78 °C. The reaction conditions and workup of the reaction mixture were same as those in the reaction with **4**. The extract was chromatographed on silica gel with chloroform as an eluent to give 170 mg (11.5%) of isoxazolidinone compound **28**: colorless leaflets; mp 116-117 °C; IR (KBr) 3300, 1760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (s, 3 H), 0.88 (d, 3 H, J = 10.0 Hz), 0.92 (s, 3 H), 0.93 (d, 3 H, J = 10.0 Hz), 1.08, 1.32 (each s, 3 H), 1.44-2.50 (m, 6 H), 2.86 (dd, 1 H, J = 2.6, 1.0 Hz), 3.26 (ddd, 1 H, J = 9.2, 4.0, 2.6 Hz), 4.08 (ddd, 1 H, J = 8.0, 5.9, 1.0 Hz), 6.43 (br, 1 H, OH); ^{13}C NMR ($CDCl_3$) δ 12.1, 13.8, 14.5, 19.6, 22.5, 25.1 (each q), 32.3 (t), 37.8, 39.7 (each d), 39.9 (t), 55.7, 64.8 (each d), 66.0 (s), 66.9 (d), 71.9 (s), 175.8 (s); mass spectrum, m/e 296 (M^+). Anal. Calcd for $C_{16}H_{28}N_2O_3$: C, 64.83; H, 9.52; N, 9.45. Found: C, 64.79; H, 9.52; N, 9.40.

Registry No. 1, 17881-80-0; **2**, 23184-28-3; **3**, 4071-88-9; **4a**, 1137-96-8; **4b**, 3585-93-1; **4c**, 3585-90-8; **4d**, 19865-55-5; **5a**, 538-49-8; **5b**, 19036-99-8; **5c**, 24470-06-2; **6a**, 17431-39-9; **6b**, 21469-81-8; **6c**, 34912-68-0; **7a**, 4192-77-2; **7c**, 24393-61-1; **7d**, 24393-49-5; **8a**, 3376-23-6; **8b**, 16089-66-0; **8c**, 16089-63-7; **8d**, 3376-26-9; *cis*-**9a**, 83511-52-8; *trans*-**9a**, 83511-69-7; **9a** dipicrate, 83511-54-0; *cis*-**9b**, 83511-55-1; *trans*-**9b**, 83511-70-0; *cis*-**9c**, 83511-56-2; *trans*-**9c**, 83511-71-1; *cis*-**9d**, 83511-57-3; *trans*-**9d**, 83511-72-2; **10a**, 83511-58-4; **10d**, 83511-59-5; **11**, 83511-75-5; **12a**, 72552-74-0; **12b**, 58751-78-3; **13a**, 83511-60-8; **13a** dipicrate, 83511-61-9; **13b**, 83511-62-0; **13b** dipicrate, 83511-65-3; **14**, 83511-63-1; **14** dipicrate, 83511-64-2; **15**, 83511-73-3; **16**, 83511-66-4; **17**, 1552-92-7; **18**, 24423-87-8; **19**, 75997-55-6; **20**, 83511-67-5; **21**, 75997-58-9; **22**, 64890-49-9; **23**, 33934-42-8; **24**, 83511-68-6; **25**, 83511-77-7; **26**, 3146-84-7; **27**, 75997-57-8; **28**, 75997-59-0; DMAD, 762-42-5; benzaldehyde, 100-52-7; *p*-anisaldehyde, 123-11-5; *p*-tolualdehyde, 104-87-0; *N*-methylhydroxylamine hydrochloride, 4229-44-1; trimethylchlorosilane, 75-77-4; phenylhydroxylamine, 100-65-2; *N*-(trimethylsiloxy)aniline, 58751-79-4; azobenzene, 103-33-3; azoxybenzene, 495-48-7.

Directed Lithiation of 2-Phenyl- and 2-(*o*-Methylphenyl)imidazoline

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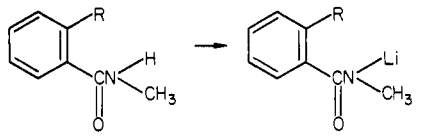
2-Phenyl- and 2-(*o*-methylphenyl)imidazoline have been converted into their ortho- and α-lithiated species, respectively, by treatment with *n*-BuLi–hexane in THF. Treatment of these reagents with a variety of nucleophiles gave ortho- and α-substituted products.

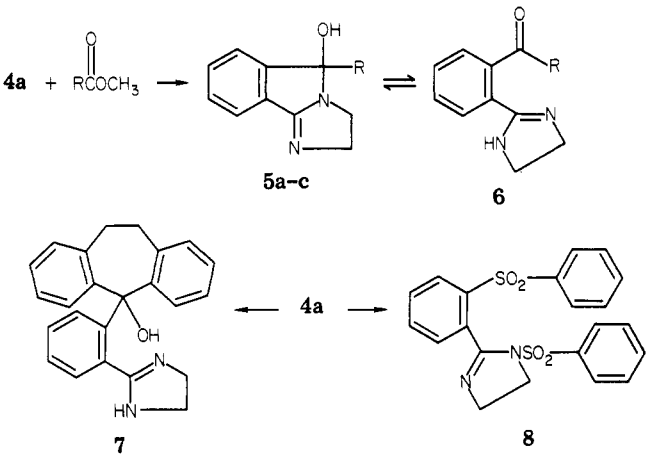
Hauser has reported that *N*-methylbenzamide[1] (**1a**) and *N*-methyl-*o*-toluamide[2] (**1b**) can undergo deprotonation



1a, R = H **2a**, R = Li
b, R = CH_3 **b**, R = CH_2Li

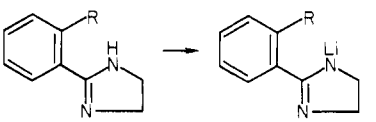
and ortho or benzylic lithiation,[3] respectively, when treated with *n*-BuLi in an inert ether solvent to form the dilithiated species **2a** or **2b**. Compounds that undergo dilithiation similar to that for **2a** have been reported for benzene derivatives with an ortho CSNHR,[4] SO_2NHR,[5] CH_2OH,[6] SO_3H,[7] or $NHCO_2$-*t*-Bu[8] group while toluene derivatives with an ortho CSNHR[4] or CO_2H[10] group give rise to dilithiated species similar to **2b**.

Scheme I



5a-c **6** **7** **8**

In the present work we report that the above lithiation reactions can be extended to 2-phenylimidazoline (**3a**) and



3a, R = H **4a**, R = Li
b, R = CH_3 **b**, R = CH_2Li

2-(*o*-methylphenyl)imidazoline (**3b**) to form the dilithiated **4a** and **4b** which can undergo reactions with a variety of nucleophiles.

The ortho lithiation of **3a** was maximized by studying the reaction of methyl *p*-chlorobenzoate to form the

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