Mono-deoxygenation of Nitroalkanes, Nitrones, and Heterocyclic *N*-Oxides by Hexamethyldisilane through 1,2-Elimination: Concept of "Counterattack Reagent"

Jih Ru Hwu,*[,†,‡] Wen Nan Tseng,[†] Himatkumar V. Patel,[†] Fong Fuh Wong,[†] Den-Nan Horng,[§] Ben Ruey Liaw,[¶] and Lung Ching Lin[¶]

Organosilicon and Synthesis Laboratory, Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China, Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan 11529, Republic of China, Department of Physics and Chemistry, Chinese Military Academy, P.O. Box 90602-6, Feng-shan, Taiwan, Republic of China, and Department of Chemistry, National Taiwan University, Taipei, Taiwan, Republic of China

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Transformation of secondary nitroalkanes to ketoximes was achieved in 40−73% yields by treatment of the corresponding nitronate anions with hexamethyldisilane. In this new mono-deoxygenation process, hexamethyldisilane acted as a "counterattack reagent". The conversion of nitrones to imines was also achieved in 82−88% yields by use of trimethylsilyllithium. Similarly, heterocyclic *N*-oxides were converted to the corresponding *N*-heterocycles in 73−86% yields. These deoxygenation processes presumably involve a 1,2-elimination.

Introduction

Functioning as a "counterattack reagent",[1,2] hexamethyldisilane can be used to bring about various organic functional group transformations. Examples include the conversion of allylic alcohols to allyltrimethylsilanes,[3] conversion of hydrazines to 2-tetrazenes,[4] polysilylation of hydrazines,[5] and oxidation of benzyl alcohols to phenones[6] or benzaldehyde.[7] This concept was also applied in a direct syntheses of ketene thioacetals and 2-trimethylsilyl-1,3-dithiane derivatives from 1,3-dithiane.[8] In addition, hexamethyldisilane can function as a reducing agent[9] and a source of trimethylsilyl anion[10] as well as halotrimethylsilanes.[11]

Hexamethyldisilane can deoxygenate pyridine *N*-oxide to give pyridine in the presence of methyllithium in a catalytic amount.[12] This reaction could go through a 1,2-elimination of α-trimethylsilyl *N*-oxide. These findings prompted us to investigate its utility as a general deoxygenation agent.

Reduction plays an important role in nitro chemistry.[13,14] A limited number of reagents can partially reduce nitroalkanes to give the corresponding oximes in appealing yields.[13,15] Herein we report on the use of hexamethyldisilane for facile mono-deoxygenation of nitroalkanes to give the corresponding ketoximes under mild conditions. Furthermore, we applied the same strategy involving 1,2-elimination in the deoxygenations of nitrones to the corresponding imines and heterocyclic *N*-oxides to the corresponding *N*-heterocycles.

Results

A new method is illustrated in Scheme 1 for the reduction of nitroalkanes **1a**−**10a** to the corresponding ketoximes. We treated secondary nitro compounds **1a**−**5a** with 1.1 equiv of *n*-BuLi in THF at 0 °C and then with 1.1 equiv of hexamethyldisilane at room temperature for 24 h. After normal workup and purification by column chromatography, we obtained the corresponding ketoximes **1b**−**5b** in 60−73% yields. By the same method, cyclic nitroalkanes **6a**−**8a** were converted to ketoximes **6b**−**8b** in 40−69% yields and bicyclic nitroalkanes **9a** and **10a** to ketoximes **9b** and **10b**, respectively, in 71−72% yields.

Different bases (such as NaH and KH) in various solvents (including ether and HMPA−THF) can also be used for accomplishment of the transformation shown in Scheme 1. Nevertheless, the oxime products were often obtained in lower yields.

† National Tsing Hua University.

‡ Academia Sinica; recipient of 1997 The Third World Academy of Sciences Award in Chemistry.

§ Chinese Military Academy.

¶ National Taiwan University.

(1) Hwu, J. R.; Gilbert, B. A. *Tetrahedron* **1989**, *45*, 1233.

(2) Hwu, J. R.; Tsay, S.-C. *Chem. Commun.* **1998**, 161.

(3) Hwu, J. R.; Lin, L. C.; Liaw, B. R. *J. Am. Chem. Soc.* **1988**, *110*, 7252.

(4) Hwu, J. R.; Wang, N.; Yung, R. T. *J. Org. Chem.* **1989**, *54*, 1070.

(5) Hwu, J. R.; Wang, N. *Tetrahedron* **1988**, *44*, 4181.

(6) Hwu, J. R. *J. Chem. Soc., Chem. Commun.* **1985**, 452.

(7) Hwu, J. R.; Tsay, S.-C.; Wang, N.; Hakimelahi, G. H. *Organometallics* **1994**, *13*, 2461.

(8) Hwu, J. R.; Lee, T.; Gilbert, B. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 3219.

(9) For representative examples, see: (a) Vorbrüggen, H.; Krolikiewicz, K. *Tetrahedron Lett.* **1984**, *25*, 1259. (b) Watanabe, H.; Saito, M.; Sutou, N.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1981**, 617. (c) Tsui, F.-P.; Vogel, T. M.; Zon, G. *J. Org. Chem.* **1975**, *40*, 761.

(10) For the generation of trimethylsilyl anions, see: (a) Hudrlik, P. F.; Waugh, M. A.; Hudrlik, A. M. *J. Organomet. Chem.* **1984**, *271*, 69. (b) Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063.

(11) For representative examples, see: (a) Olah, G. A.; Gupta, B. G. B.; Malhotra, R.; Narang, S. C. *J. Org. Chem.* **1980**, *45*, 1638. (b) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 612. (c) Sakurai, H.; Shirahata, A.; Sasaki, K.; Hosomi, A. *Synthesis* **1979**, 740.

(12) (a) Hwu, J. R.; Wetzel, J. M. *J. Org. Chem.* **1985**, *50*, 400. (b) Tsay, S.-C.; Patel, H. V.; Hwu, J. R. *Synlett* **1998**, 939.

(13) Hudlicky, M. *Reduction in Organic Chemistry*; John Wiley: New York, 1984; pp 69−76.

(14) Brown, B. R. *The Organic Chemistry of Aliphatic Nitrogen Compounds*; Oxford University Press: New York, 1994; pp 433−443.

(15) For representative examples, see: (a) Albanese, D.; Landini, D.; Penso, M. *Synthesis* **1990**, 333. (b) Barton, D. H. R.; Fernandez, I.; Richard, C. S.; Zard, S. Z. *Tetrahedron* **1987**, *43*, 551. (c) Olah, G. A.; Narang, S. C. Field, L. D.; Fung, A. P. *J. Org. Chem.* **1983**, *48*, 2766. (d) Hanson, J. R. *Synthesis* **1974**, 1.

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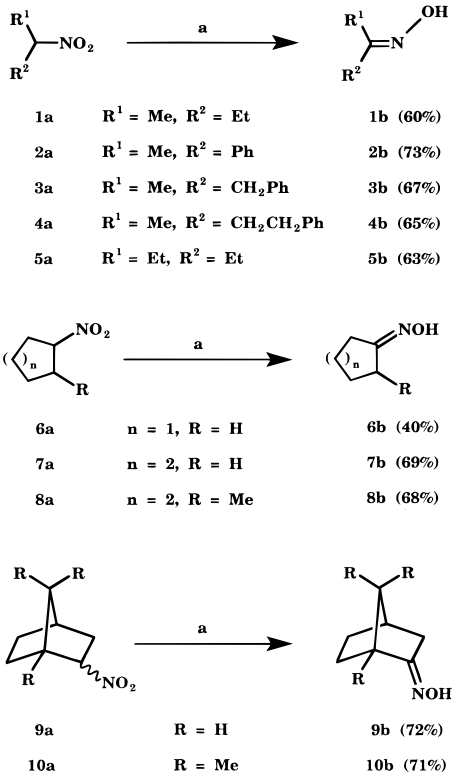
Scheme 1



(a) *n*-BuLi (1.1 equiv), $Me_3SiSiMe_3$ (1.1 equiv), 0–25 °C, 24 h

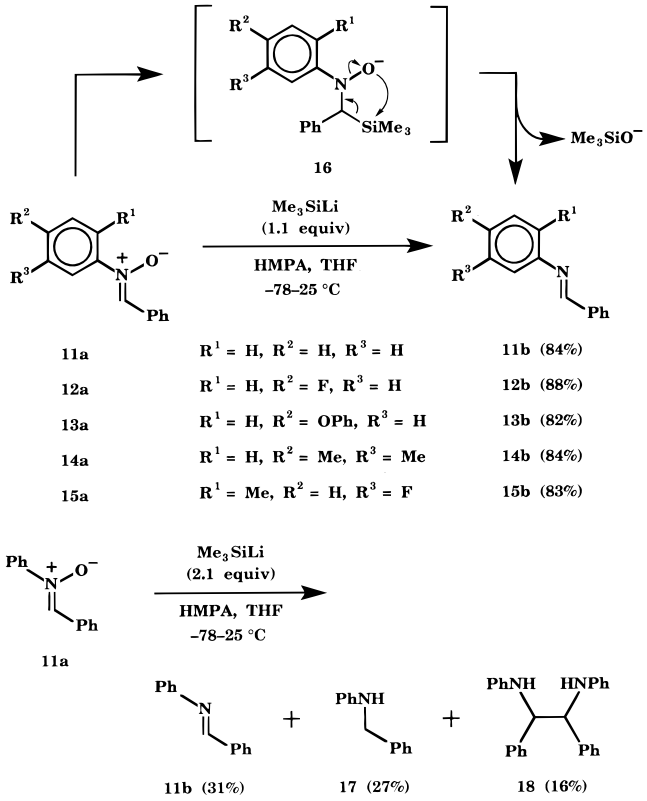
Furthermore, we treated hexamethyldisilane with methyllithium in HMPA−THF at 0 °C to generate Me_3SiLi.[10] In situ, we allowed Me_3SiLi (∼1.1 equiv) to react with nitrones **11a**−**15a**[16] at −78 °C for 20 min and at room temperature for 4−6 h (Scheme 2). The corresponding imines **11b**−**15b** were obtained in 82−88% yields after normal workup and purification. Reduction of nitrone **11a** by use of a catalytic amount of trimethylsilyllithium (0.10 equiv) and hexamethyldisilane (1.0 equiv) in HMPA−THF, however, afforded the corresponding imine **11b** in poor yield. On the other hand, reaction of nitrone **11a** with an excess of Me_3SiLi (2.1 equiv) afforded a mixture containing *N*-benzylaniline (**17**, 27%), the dimer 1,2-dianilino-1,2-diphenylethane (**18**, 16%), and the expected mono-deoxygenated product imine **11b** (31%).

In studies on the use of hexamethyldisilane as a versatile reagent in organic synthesis, we have reported the deoxygenation of pyridine *N*-oxide (**19a**) to pyridine (**19b**).[12] To realize the generality of this deoxygenation process, we subjected various heterocyclic *N*-oxides to the same reaction conditions (see Scheme 3).

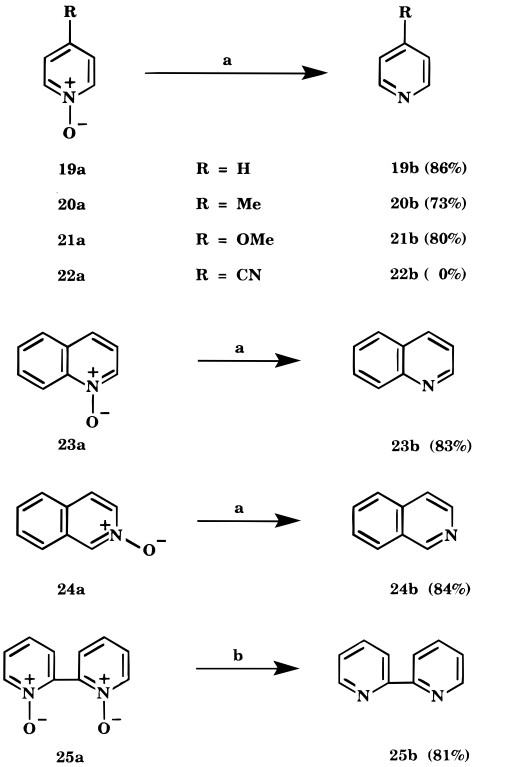
We found that deoxygenation by Me_3SiLi proceeded smoothly for a pyridine *N*-oxide bearing an electron-donating group, such as Me (i.e., **20a**) and OMe (i.e., **21a**). Deoxygenation, however, did not occur to a pyridine *N*-oxide bearing an electron-withdrawing cyano group (i.e., **22a**).

Furthermore, we treated quinoline *N*-oxide (**23a**) and isoquinoline *N*-oxide (**24a**) with Me_3SiLi in HMPA−THF. The corresponding quinoline (**23b**) and isoquinoline (**24b**)

Scheme 2



Scheme 3

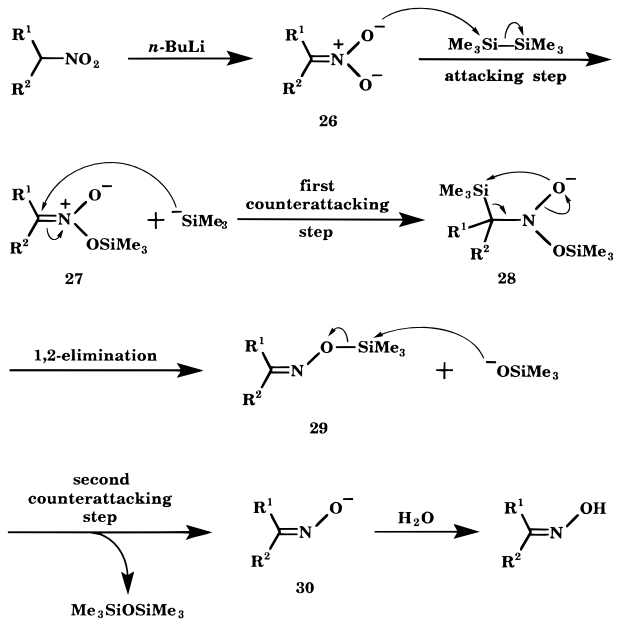


(a) Me_3SiLi (1.1 equiv), HMPA, THF, –78–25 °C
(b) Me_3SiLi (2.1 equiv), HMPA, THF, –78–25 °C

were obtained in 83% and 84% yields, respectively. We also extended the above strategy to the deoxygenation of dipyridine*N*-oxide **25a**. Thus reaction of 2,2′-bipyridine *N*,*N*′-dioxide (**25a**) with hexamethyldisilane (2.2 equiv)

(16) For their preparation, see: Brüning, I.; Grashey, R.; Hauck, H.; Huisgen, R.; Seidl, H. *Organic Syntheses;* Wiley: New York, 1973; Collect. Vol. V, p 1124.
(17) Hwu, J. R.; Tsay, S.-C. *Tetrahedron* **1990**, *46*, 7413.

Scheme 4



in the presence of methyllithium (2.1 equiv) in HMPA−THF afforded the 2,2′-bipyridine (**25b**) in 81% yield.

Discussion

Recently, we have reported a general procedure for the conversion of primary nitro compounds into the corresponding thiohydroxamic acids using $Me_3SiSSiMe_3$ under alkaline conditions.[17] Analogy was extended for the transformation of primary nitro compounds to nitriles by use of $Me_3SiSSiMe_3$ as a counterattack reagent.[18] We have also reported the conversion of secondary nitro compounds to ketoximes by using sulfur-containing reagents $Me_3SiSSiMe_3$ or $MeSSiMe_3$ in the presence of base.[17] To avoid the use of the noxious sulfur-containing reagents, we successfully developed a new method for the conversion of secondary nitro compounds to ketoximes, in which the nontoxic reagent $Me_3SiSiMe_3$ functioned as a counterattack reagent.

Halogenated silanes or disilanes can be used in the deoxygenation of organic oxides, such as phosphine oxides, sulfoxides, and amine oxides.[19] These halogenated silicon-containing reagents are often corrosive and moisture-sensitive. It would be advantageous to accomplish the mono-deoxygenations of nitro compounds, nitrones, and heterocyclic *N*-oxides by use of the mild and neutral $Me_3SiSiMe_3$.

Deoxygenation of Secondary Nitroalkanes to Ketoximes. A plausible mechanism associated with the new method for mono-deoxygenation of nitroalkanes is depicted in Scheme 4. The nitronates **26**, generated from a secondary nitro compound under basic condition, attacks hexamethyldisilane to give silyl nitronates **27** and Me_3Si^-.[20] Colvin et al.[21] reported the nucleophilic attack of primary silyl nitronates by organolithium reagents to give ketoximes. Secondary silyl nitronates, however, react with organolithium reagents in a different manner to afford α-alkylated oximes via a nitroso intermediate.[21]

We believe that the Me_3Si^- formed in situ can counterattack the electrophilic carbon center in **27** to form the adducts **28**, which undergo a 1,2-*syn*-elimination to give intermediates **29**. This process is similar to the Peterson olefination.[22] The resultant intermediates **29**, in turn, can undergo counterattack by Me_3SiO^- to form **30**. Protonation of **30** by water during workup gives the desired ketoximes. Alternatively, we cannot rule out the possibility that Me_3Si^- formed in situ attacks the silylated *O*-atom of silyl nitronates **27** to give **30** directly.

This newly developed mono-deoxygenation of secondary nitroalkanes to ketoximes can be regarded as a "reductive Nef reaction".[23] In the entire transformation, hexamethyldisilane acts as a "counterattack reagent".

Both cyclic and acyclic secondary nitroalkanes gave the desired ketoximes in good yields under the applied conditions. Nevertheless, attempts to convert primary nitroalkanes to the corresponding aldoximes under the same conditions failed. The failure of this transformation could be attributed to the elimination of Me_3SiOH and thus results in the formation of labile nitrile oxides.

Deoxygenation of Nitrones to Imines. Nitrones can be deoxygenated by phosphines or phosphites.[24] Use of lithium aluminum hydride, sodium borohydride, or Raney nickel leads to reduction of the C−N double bond in nitrones.[24] We considered that nitrones and silyl nitronates **27** possess a similar electronic structure. Thus conditions for mono-deoxygenation of nitro compounds could be applicable to the conversion of nitrones to imines (Scheme 2).

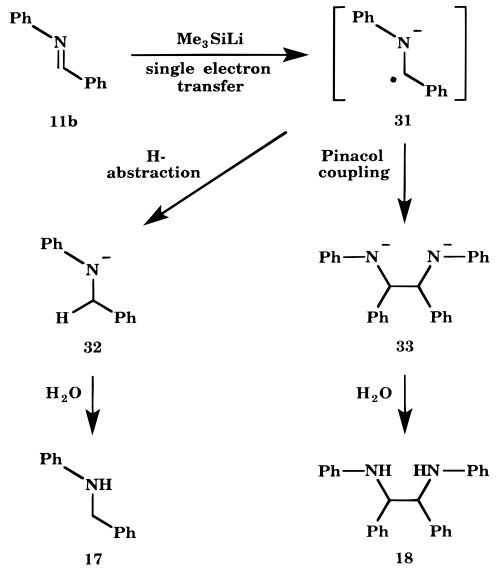
Nitrones react easily with alkyllithium or Grignard reagents to give 1,3-addition products.[24,25] In the deoxygenation process, the first step involves the attack of Me_3Si^- on the electrophilic carbon atom in nitrones **11a**−**15a** (Scheme 2). Then the 1,3-addition intermediates **16** may undergo a 1,2-elimination to form imines **11b**−**15b**.

Deoxygenation of nitrones **11a**−**15a** generated Me_3SiO^- as a side species. It can cleave the Si−Si bond of the remaining hexamethyldisilane to regenerate Me_3Si^- along with $Me_3SiOSiMe_3$.[20] Accordingly, it is possible to propagate the reaction further and result in complete conversion of nitrones to imines by initiation of the deoxygenation process with base in a catalytic amount. To explore the possibility of the catalytic cycle, we carried out the reduction of nitrone **11a** with a catalytic amount of MeLi and an equimolar amount of hexamethyldisilane at room temperature. Isolation of the corresponding imine **11b** in a modest yield (26%) indicates the catalytic cycle is feasible, but not efficient enough for organic synthesis.

We found that reaction of nitrone **11a** with an excess of Me_3SiLi afforded the desired imine **11b** in only 31%

(18) Tsay, S.-C.; Gani, P.; Hwu, J. R. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1493.
(19) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 328−336.
(20) For reports on the cleavage of the Si−Si bond by alkoxide anions, see: (a) Sakurai, H.; Okada, A.; Kira, M.; Yonezawa, K. *Tetrahedron Lett.* **1971**, 1511. (b) Watanabe, H.; Higuchi, K.; Kobayashi, M.; Hara, M.; Koike, Y.; Kitahara, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1977**, 534.
(21) Colvin, E. W.; Robertson, A. D.; Seebach, D.; Beck, A. K. *J. Chem. Soc., Chem. Commun.* **1981**, 952.
(22) For reviews, see: (a) Ager, D. J. *Org. React.* **1990**, *38*, 1. (b) Hudrlik, P. F.; Agwaramgbo, E. L. O. In *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Eds.; Ellis Horwood: Chichester, 1988; pp 95−104.
(23) Pinnick, H. W. *Org. React.* **1990**, *38*, 655.
(24) Torssell, K. B. G. *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*; VCH: New York, 1988; pp 75−93.
(25) Breuer, E. In *The Chemistry of Amino, Nitroso and Nitro Compounds and their Derivatives*; Patai, S., Ed.; John Wiley: New York, 1982; pp 459−564.

Scheme 5



yield. The unexpected byproducts include *N*-benzylaniline (**17**) through over-reduction and 1,2-dianilino-1,2-diphenylethane (**18**) through dimerization. Sakurai et al.[26] reported that Me_3Si^- can donate one electron to certain organic compounds. Thus a single electron transfer from Me_3Si^- to the primary product imine **11b** could occur to give the radical anion **31** (see Scheme 5). Then H-abstraction by radical anion **31** followed by protonation of the resultant anionic intermediate **32** affords benzylamine **17**. On the other hand, intermediate **31** undergoes a Pinacol coupling[27] to give bisamine **18** via the dianionic intermediate **33**. Hence it is necessary to use an equimolar amount of Me_3SiLi, not in excess, in the mono-deoxygenation of nitrones to give imines in high yields.

Deoxygenation of Heterocyclic *N*-Oxides to *N*-Heterocycles. Heterocyclic *N*-oxides can be deoxygenated by many reagents, including hydrides, trivalent phosphorus compounds, sulfur compounds, dissolved metals, titanium trichloride, hydrogen gas, etc.[28,29] In general, methods are limited for the specifically reductive cleavage of the *N*-oxide bond because of interference resulting from side reactions, relatively high reaction temperatures, and the difficulties associated with product isolation.

In the course of finding solutions to this problem, we have reported our preliminary results on the deoxygenation of pyridine *N*-oxide to pyridine with hexamethyldisilane in the presence of methyllithium.[12a] To explore the generality and to study the scope of this deoxygenation process, we found that *N*-oxides of substituted pyridines, quinoline, and isoquinoline can be deoxygenated with hexamethyldisilane in the presence of methyllithium. The resultant deoxygenated *N*-heterocycles were obtained in good yields for almost all substrates, including **19b**−**21b** and **23b**−**25b**. The only exception was the failure on the formation of 4-cyanopyridine (**22b**) from 4-cyanopyridine *N*-oxide (**22a**), which bears an electron-withdrawing group.

Conclusions

New mono-deoxygenation processes were established by use of hexamethyldisilane under basic conditions. They were applied successfully in the reductions of secondary nitroalkanes, nitrones, and heterocyclic *N*-oxides to the corresponding ketoximes, imines, and *N*-heterocycles, respectively. These mono-deoxygenation processes may involve a 1,2-elimination of intermediates containing the Si−C−N−O^- moiety. In the conversion of secondary nitroalkanes to ketoximes, hexamethyldisilane acted as a "counterattack reagent". Advantages associate with these processes include mild reaction conditions and generation of the desired products in appealing yields.

Experimental Section

General Procedure. All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen, unless indicated otherwise. Tetrahydrofuran (reagent grade) from Mallinckrodt was dried by distillation from sodium and benzophenone under an atmosphere of nitrogen. Ethyl acetate and hexanes from Mallinckrodt Chemical Co. were dried and distilled from CaH_2. Benzaldehyde, dimethyl sulfoxide (DMSO), and sodium nitrite were purchased from Merck Inc. The following compounds and reagents were purchased from Aldrich Chemical Co.: 2-bromobutane, 3-bromopentane, *n*-butyllithium (1.6 M solution in hexanes), (±)-camphor, 2,2′-bipyridine *N*,*N*′-dioxide, 1-fluoro-4-nitrobenzene, 4-fluoro-2-nitrotoluene, hexamethyldisilane, hexamethylphosphoric triamide (HMPA), isoquinoline *N*-oxide, 4-methoxypyridine *N*-oxide hydrate, methyllithium (1.4 M solution in diethyl ether), 4-methylpyridine *N*-oxide, nitrocyclohexane, nitrocyclopentane, 4-nitrophenyl phenyl ether, 4-nitro-*o*-xylene, (±)-2-norboranone, 4-phenyl-2-butanone, and quinoline *N*-oxide hydrate.

Analytical thin-layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a 25-m cross-linked methyl silicone gum capillary column (0.32-mm i.d.). Nitrogen gas was used as the carrier gas, and the flow rate was kept constant at 14.0 mL/min. The retention time t_R was measured under the following conditions: injector temperature 260 °C, initial temperature for column 70 °C, duration 2.00 min, increment rate 10 °C/min, and final temperature for column 250 °C. Gas chromatography and low-resolution mass spectral analyses were performed on a Hewlett-Packard 5890 Series II instrument equipped with a Hewlett-Packard 5971A mass selective detector and a capillary HP-1 column. Purification by gravity column chromatography packed with Merck Reagents silica gel 60 (particle size 0.063−0.200 mm, 70−230 mesh ASTM) provided the desired product with purity >99.5%. The yields reported were based on the isolated, pure fraction from column chromatography.

Preparation of Nitro Compounds. 1-Methyl-2-nitrocyclohexane (**8a**), 3-nitrophenylbutane (**4a**), 1-nitrophenylethane (**2a**), and 1,7,7-trimethyl-2-nitrobicyclo[2.2.1]heptane (**10a**) were prepared by the literature method.[17] 2-Nitrobutane (**1a**) and 3-nitropentane (**5a**) were synthesized from the corresponding alkyl bromide and sodium nitrite in DMSO.[30] 2-Nitronorborane (**9a**) and 2-nitrophenylpropane (**3a**) were produced by condensation of the corresponding ketones and

(26) Sakurai, H.; Okada, A.; Umino, H.; Kira, M. *J. Am. Chem. Soc.* **1973**, *95*, 955.
(27) Robertson, G. M. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Pattenden, G., Eds.; Pergamon: Oxford, 1991; Vol. 3, pp 563−611.
(28) Katritzky, A. R.; Lagowski, J. M. *Chemistry of the Heterocyclic N-Oxides*; Academic: London, 1971; pp 166−226.
(29) Albini, A.; Pietra, S. *Heterocyclic N-Oxides*; CRC: Boca Raton, 1991; pp 120−134.
(30) Asaro, M. F.; Nakayama, I.; Wilson, R. B., Jr. *J. Org. Chem.* **1992**, *57*, 778.

hydroxylamine, followed by oxidation of the resultant ketoximes with peroxytrifluoroacetic acid.[31]

Standard Procedure 1 for the Reduction of Nitroalkanes to Oximes. To a solution of nitroalkanes (1.0 equiv) in THF (10.0 mL) was added *n*-butyllithium (1.6 M in hexanes, 1.1 equiv) at 0 °C. After the solution was stirred at 0 °C for 10 min, hexamethyldisilane (1.1 equiv) was added and the mixture was stirred at room temperature for 24 h. The reaction mixture was quenched with water at 0 °C, neutralized with 10% aqueous HCl, and extracted with ether (3 × 50 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to provide the desired oximes.

(*Z*)- and (*E*)-2-Butanone Oximes (1b). The standard procedure 1 was followed by use of 2-nitrobutane (**1a**, 432 mg, 4.19 mmol, 1.0 equiv), hexamethyldisilane (675 mg, 4.61 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.9 mL, 4.6 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (20% EtOAc in hexanes as eluant). Oximes **1b** (as a *Z*- and *E*-mixture, 223 mg, 2.56 mmol) were obtained as a colorless oil in 61% yield: TLC R_f 0.52 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.04−1.09 (m, 3 H), 1.88 (s, 3 H), 2.18−2.45 (m, 2 H), 8.49 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.68, 10.71, 13.29, 19.01, 21.92, 29.00, 159.78, 160.52; IR (neat) 3251 (br s, OH), 1663 (m, C=N), 935 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 87 (M^+, 1), 42 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[32]

Acetophenone Oxime (2b). The standard procedure 1 was followed by use of 1-nitrophenylethane (**2a**, 455 mg, 3.01 mmol, 1.0 equiv), hexamethyldisilane (485 mg, 3.31 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.1 mL, 3.4 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (15% EtOAc in hexanes as eluant). Oxime **2b** (297 mg, 2.20 mmol) was obtained as a white solid in 73% yield: mp (recrystallized from hexanes) 58.0−59.0 °C (lit.[33] mp 58 °C); TLC R_f 0.67 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3 H), 7.24−7.66 (m, 5 H), 9.19 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.40, 126.03, 128.48, 129.24, 136.36, 156.02; IR (KBr) 3221 (br s, OH), 1644 (m, C=N), 1006 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 135 (M^+, 77), 77 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[17]

(*Z*)- and (*E*)-1-Phenyl-2-propanone Oximes (3b). The standard procedure 1 was followed by use of 2-nitrophenylpropane (**3a**, 568 mg, 3.44 mmol, 1.0 equiv), hexamethyldisilane (553 mg, 3.78 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.3 mL, 3.7 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (20% EtOAc in hexanes as eluant). Oximes **3b** (as a *Z*- and *E*-mixture, 344 mg, 2.31 mmol) were obtained as a colorless oil in 67% yield: TLC R_f 0.55 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.81 (s, 3 H), 1.82 (s, 3 H), 3.75 (s, 2 H), 3.49 (s, 2 H), 7.21−7.33 (m, 5 H), 9.06 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.19, 19.68, 34.76, 42.11, 126.45, 126.74, 128.75, 129.14, 129.99, 136.49, 136.66, 156.92, 157.64; IR (neat) 3250 (br s, OH), 1662 (s, C=N), 922 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 149 (M^+, 70), 91 (100). Its physical properties and spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of an authentic sample prepared from the corresponding ketone and hydroxylamine.

(*Z*)- and (*E*)-4-Phenyl-2-butanone Oximes (4b). The standard procedure 1 was followed by use of 3-nitrophenylbutane (**4a**, 547 mg, 3.05 mmol, 1.0 equiv), hexamethyldisilane (491 mg, 3.35 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.1 mL, 3.4 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (15% EtOAc in hexanes as eluant). Oximes **4b** (as a *Z*- and *E*-mixture, 323 mg, 1.98 mmol) were obtained as a white solid in 65% yield: mp (recrystallized from ethanol) 85.0−86.0 °C (lit.[34] mp 85−86 °C); TLC R_f 0.62 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.98 (s, 3 H), 2.55−2.77 (m, 2 H), 2.87−2.92 (m, 2 H), 7.23−7.37 (m, 5 H), 8.45 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.87, 20.22, 30.81, 31.47, 32.02, 37.70, 126.12, 128.33, 128.46, 141.10, 141.27, 157.87, 158.20; IR (KBr) 3222 (br s, OH), 1682 (m, C=N), 953 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 163 (M^+, 16), 91 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[17]

3-Pentanone Oxime (5b). The standard procedure 1 was followed by use of 3-nitropentane (**5a**, 541 mg, 4.62 mmol, 1.0 equiv), hexamethyldisilane (744 mg, 5.08 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 3.2 mL, 5.1 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (20% EtOAc in hexanes as eluant). Oxime **5b** (294 mg, 2.91 mmol) was obtained as a colorless oil in 63% yield: TLC R_f 0.62 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, J = 6.0 Hz, 6 H), 2.13−2.35 (m, 4 H), 9.89 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 9.87, 10.54, 20.67, 26.81, 163.25; IR (neat) 3249 (br s, OH), 1661 (m, C=N), 935 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 101 (M^+, 2), 59 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[32]

Cyclopentanone Oxime (6b). The standard procedure 1 was followed by use of nitrocyclopentane (**6a**, 455 mg, 3.95 mmol, 1.0 equiv), hexamethyldisilane (636 mg, 4.34 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.7 mL, 4.3 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (25% EtOAc in hexanes as eluant). Oxime **6b** (157 mg, 1.58 mmol) was obtained as a white solid in 40% yield: mp (recrystallized from hexanes) 57.0−58.0 °C (lit.[34] mp 57−58.5 °C); TLC R_f 0.38 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.26−1.69 (m, 4 H), 2.22−2.35 (m, 4 H), 9.91 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.22, 24.87, 26.82, 30.42, 166.80; IR (KBr) 3218 (br s, OH), 1689 (m, C=N), 942 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 99 (M^+, 70), 55 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[32]

Cyclohexanone Oxime (7b). The standard procedure 1 was followed by use of nitrocyclohexane (**7a**, 452 mg, 3.50 mmol, 1.0 equiv), hexamethyldisilane (563 mg, 3.85 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.4 mL, 3.8 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (20% EtOAc in hexanes as eluant). Oxime **7b** (273 mg, 2.41 mmol) was obtained as a white solid in 69% yield: mp (recrystallized from ethanol) 89.0−90.0 °C (lit.[34] mp 89.5−90.5 °C); TLC R_f 0.52 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.54−1.60 (m, 6 H), 2.14−2.47 (m, 4 H), 9.91 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 24.34, 25.39, 25.63, 26.69, 31.66, 160.37; IR (KBr) 3221 (br s, OH), 1691 (m, C=N), 942 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 113 (M^+, 100), 59 (56). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported.[17]

(*Z*)- and (*E*)-2-Methylcyclohexanone Oximes (8b). The standard procedure 1 was followed by use of 1-methyl-2-nitrocyclohexane (**8a**, 467 mg, 3.26 mmol, 1.0 equiv), hexamethyldisilane (525 mg, 3.59 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.3 mL, 3.7 mmol, 1.1 equiv). After

(31) Olah, G. A.; Ramaiah, P.; Prakash, G. K. S.; Gilardi, R. *J. Org. Chem.* **1993**, *58*, 763.

(32) Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017.

(33) Ohwada, T.; Yamagata, N.; Shudo, K. *J. Am. Chem. Soc.* **1991**, *113*, 1364.

(34) Barber, G. N.; Olofson, R. A. *J. Org. Chem.* **1978**, *43*, 3015.

the reaction was worked up, the residue was purified by column chromatography on silica gel (10% EtOAc in hexanes as eluant). Oximes **8b** (as a *Z*- and *E*-mixture, 282 mg, 2.22 mmol) were obtained as a white solid in 68% yield: mp (recrystallized from hexanes) 42.0−43.0 °C (lit.[34] mp 41.5−43 °C); TLC R_f 0.75 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.07 (d, J = 6.0 Hz, 3 H), 1.40−3.57 (m, 9 H), 9.80 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.13, 16.77, 20.37, 23.84, 24.65, 25.95, 26.61, 26.69, 28.30, 31.57, 35.54, 37.13, 163.06, 163.66; IR (neat) 3282 (br s, OH), 1659 (m, C=N), 942 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 127 (M^+, 34), 41 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[17]

(*Z*)- and (*E*)-2-Norboranone Oximes (9b). The standard procedure 1 was followed by use of 2-nitronorborane (**9a**, 452 mg, 3.20 mmol, 1.0 equiv), hexamethyldisilane (516 mg, 3.53 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.2 mL, 3.5 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (20% EtOAc in hexanes as eluant). Oximes **9b** (as a *Z*- and *E*-mixture, 289 mg, 2.31 mmol) were obtained as a white solid in 72% yield: mp (recrystallized from hexanes) 51.0−52.0 °C (lit.[35] mp 50−51.5 °C); TLC R_f 0.48 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.05−3.42 (m, 10 H), 9.81 (br s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 25.67, 26.81, 27.10, 27.51, 34.57, 35.18, 36.87, 38.02, 38.24, 38.78, 41.96, 42.15, 166.38, 167.32; IR (KBr) 3249 (br s, OH), 1690 (m, C=N), 952 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 125 (M^+, 7), 79 (100). Its physical properties and spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of an authentic sample prepared from the corresponding ketone and hydroxylamine.

Camphor Oxime (10b). The standard procedure 1 was followed by use of 1,7,7-trimethyl-2-nitrobicyclo[2.2.1]heptane (**10a**, 603 mg, 3.29 mmol, 1.0 equiv), hexamethyldisilane (531 mg, 3.63 mmol, 1.1 equiv), and *n*-butyllithium (1.6 M in hexanes, 2.3 mL, 3.7 mmol, 1.1 equiv). After the reaction was worked up, the residue was purified by column chromatography on silica gel (15% EtOAc in hexanes as eluant). Oxime **10b** (391 mg, 2.34 mmol) was obtained as a white solid in 71% yield: mp (recrystallized from ethanol) 116.0−117.0 °C (lit.[36] mp 116.5−117.5 °C); TLC R_f 0.68 (30% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.67 (s, 3 H), 0.88 (s, 3 H), 0.97 (s, 3 H), 1.16−2.56 (m, 7 H), 9.45 (br s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 11.07, 18.49, 19.41, 27.22, 32.59, 33.04, 43.70, 48.24, 51.78, 169.67; IR (KBr) 3304 (br s, OH), 1685 (m, C=N), 923 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 167 (M^+, 100), 124 (94). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[17]

Standard Procedure 2 for the Preparation of Substituted *N*-Aryl-α-phenylnitrones.[16] Benzaldehyde (1.05 equiv) was added into an ethanolic solution containing *N*-arylhydroxylamines[37] (1.0 equiv) with stirring at 50−60 °C for 10 min. After the reaction mixture was kept at room temperature in the dark overnight, *N*-aryl-α-phenylnitrones were crystallized from the reaction mixture. The crystals of nitrone were collected on a Büchner funnel, washed with cold ethanol, and dried under reduced pressure in the presence of P_2O_5. Their structures were determined by spectroscopic methods. For nitrones **11a** and **12a**, their physical properties and spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[38]

***N*-(4-Phenoxyphenyl)-α-phenylnitrone (13a).** The standard procedure 2 was followed by use of *N*-(4-phenoxyphenyl)-hydroxylamine (812 mg, 4.04 mmol, 1.0 equiv), benzaldehyde (449 mg, 4.23 mmol, 1.05 equiv), and ethanol (3.0 mL). Nitrone **13a** (992 mg, 3.63 mmol) was obtained as colorless crystals in 90% yield: mp 135.0−136.0 °C; TLC R_f 0.17 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.05−7.22 (m, 5 H), 7.37−7.41 (m, 2 H), 7.47−7.49 (m, 3 H), 7.74−7.76 (m, 2 H), 7.89 (s, 1 H), 8.37−8.40 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 118.12, 119.33, 123.03, 124.04, 128.41, 128.77, 129.80, 130.53, 130.62, 133.84, 143.82, 155.90, 158.51; IR (neat) 1536 (m, C=N), 1064 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 289 (M^+, 18), 183 (100); HRMS calcd for $C_{19}H_{15}NO_2$ 289.1103, found 289.1104. Anal. Calcd for $C_{19}H_{15}NO_2$: C, 78.86; H, 5.23; N, 4.84. Found: C, 78.82; H, 5.25; N, 4.82.

***N*-(3,4-Dimethylphenyl)-α-phenylnitrone (14a).** The standard procedure 2 was followed by use of *N*-(3,4-dimethylphenyl)hydroxylamine (1.22 g, 8.89 mmol, 1.0 equiv), benzaldehyde (991 mg, 9.34 mmol, 1.05 equiv), and ethanol (7.0 mL). Nitrone **14a** (1.65 g, 7.32 mmol) was obtained as yellow crystals in 82% yield: mp 61.0−62.0 °C; TLC R_f 0.23 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3 H), 2.34 (s, 3 H), 7.20−7.23 (m, 1 H), 7.46−7.49 (m, 3 H), 7.58 (s, 1 H), 7.89 (s, 1 H), 8.37−8.41 (m, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.10, 19.46, 118.33, 122.25, 128.13, 128.62, 129.59, 130.26, 130.50, 133.63, 137.27, 138.33, 146.55; IR (neat) 1548 (s, C=N), 1078 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 225 (M^+, 26), 119 (100); HRMS calcd for $C_{15}H_{15}NO$ 225.1154, found 225.1146. Anal. Calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.95; H, 6.80; N, 6.25.

***N*-(5-Fluoro-2-methylphenyl)-α-phenylnitrone (15a).** The standard procedure 2 was followed by use of *N*-(5-fluoro-2-methylphenyl)hydroxylamine (827 mg, 5.86 mmol, 1.0 equiv), benzaldehyde (653 mg, 6.15 mmol, 1.05 equiv), and ethanol (2.0 mL). Nitrone **15a** (1.22 g, 5.32 mmol) was obtained as colorless crystals in 91% yield: mp 116.0−117.0 °C; TLC R_f 0.19 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.37 (s, 3 H), 7.07 (dt, J = 8.3, 2.6 Hz, 1 H), 7.17 (dd, J = 8.3, 2.6 Hz, 1 H), 7.27 (dd, J = 8.3, 7.1 Hz, 1 H), 7.48−7.51 (m, 3 H), 7.54 (s, 1 H), 8.33−8.36 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 16.13. 110.78, 116.01, 127.10, 128.38, 128.59, 129.89, 130.83, 132.37, 137.45, 148.56, 160.35; IR (neat) 1568 (m, C=N), 1055 (s, N−O) cm^{-1}; MS *m*/*z* (relative intensity) 229 (M^+, 100), 212 (84); HRMS calcd for $C_{14}H_{12}FNO$ 229.0903, found 229.0909. Anal. Calcd for $C_{14}H_{12}FNO$: C, 73.33; H, 5.28; N, 6.11. Found: C, 73.34; H, 5.28; N, 6.16.

Standard Procedure 3 for the Deoxygenation of *N*,α-Diarylnitrones and Pyridine *N*-Oxides. A solution of hexamethyldisilane in HMPA (1.6 mL) was cooled to −78 °C under argon, whereupon the mixture solidified. Low-halide MeLi and THF (8.0 mL) were added slowly onto the frozen mixture, which was then warmed to 0 °C for 5.0 min. The resultant orange-red solution was cooled to −78 °C. A solution of *N*,α-diarylnitrones or pyridine *N*-oxides in THF (2.0 mL) was injected slowly into the reaction flask. The reaction mixture was stirred at −78 °C for 20 min and at room temperature for 4−15 h and then quenched with water. The solution was extracted with ether (3 × 25 mL), and the combined ether layers were washed with saturated ammonium chloride solution (1 × 3 mL) and water (3 × 3 mL). After the ether solution was dried ($MgSO_4$), the solvent was removed to give the crude product. The residue was purified by column chromatography on silica gel to provide the desired products.

***N*-Benzylideneaniline (11b). Method 1.** The standard procedure 3 was followed by use of *N*,α-diphenylnitrone (**11a**, 211 mg, 1.07 mmol, 1.0 equiv), hexamethyldisilane (172 mg, 1.18 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 0.85 mL, 1.1 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 5.0 h, it was worked up and the residue was purified by column chromatography on silica gel (5% EtOAc in hexanes as eluant) to give **11b** (163 mg, 0.899 mmol) as a yellow solid in 84% yield: mp (recrystallized from ethanol) 50.0−51.0 °C (lit.[39] mp 51 °C); GC t_R 15.56 min; TLC

(35) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1960**, *82*, 1209.
(36) Hutchins, R. O.; Adams, J.; Rutledge, M. C. *J. Org. Chem.* **1995**, *60*, 7396.
(37) Oxley, P. W.; Adger, B. M.; Sasse, M. J.; Forth, M. A. *Org. Synth.* **1988**, *67*, 187.
(38) Suda, K.; Tsujimoto, T.; Yamauchi, M. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3607.
(39) *Dictionary of Organic Compounds*, 5th ed.; Buckingham, J., Ed.; Chapman and Hall: New York, 1982; Vol. 1, p 372.

R_f 0.62 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.20−7.26 (m, 3 H), 7.37−7.42 (m, 2 H), 7.47−7.49 (m, 3 H), 7.89−7.92 (m, 2 H), 8.46 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 120.82, 125.89, 128.71, 128.77, 129.10, 131.32, 136.15, 152.02, 160.33; IR (neat) 1626 (s, C=N), 1584 (s, C=C), 1182 (m, C−N) cm^{-1}; MS *m*/*z* (relative intensity) 181 (M^+, 89), 180 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[40]

Method 2. The standard procedure 3 was followed by use of *N*,α-diphenylnitrone (**11a**, 828 mg, 4.20 mmol, 1.0 equiv), hexamethyldisilane (676 mg, 4.62 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 0.30 mL, 0.42 mmol, 0.10 equiv). After the reaction mixture was stirred at room temperature for 30 h, it was worked up and the residue was purified to give **11b** (198 mg, 1.09 mmol) in 26% yield.

***N*-Benzylidene-4-fluoroaniline (12b).** The standard procedure 3 was followed by use of *N*-(4-fluorophenyl)-α-phenylnitrone (**12a**, 254 mg, 1.18 mmol, 1.0 equiv), hexamethyldisilane (191 mg, 1.30 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 0.95 mL, 1.3 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 4.0 h, it was worked up and the residue was purified by column chromatography on silica gel (5% EtOAc in hexanes as eluant) to give **12b** (207 mg, 1.04 mmol) as a yellow solid in 88% yield: mp (recrystallized from ethanol) 56.0−57.0 °C (lit.[41] mp 56 °C); GC t_R 15.52 min; TLC R_f 0.62 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.05−7.11 (m, 2 H), 7.18−7.23 (m, 2 H), 7.47−7.51 (m, 3 H), 7.89−7.93 (m, 2 H), 8.45 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 115.83, 122.28, 128.71, 128.76, 131.40, 136.08, 148.02, 160.13, 161.24; IR (neat) 1627 (s, C=N), 1499 (s, C=C), 1225 (s, C−F), 1186 (m, C−N) cm^{-1}; MS *m*/*z* (relative intensity) 199 (M^+, 90), 198 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[42]

***N*-Benzylidene-4-phenoxyaniline (13b).** The standard procedure 3 was followed by use of *N*-(4-phenoxyphenyl)-α-phenylnitrone (**13a**, 201 mg, 0.735 mmol, 1.0 equiv), hexamethyldisilane (118 mg, 0.806 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 0.60 mL, 0.84 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 6.0 h, it was worked up and the residue was purified by column chromatography on silica gel (5% EtOAc in hexanes as eluant) to give **13b** (155 mg, 0.602 mmol) as a yellow solid in 82% yield: mp (recrystallized from ethanol) 62.0−63.0 °C; GC t_R 25.85 min; TLC R_f 0.59 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.02−7.13 (m, 5 H), 7.21−7.37 (m, 4 H), 7.46−7.49 (m, 3 H), 7.89−7.92 (m, 2 H), 8.49 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 118.64, 119.57, 122.25, 123.15, 128.68, 128.72, 129.72, 131.23, 136.22, 147.30, 155.49, 157.41, 159.45; IR (neat) 1624 (m, C=N), 1586 (m, C=C), 1491 (m, C=C), 1238 (m, C−O) cm^{-1}; MS *m*/*z* (relative intensity) 273 (M^+, 100), 272 (44). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12; O, 5.86. Found: C, 83.37; H, 5.54; N, 5.20; O, 6.00.

***N*-Benzylidene-3,4-dimethylaniline (14b).** The standard procedure 3 was followed by use of *N*-(3,4-dimethylphenyl)-α-phenylnitrone (**14a**, 147 mg, 0.652 mmol, 1.0 equiv), hexamethyldisilane (105 mg, 0.717 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 0.53 mL, 0.74 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 5.0 h, it was worked up and the residue was purified by column chromatography on silica gel (5% EtOAc in hexanes as eluant) to give **14b** (115 mg, 0.549 mmol) as a yellow solid in 84% yield: mp (recrystallized from ethanol) 43.0−44.0 °C; GC t_R 18.42 min; TLC R_f 0.65 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.27 (s, 3 H), 2.29 (s, 3 H), 6.98 (dd, J = 7.8, 2.2 Hz, 1 H), 7.03 (d, J = 2.2 Hz, 1 H), 7.14 (d, J = 7.8 Hz, 1 H), 7.44−7.46 (m, 3 H), 7.86−7.90 (m, 2 H), 8.46 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 19.20, 19.74, 118.01, 122.24, 128.61, 128.66, 130.19, 130.99, 134.32, 136.37, 137.19, 149.73, 159.19; IR (neat) 1627 (s, C=N), 1497 (s, C=C), 1199 (w, C−N) cm^{-1}; MS *m*/*z* (relative intensity) 209 (M^+, 100), 208 (74); HRMS calcd for $C_{15}H_{15}N$ 209.1204, found 209.1211. Anal. Calcd for $C_{15}H_{15}N$: C, 86.07; H, 7.23; N, 6.70. Found: C, 86.11; H, 7.28; N, 6.70. Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[43]

***N*-Benzylidene-5-fluoro-2-methylaniline (15b).** The standard procedure 3 was followed by use of *N*-(5-fluoro-2-methylphenyl)-α-phenylnitrone (**15a**, 226 mg, 0.986 mmol, 1.0 equiv), hexamethyldisilane (159 mg, 1.09 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 0.80 mL, 1.12 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 5.0 h, it was worked up and the residue was purified by column chromatography on silica gel (5% EtOAc in hexanes as eluant) to give **15b** (174 mg, 0.816 mmol) as a yellow solid in 83% yield: mp (recrystallized from ethanol) 42.0−43.0 °C; GC t_R 16.35 min; TLC R_f 0.68 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.30 (s, 3 H), 6.67 (dd, J = 9.8, 2.6 Hz, 1 H), 6.82 (dt, J = 2.6, 8.4 Hz, 1 H), 7.14 (dd, J = 8.1, 6.3 Hz, 1 H), 7.46−7.49 (m, 3 H), 7.90−7.93 (m, 2 H), 8.33 (s, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 17.05, 104.85, 111.80, 127.46, 128.74, 128.83, 130.98, 131.50, 136.09, 152.05, 160.14, 161.64; IR (neat) 1632 (s, C=N), 1596 (s, C=C), 1496 (s, C=C), 1261 (m, C−F), 1146 (m, C−N) cm^{-1}; MS *m*/*z* (relative intensity) 213 (M^+, 74), 136 (100); HRMS calcd for $C_{14}H_{12}NF$ 213.0954, found 213.0955. Anal. Calcd for $C_{14}H_{12}FN$: C, 78.84; H, 5.68; N, 6.57. Found: C, 78.78; H, 5.66; N, 6.60.

***N*-Benzylaniline (17) and 1,2-Dianilino-1,2-diphenylethane (18).** The standard procedure 3 was followed by use of *N*,α-diphenylnitrone (**11a**, 205 mg, 1.04 mmol, 1.0 equiv), hexamethyldisilane (334 mg, 2.28 mmol, 2.2 equiv), and methyllithium (1.4 M in ether, 1.6 mL, 2.2 mmol, 2.1 equiv). After the reaction mixture was stirred at room temperature for 4.0 h, it was worked up. The crude products were separated by column chromatography on silica gel (8% EtOAc in hexanes as eluant) to give pure **11b** (58.4 mg, 0.322 mmol) in 31% yield, pure **17** (51.5 mg, 0.281 mmol) in 27% yield, and **18** (60.7 mg, 0.167 mmol) in 16% yield.

For **17**: GC t_R 16.26 min; TLC R_f 0.59 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.01 (br s, 1 H), 4.32 (s, 2 H), 6.62−7.38 (m, 10 H); IR (neat) 3405 (s, NH), 1599 (s, C=C), 1498 (s, C=C), 1321 (m, C−N) cm^{-1}; MS *m*/*z* (relative intensity) 183 (M^+, 71), 91 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and MS are consistent with those of the same compound reported in the literature.[44]

For **18**: TLC R_f 0.55 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.54 (s, 2 H), 4.95 (s, 2 H), 6.49−7.21 (m, 20 H); IR (neat) 3396 (s, NH), 1599 (s, C=C), 1498 (s, C=C), 1309 (m, C−N) cm^{-1}; MS (FAB) *m*/*z* (relative intensity) 365 (M^+ + H, 12), 182 (100). Its spectroscopic characteristics in IR, ^{1}H NMR, and MS are consistent with those of the same compound reported in the literature.[45]

Pyridine (19b). The standard procedure 3 was followed by use of pyridine *N*-oxide (**19a**, 191 mg, 2.01 mmol, 1.0 equiv), hexamethyldisilane (324 mg, 2.21 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 1.6 mL, 2.2 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 8.0 h, it was worked up and the residue was purified by column chromatography on silica gel (1% triethylamine in

(40) Ishihara, K.; Miyata, M.; Hattori, K.; Tada, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1994**, *116*, 10520.
(41) Dayal, S. K.; Ehrenson, S.; Taft, R. W. *J. Am. Chem. Soc.* **1972**, *94*, 9113.
(42) Akaba, R.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1186.
(43) García-Vázquez, J. A.; López-Becerra, M.; Masaguer, J. R. *Polyhedron* **1983**, *2*, 1081.
(44) Katritzky, A. R.; Yao, G.; Lan, X.; Zhao, X. *J. Org. Chem.* **1993**, *58*, 2086.
(45) Katritzky, A. R.; Fan, W.-Q.; Fu, C. *J. Org. Chem.* **1990**, *55*, 3209.
(46) Its physical properties and spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of authentic samples available from Aldrich Chemical Co.
(47) Barlin, G. B.; Brown, D. J.; Fenn, M. D. *Aust. J. Chem.* **1984**, *37*, 2391.

dichloromethane as eluant) to give pyridine[46] (**19b**, 137 mg, 1.73 mmol) in 86% yield.

4-Methylpyridine (20b). The standard procedure 3 was followed by use of 4-methylpyridine *N*-oxide (**20a**, 229 mg, 2.10 mmol, 1.0 equiv), hexamethyldisilane (338 mg, 2.31 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 1.7 mL, 2.4 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 10 h, it was worked up and the residue was purified by column chromatography on silica gel (1% triethylamine in dichloromethane as eluant) to give 4-methylpyridine[46] (**20b**, 143 mg, 1.54 mmol) in 73% yield.

4-Methoxypyridine (21b). The standard procedure 3 was followed by use of 4-methoxypyridine *N*-oxide (**21a**, 187 mg, 1.49 mmol, 1.0 equiv), hexamethyldisilane (241 mg, 1.65 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 1.2 mL, 1.7 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 12 h, it was worked up and the residue was purified by column chromatography on silica gel (1% triethylamine in dichloromethane as eluant) to give 4-methoxypyridine (**21b**, 129 mg, 1.18 mmol) in 79% yield: TLC R_f 0.45 (40% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.88 (s, 3 H), 6.87 (d, J = 5.4 Hz, 2 H), 8.42 (d, J = 5.4 Hz, 2 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 55.01, 109.89, 151.10, 165.62; MS *m*/*z* (relative intensity) 109 (M^+, 100), 79 (44). Its spectroscopic characteristics in IR, ^{1}H NMR, and ^{13}C NMR are consistent with those of the same compound reported in the literature.[47]

Quinoline (23b). The standard procedure 3 was followed by use of quinoline *N*-oxide (**23a**, 189 mg, 1.30 mmol, 1.0 equiv), hexamethyldisilane (209 mg, 1.43 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 1.0 mL, 1.4 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 8.0 h, it was worked up and the residue was purified by column chromatography on silica gel (1% triethylamine in dichloromethane as eluant) to give quinoline[46] (**23b**, 139 mg, 1.08 mmol) in 83% yield.

Isoquinoline (24b). The standard procedure 3 was followed by use of isoquinoline *N*-oxide (**24a**, 218 mg, 1.50 mmol, 1.0 equiv), hexamethyldisilane (242 mg, 1.65 mmol, 1.1 equiv), and methyllithium (1.4 M in ether, 1.2 mL, 1.7 mmol, 1.1 equiv). After the reaction mixture was stirred at room temperature for 10 h, it was worked up and the residue was purified by column chromatography on silica gel (1% triethylamine in dichloromethane as eluant) to give isoquinoline[46] (**24b**, 163 mg, 1.26 mmol) in 84% yield.

2,2′-Bipyridine (25b). The standard procedure 3 was followed by use of 2,2′-bipyridine *N*,*N*′-dioxide (**25a**, 244 mg, 1.30 mmol, 1.0 equiv), hexamethyldisilane (417 mg, 2.85 mmol, 2.2 equiv), and methyllithium (1.4 M in ether, 1.9 mL, 2.7 mmol, 2.1 equiv). After the reaction mixture was stirred at room temperature for 15 h, it was worked up and the residue was purified by column chromatography on silica gel (1% triethylamine in dichloromethane as eluant) to give 2,2′-bipyridine[46] (**25b**, 164 mg, 1.05 mmol) in 81% yield.

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