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COUNTERATTACK REAGENTS: THIOSILANES IN THE CONVERSION OF NITRO COMPOUNDS TO THIOHYDROXAMIC ACIDS AND THIOHYDROXIMATES

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Abstract—Various primary nitro compounds were reacted sequentially with KH and $Me_3SiSSiMe_3$ in THF to give thiohydroxamic acids in 56–92% yields. By the same strategy, a thiohydroxamic acid was obtained in 50% yield by treatment of *trans*-β-nitrostyrene with *i*-PrSLi in THF and then with $Me_3SiSSiMe_3$. Reaction of primary nitro compounds with *n*-BuLi and then with $MeSSiMe_3$ or $PhSSiMe_3$ produced the corresponding thiohydroximates in 61–78% yields. Secondary nitro compounds were converted to oximes in 68–96% yields by reaction with KH and $Me_3SiSSiMe_3$ or $MeSSiMe_3$ in THF or 1,4-dioxane. In these "one-flask" reactions, thiosilanes $Me_3SiSSiMe_3$, $MeSSiMe_3$, and $PhSSiMe_3$ acted as "counterattack reagents."

INTRODUCTION

Thiohydroxamic acids [RC(=S)NHOH] and thiohydroximates [RC(SR')=NOH] contain a moiety with three adjacent nucleophilic atoms (i.e., N, O, and S). These compounds play various roles in analytical and biological chemistry. Thiohydroxamic acids can coordinate with metal ions, including Fe^{3+}, Ni^{2+}, and Cu^{2+},[1,2] to form colored metal complexes by use of the sulfur and oxygen atoms. Thus thiohydroxamic acids are utilized in the detection and quantitative determination of metals.[3] Also, the tris-chelates of thiohydroxamic acids and Fe^{3+} are believed to participate in bacterial iron-transport systems.[1] The thiohydroximate unit exists in natural occurring mustard oil glucosides, such as glucoapparin,[4] glucotropaeolin,[5] and sinigrin.[6] In a separate study, Matsuo and Underhill found that phenylacetothiohydroximate exists in *Tropaeolum majus*.[7,8] They also concluded that phenylacetothiohydroximate is an intermediate in the biosynthesis of benzyl glucosinolate, a mustard oil glucoside.[7] Thiohydroximates and isocyanates are used as starting materials for the synthesis of the carbamate derivatives $R^1C(SR^2)=NOC(=O)NR^3R^4$.[9] Some carbamates can be utilized as pesticides.

Several conventional methods have been developed for the preparation of thiohydroxamic acids.[3] These include the thioacylation of hydroxylamines with dithiocarboxylic acids, dithiocarboxylic acid esters, thionocarboxylic acid esters, or thioacyl chlorides; and the reaction of hydroximic acid chlorides or nitrile oxides with hydrogen sulfide. Traditional methods[3] to prepare thiohydroxamate esters involve the reactions of hydroximic acid chlorides or nitrile oxides with thiols, the thioacylation of hydroxylamines with alkyl thiocarboximidates, the reaction of nitro compounds with thiols, and the *S*-alkylation of thiohydroxamic acids.

†Research fellow of the Alfred P. Sloan Foundation (1986–1990)

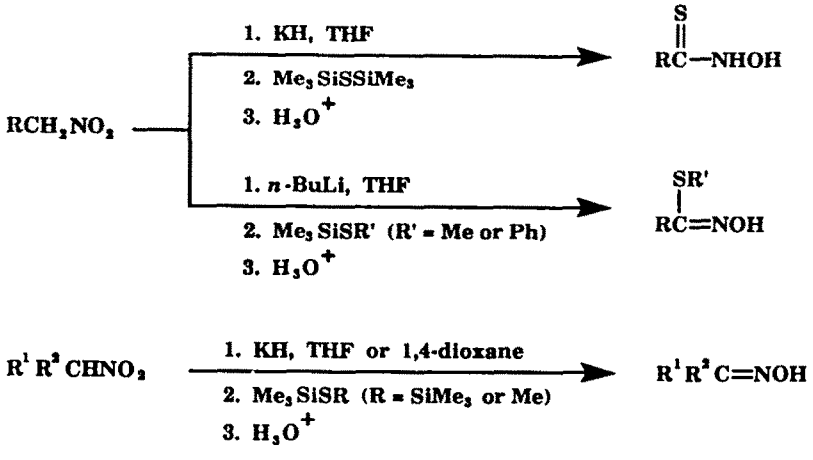
Recognizing the multiple roles of thiohydroxamic acids and thiohydroximates, we have developed new methods for the preparation of these compounds. Our methods involve applications of the "counterattack reagent" concept.[10,11] The procedures are experimentally simple since they involve facile manipulations and the use of readily available reagents.

RESULTS

We have developed efficient methods for the synthesis of thiohydroxamic acids and thiohydroximates from primary nitro compounds. In addition, we found a new way to convert secondary nitro compounds into oximes. The procedures are described as follows.

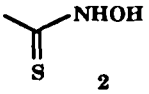
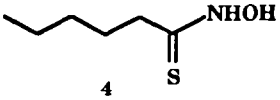
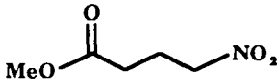
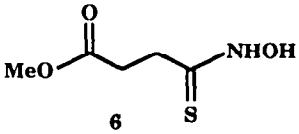
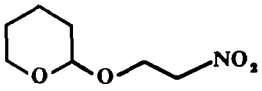
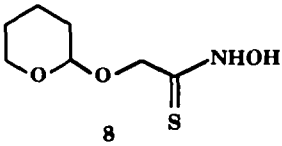
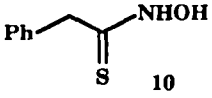
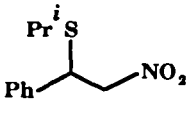
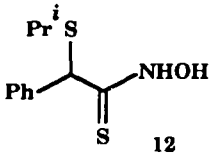
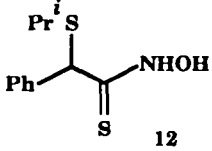
The Conversion of Primary Nitro Compounds into Thiohydroxamic Acids (Scheme I, Table I). We reacted simple aliphatic nitro compounds **1** and **3** with 1.1 equiv of KH in THF at 0 °C to room temperature. Hexamethyldisilathiane was added to the resultant nitronate in the dark to provide the thiohydroxamic acids **2** and **4** in 81% and 87% yields, respectively. In the same manner, we converted other primary nitro compounds (**5**, **7**, **9**, and **11**) into the corresponding thiohydroxamic acids (**6**, **8**, **10**, and **12**) in 56–92% yields. These results demonstrate that esters, acetals, arenes, and sulfides were all stable to the reaction conditions.

Scheme I



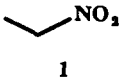
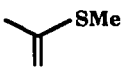
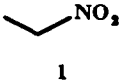
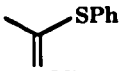
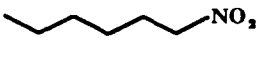
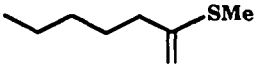
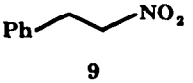
The Conversion of *trans*-β-Nitrostyrene into a Thiohydroxamic Acid. *trans*-β-Nitrostyrene (**13**) was allowed to react with ~1.5 equiv of *i*-PrSLi, generated in situ from *i*-PrSH and *n*-BuLi, in THF and then with 1.5 equiv of Me3SiSSiMe3. After heating the reaction mixture to reflux, thiohydroxamic acid **12** was obtained in 50% yield.

Table I. Preparation of Thiohydroxamic Acids from $Me_3SiSSiMe_3$ and Nitroalkanes or a Nitroalkene Under Alkaline Conditions

nitro compound	thiohydroxamic acid	yield
 1	 2	81%
 3	 4	87%
 5	 6	92%
 7	 8	87%
 9	 10	70%
 11	 12	56%
 13	 12	50%

The Conversion of Primary Nitro Compounds into Thiohydroximates (Scheme I, Table II). Primary nitro compounds were converted into thiohydroximates by reaction with *n*-BuLi and thiosilanes (i.e., MeSSiMe3 and PhSSiMe3). In this way **1**, **3**, and **9** gave **14–17** in 61–78% yields. These reactions were successfully carried out without the need to avoid light.

Table II. Preparation of Thiohydroximates from Nitro Compounds and $MeSSiMe_3$ or $PhSSiMe_3$ Under Alkaline Conditions

nitro compound	thiohydroximate	yield
 1	 14	78%
 1	 15	62%
 3	 16	61%
 9	 17	63%

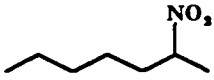
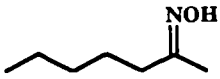
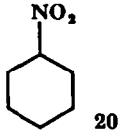
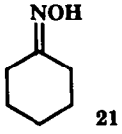
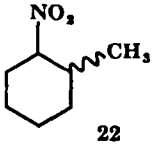
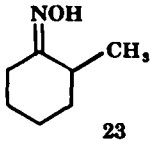
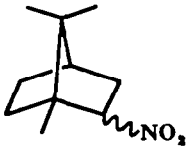
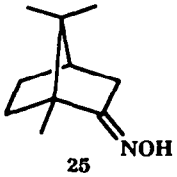
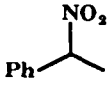
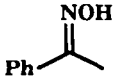
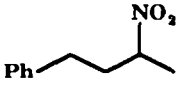
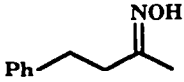
The Conversion of Secondary Nitro Compounds into Oximes (Scheme I, Table III). We have found that secondary nitro compounds **18**, **20**, **22**, **24**, **26**, and **28** reacted with KH and then with $Me_3SiSSiMe_3$ in THF or 1,4-dioxane to yield the corresponding oximes (**19**, **21**, **23**, **25**, **27**, and **29**) upon heating. The yields ranged from 80% to 96%. Similarly, treatment of nitrocyclohexane (**20**) or 2-nitropropane (**30**) with $MeSSiMe_3$ in THF under alkaline conditions afforded the oximes **21** (69%) and **31** (68%), respectively.

DISCUSSION

Reaction Products and Conditions. In the presence of light, thiohydroxamic acids decompose to produce nitriles, sulfur, and water.[12-15] Thus we carried out the transformation of nitro compounds to thiohydroxamic acids in the dark. Although thiohydroxamic acids **2**, **4**, **6**, and **8** were isolated in high yields (81–92%, see Table I), we obtained **10** in only 70% yield from **9**. In the conversion of **9** into **10**, we also isolated phenylacetonitrile in 15% yield. Similarly, in the preparation of **12** from **11**, or **13**, the by-product Ph(*i*-PrS)CHCN was generated in 21% and 12% yields, respectively. We believe that both nitriles are "secondary" products, which were derived from **10** and **12** via decomposition. We obtained **6** from **5** in 92% yield at room temperature in THF. On heating the reaction mixture at reflux, however, **5** gave a mixture of ester **6** and the corresponding acid ($HO_2CCH_2CH_2C(=S)NHOH$) in 85% overall yield. The ratio of the ester to the acid was 2:3.

By reacting a primary nitronate with $Me_3SiSSiMe_3$ and then with an alkyl iodide, we were able to obtain an *S*-alkylated product (i.e., thiohydroximate).[16] This transformation is, however, not efficient. For example, the nitro compound **3** gave the thiohydroximate **16** in <20% yield by this method. However, utilization of the reaction of $RSSiMe_3$ with primary nitro compounds provides a better and easier method to synthesize thiohydroximates (see results in Table II). We

Table III. Conversion of 2°-Nitro Compounds to Oximes with $Me_3SiSSiMe_3$ or $MeSSiMe_3$ Under Alkaline Conditions

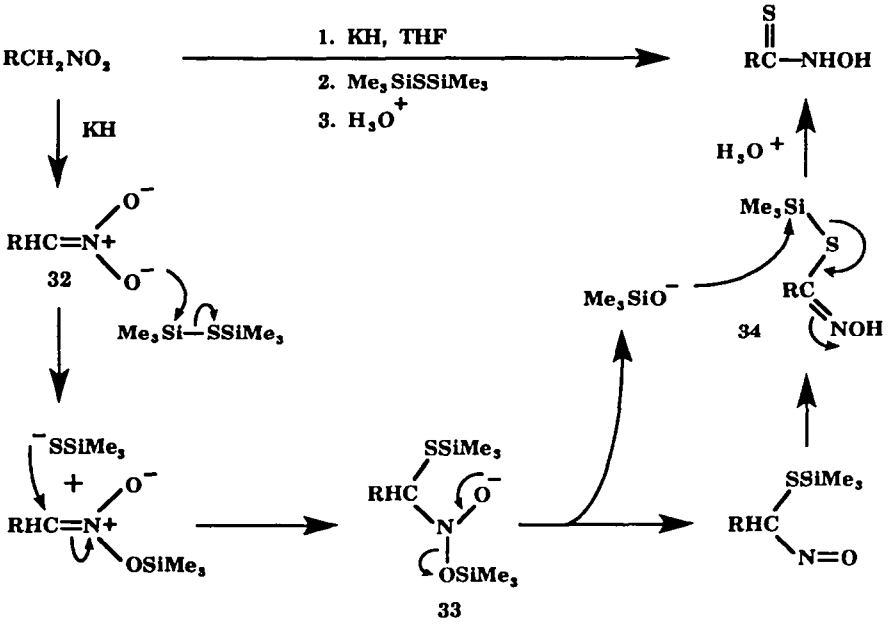
nitro compound	thiosilane	oxime	yield
 18	$Me_3SiSSiMe_3$	 19	96%
 20	$Me_3SiSSiMe_3$	 21	83%
20	$MeSSiMe_3$	21	69%
 22	$Me_3SiSSiMe_3$	 23	81%
 24	$Me_3SiSSiMe_3$	 25	80%
 26	$Me_3SiSSiMe_3$	 27	81%
 28	$Me_3SiSSiMe_3$	 29	83%
 30	$MeSSiMe_3$	 31	68%

have found that control of the reaction temperature is crucial in the conversion of secondary nitro compounds to oximes with $Me_3SiSSiMe_3$. When the reaction temperature was higher than 95 °C, significant amounts of ketones were produced. Among various secondary nitro compounds shown in Table III, **26** and **28** could be easily converted to acetophenone and 4-phenyl-2-butanone, respectively. In a control experiment, we worked up the reaction mixture without an aqueous quench and the mixture was then filtered through anhydrous Celite. In the filtrate, we did not detect any thioketone. Thus we conclude that thioketones are not intermediates in the formation of ketones.

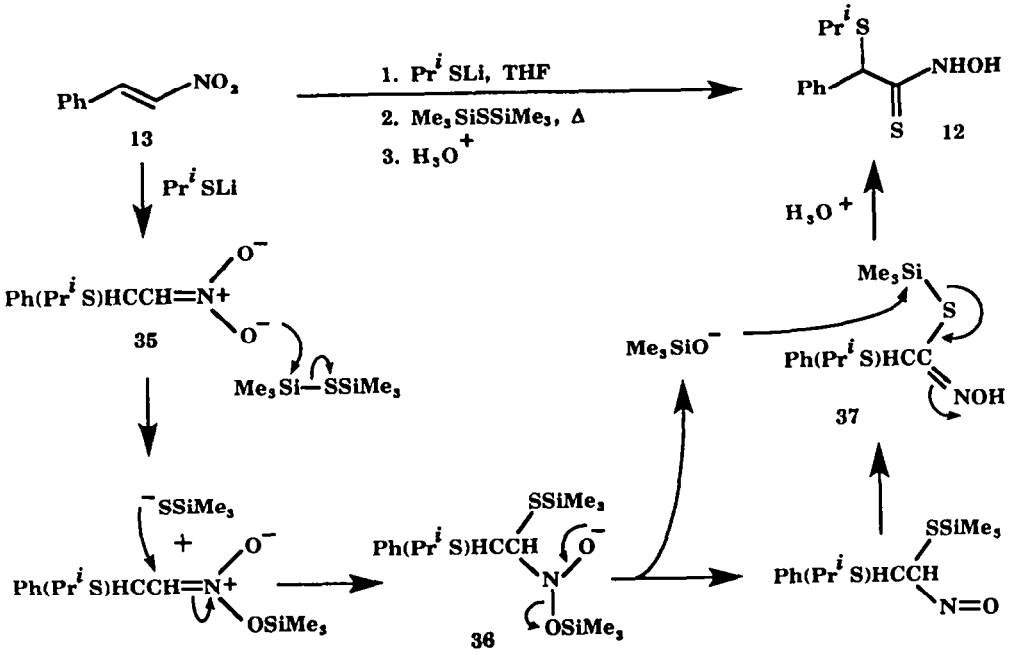
Thiohydroximates can exist in *E*- and *Z*-forms. Generally the *E*-isomer is more soluble in petroleum ether than the *Z*-isomer.[17] Under our reaction conditions, the thiohydroximate products with a small alkyl group (e.g., CH_3) attached to the C=N carbon were generated as a mixture of *E*- and *Z*-isomers. For example, nitroethane (**1**) gave *E*-**14** and *Z*-**14** in a ratio of 1:1.9. Thiohydroximates with a larger alkyl group (e.g., *n*-C_5H_{11}) could be produced predominantly in the *Z*-form. An example is the conversion of **3** to *Z*-**16**. On the other hand, the thiohydroximate **15** possesses a small methyl group on the C=N carbon and a large phenyl group on sulfur. In this case the *E*-isomer was generated predominantly. These geometric isomers were, in many cases, readily separated by chromatography and recrystallization from hexanes.

Mechanism. Scheme II shows a mechanism, which can describe the "one-flask" conversion of primary nitro compounds into thiohydroxamic acids. It is reasonable to propose that the thiohydroxamates were formed by similar transformations. Scheme III illustrates a pathway to thiohydroxamic acid **12**. These reactions involve multistep processes and the formation of several intermediates. Nevertheless, isolation of the intermediates is unnecessary for the generation of the final products. Thus these reactions are efficient for the preparation of compounds with complex functionalities from simple starting materials.

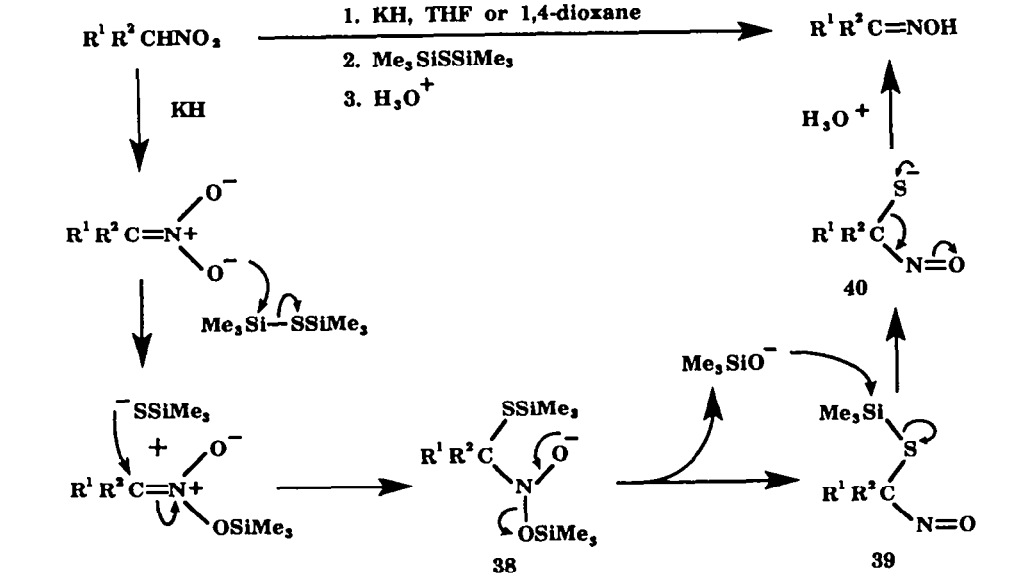
Scheme II



Scheme III



Scheme IV



A common feature of the mechanisms shown in Schemes II and III is the generation of a nitronate intermediate (i.e., **32** and **35**). Because proton sensitive silicon-containing reagents are used in the sequential steps, generation of nitronates must be carried out under aprotic conditions. The formation of nitronate **32** from RCH_2NO_2 and KH was straightforward. The nitronate **35** was readily prepared from **13** by the Michael addition of Pr^iSLi.[18] Scheme IV illustrates a plausible mechanism for the conversion of secondary nitro compounds into oximes by reaction with $Me_3SiSSiMe_3$. The intermediate $R^1R^2C(N{=}O)S^-$ **40** may decompose by either of two pathways. First, **40** might undergo 1,2-elimination to give a thioketone and hyponitrite. The results from our control experiment do not support this mechanistic hypothesis, however, since we did not detect any thioketone in the reaction mixture. Second, 1,1-elimination could occur in **40** to give sulfur and an oxime. In 1978, Soysa and Weber developed a method for the deoxygenation of sulfoxides.[19a] For this reaction, they proposed a novel mechanism involving the 1,1-elimination of thiosulfoxides (i.e., $R^1R^2S^+{-}S^-$).

Counterattack Reagents $RSSiMe_3$. Hexamethyldisilthiane, (alkylthio)trimethylsilanes, and (arylthio)trimethylsilanes have been utilized in various synthetic organic reactions.[19] In the preparation of thiohydroxamic acids and thiohydroximates (Scheme II and III), the reagents $Me_3SiSSiMe_3$, $MeSSiMe_3$, and $PhSSiMe_3$ are first attacked by nitronates at a silicon center. The leaving group, Me_3SiS^- or RS^-, then counterattacks the silylated nitronate intermediates. Thus $Me_3SiSSiMe_3$, $MeSSiMe_3$, and $PhSSiMe_3$ can be regarded as "counterattack reagents."[10,11] In Schemes II - IV, the Me_3SiO^- species was expelled from oxides **33**, **36**, and **38**. At a later step, the Me_3Si moiety in thiosilanes **34**, **37**, and **39** was attacked by Me_3SiO^- at the Si center. Thus the two electrophilic silicon centers and the one nucleophilic sulfur center in reagent $Me_3SiSSiMe_3$ are employed in the overall process. These "one flask" reactions represent an efficient method to prepare thiohydroxamic acids and esters and oximes. Schemes II, III, and IV are examples of the "tandem double-counterattack process."[10]

CONCLUSION

Thiohydroxamic acids and thiohydroximates were generated in high yields from primary nitro compounds and thiosilanes $Me_3SiSSiMe_3$, $MeSSiMe_3$, or $PhSSiMe_3$ under basic conditions. Similarly, secondary nitro compounds were reacted with thiosilanes to produce oximes in good to excellent yields. The design of these reactions involves the concept of a "counterattack reagent".

EXPERIMENTAL SECTION

General Procedure. All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen, unless otherwise indicated. Ethyl acetate and hexanes from Tilley Chemical Co. were dried and distilled from CaH_2. Tetrahydrofuran and 1,4-dioxane from J. T. Baker Chemical Co. were freshly distilled from Na and benzophenone. The following compounds and reagents were purchased from Aldrich Chemical Co.: nitroethane, 1-nitrohexane, methyl 4-nitrobutyrate, 2-(2-nitroethoxy)tetrahydropyran, *trans*-β-nitrostyrene, nitrocyclohexane, 2-nitropropane, 1-nitro-1-cyclohexene, 2-bromoheptane, (±)-camphor, acetophenone, benzylacetone, (phenylthio)trimethylsilane, L-selectride (1.0 M in tetrahydrofuran), 2-propanethiol, *n*-BuLi (2.5 M solution in hexanes), sodium nitrite, MeLi (1.4 M solution in diethyl ether), hydroxylamine hydrochloride, trifluoroacetic anhydride, hydrogen

peroxide (30 wt. % solution in water), and potassium hydride (KH, 35 wt. % dispersion in mineral oil). Hexamethyldisilathiane and (methylthio)trimethylsilane from Fluka Chemical Co. were stored in serum capped bottles under argon over molecular sieves 4Å. Melting points were obtained with a Büchi 510 melting point apparatus. Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel GHLF), purchased from Analtech Inc. Visualization of spots on TLC plates was done by use of UV light or 2.5% phosphomolybdic acid in ethanol with heating. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatography analyses were performed on a Hewlett–Packard 5794 instrument equipped with a 12.5-m cross-linked methyl silicone gum capillary column (0.2-mm i.d.); the injector temperature was set up at 260 °C. Purification by gravity column chromatography was carried out by use of EM Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM). Separations by radial thin-layer chromatography were performed on a model 7924T Chromatotron from Harrison Research. The plate with 1-mm thickness was coated with EM Reagents Silica Gel 60 PF_{254} containing gypsum. Infrared (IR) spectra were measured on a Perkin–Elmer 599B or 1600 Series FT-IR. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak; br, broad. Proton NMR spectra were obtained on a Varian CFT-20 (80 MHz) spectrometer by use of chloroform-*d* as solvent and tetramethylsilane as an internal standard. Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; hep, heptet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra and electron impact mass spectra (EIMS) were obtained with a VG Analytical 70-S mass spectrometer.

Preparation of Nitro Compounds 9, 11, 18, 22, 24, 26, and 28. (2-Nitroethyl)benzene (**9**) was prepared by reduction of *trans*-β-nitrostyrene with L-selectride.[20] (1-Isopropylthio-2-nitro)ethylbenzene (**11**) was generated by thiolation of *trans*-β-nitrostyrene with *i*-PrSLi in THF.[18] 2-Nitroheptane (**18**) was synthesized from 2-bromoheptane and sodium nitrite in DMF.[21] 2-Methyl-1-nitrocyclohexane (**22**) was obtained by alkylation of 1-nitro-1-cyclohexene with MeLi at –20°C to room temperature in THF.[22] Nitro compounds **24**, **26**, and **28** were produced by condensation of the corresponding ketones and hydroxylamine,[23] followed by oxidation of the resulting ketoximes with peroxytrifluoroacetic acid.[24]

Standard Procedure for the Preparation of Thiohydroxamic Acids. In a one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum, KH was washed with hexanes (3 x 5 mL). Hexanes were then removed to give KH as a white powder. A nitro compound and THF were added. After 30 min of stirring at 0 °C and then 1.0 h of stirring at room temperature under an atmosphere of nitrogen, hexamethyldisilathiane was added. This flask was surrounded with aluminum foil to avoid light. Stirring was continued at room temperature and then the mixture was heated if necessary. The reaction mixture was diluted with water at 0 °C, neutralized with 10% aqueous HCl, and extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was chromatographed to give the desired thiohydroxamic acid.

Acetothiohydroxamic Acid (2). The standard procedure was followed, using KH (61 mg, 1.5 mmol, 1.1 equiv), nitroethane (**1**, 101 μL, 1.39 mmol, 1.0 equiv), hexamethyldisilathiane (447 μL, 2.08 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 7 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **2** was obtained as a white solid in 81% yield (102 mg, 1.12 mmol): ^1H NMR ($CDCl_3$, 80 MHz) δ 2.34 (s, 3 H, CH_3), 7.92–8.55 (br, 2 H, NHOH); IR (CCl_4) 3565 (m, OH), 3400 (m, NH), 3195 (br, OH), 3064 (m), 2948 (m), 2900 (m), 2845 (m), 2550 (w, SH), 1540 (s, C=N),

1402 (s, C=S), 1364 (m), 1327 (w), 1240 (m), 1189 (m), 1062 (m), 995 (m), 964 (m), 900 (m) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[1,25,26]

Hexanothiohydroxamic Acid (4). The standard procedure was followed using KH (31 mg, 0.77 mmol, 1.1 equiv), 1-nitrohexane (**3**, 101 μL, 0.703 mmol, 1.0 equiv), hexamethyldisilathiane (227 μL, 1.05 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 24 h and then refluxed for 6 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **4** was obtained as a pale yellow solid in 87% yield (90 mg, 0.61 mmol): ^1H NMR ($CDCl_3$, 80 MHz) δ 0.90 (t, J = 5.3 Hz, 3 H, CH_3), 1.25–1.50 (m, 4 H, 2 x CH_2), 1.50–1.89 (m, 2 H, CH_2), 2.53 (t, J = 7.9 Hz, 2 H, CH_2C=S), 7.40–8.22 (br, 2 H, NHOH); IR (CCl_4) 3579 (w, OH), 3410 (m, NH), 3185 (br, OH), 3080 (m), 2945 (s), 2920 (s), 2857 (s), 2570 (w, SH), 1546 (s, C=N), 1445 (m, C=S), 1378 (m), 1249 (m), 1201 (m), 1100 (m), 1046 (m), 995 (m) cm^{-1}; exact mass calcd for $C_6H_{13}NOS$ 147.0718, found 147.0718.

3-(Methoxycarbonyl)propanothiohydroxamic Acid (6). The standard procedure was followed using KH (33 mg, 0.83 mmol, 1.1 equiv), methyl 4-nitrobutyrate (**5**, 101 μL, 0.759 mmol, 1.0 equiv), hexamethyldisilathiane (245 μL, 1.14 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 24 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **6** was obtained as a yellow solid in 92% yield (114 mg, 0.697 mmol): ^1H NMR ($CDCl_3$, 80 MHz) δ 2.66 (br, 4 H, CH_2CH_2), 3.74 (s, 3 H, CH_3), 5.70–6.18 (br, 2 H, NHOH); IR (CCl_4) 3581 (w, OH), 3444 (w, NH), 3220 (br, OH), 2938 (w), 2839 (w), 1725 (s, C=O), 1543 (s, C=N), 1431 (m, C=S), 1360 (w), 1309 (w), 1260 (m), 1216 (s, C–O), 1171 (m, C–O), 1001 (w), 975 (w) cm^{-1}.

Thiohydroxamic Acid 8. The standard procedure was followed using KH (29 mg, 0.72 mmol, 1.1 equiv), 2-(2-nitroethoxy)tetrahydropyran (**7**, 99 μL, 0.65 mmol, 1.0 equiv), hexamethyldisilathiane (211 μL, 0.978 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 46 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **8** was obtained as a yellow solid in 87% yield (108 mg, 0.567 mmol): ^1H NMR ($CDCl_3$, 80 MHz) δ 1.26–1.98 (m, 6 H, 3 x CH_2), 3.40–3.71 (m, 2 H, CH_2O), 4.61 (s, 2 H, CH_2C=S), 4.90 (t, J = 4.5 Hz, 1 H, OCHO); IR (CCl_4) 3561 (w, OH), 3380 (w, NH), 3250 (br, OH), 2924 (s), 2859 (s), 2833 (s), 1536 (s, C=N), 1457 (w), 1445 (w), 1432 (m, C=S), 1378 (w), 1344 (w), 1250 (m), 1195 (m), 1172 (w), 1118 (s, C–O), 1069 (s, C–O), 1029 (s, C–O), 1007 (s), 966 (s), 901 (s), 862 (m) cm^{-1}.

Phenylacetothiohydroxamic Acid (10). The standard procedure was followed using KH (29 mg, 0.73 mmol, 1.1 equiv), (2-nitroethyl)benzene (**9**, 101 mg, 0.662 mmol, 1.0 equiv), hexamethyldisilathiane (214 μL, 0.993 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 24 h and then refluxed for 48 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **10** was obtained as a yellow oil in 70% yield (77 mg, 0.46 mmol) and the by-product phenylacetonitrile was isolated in 15% yield (12 mg, 0.10 mmol).

For **10**: ^1H NMR ($CDCl_3$, 80 MHz) δ 3.95 (s, 2 H, CH_2), 7.05–7.55 (m, 5 H, C_6H_5), 7.64–8.25 (br, 2 H, NHOH); IR (CCl_4) 3589 (m, OH), 3389 (m, NH), 3260 (br, OH), 3072 (m, =C–H), 3025 (m, =C–H), 2955 (s), 2919 (m), 2578 (w, SH), 1602 (w, C=C), 1496 (s, C=N), 1449 (s, C=S), 1414 (m, C=C), 1343 (w), 1261 (m), 1091 (s), 1073 (s), 1026 (m), 809 (s), 779 (s, =C–H) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[3,25,26]

For Phenylacetonitrile: GC (column program: initial temperature 70 °C, duration 2.00 min;

increment rate 15 °C/min; final temperature 200 °C) t_R 4.60 min; TLC R_f 0.41 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 3.58 (s, 2 H, CH_2), 7.18 (s, 5 H, C_6H_5); IR (neat) 3049 (m, =C–H), 3037 (m, =C–H), 2943 (w), 2919 (w), 2243 (m, CN), 1600 (m, C=C), 1494 (s, C=C), 1453 (s), 1413 (s), 1075 (m), 1026 (m), 939 (w), 733 (s, =C–H), 693 (s, =C–H) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with those of an authentic sample.[27a]

2-Isopropylthio-2-phenylacetothiohydroxamic Acid (12). Method A. The standard procedure was followed using KH (29 mg, 0.73 mmol, 1.1 equiv), (1-isopropylthio-2-nitro)ethylbenzene (**11**, 151 mg, 0.666 mmol, 1.0 equiv), hexamethyldisilathiane (215 μL, 0.999 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 24 h and then refluxed for 48 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **12** was obtained as a yellow oil in 56% yield (90 mg, 0.37 mmol) and the by-product α-(isopropylthio)phenylacetonitrile was obtained as a yellow oil in 21% yield (27 mg, 0.14 mmol).

For **12**: ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.29 (d, J = 6.7 Hz, 6 H, 2 x CH_3), 2.96 (hep, J = 6.7 Hz, 1 H, SCH), 5.28 (s, 1 H, CHC=S), 7.32 (s, 5 H, C_6H_5), 7.64–8.25 (br, 2 H, NHOH); IR (CCl_4) 3561 (w, OH), 3440 (w, NH), 3263 (br, OH), 3042 (w, =C–H), 3010 (w, =C–H), 2958 (s), 2911 (s), 2845 (s), 2575 (w, SH), 1535 (s, C=N), 1438 (m, C=S), 1371 (m), 1240 (m), 1112 (s), 995 (m), 972 (m), 690 (m, =C–H) cm^{-1}.

For α-(Isopropylthio)phenylacetonitrile: GC (column program: initial temperature 70 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 7.94 min; TLC R_f 0.20 (20% EtOAc in hexanes); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.22 (d, J = 6.7 Hz, 6 H, 2 x CH_3), 2.85 (hep, J = 6.7 Hz, 1 H, CH), 5.12 (s, 1 H, CHCN), 7.00–7.65 (m, 5 H, C_6H_5); IR (CCl_4) 3042 (w, =C–H), 3010 (w, =C–H), 2966 (s), 2931 (s), 2861 (s), 2225 (w, CN), 1443 (m, C=C), 1437 (m), 1378 (m), 1343 (m), 1237 (m), 1149 (m), 1114 (s), 1067 (m), 903 (m), 711 (s, =C–H), 690 (s, =C–H) cm^{-1}; exact mass calcd for $C_{11}H_{13}NS$ 191.0769, found 191.0768.

Method B. Preparation of Thiohydroxamic Acid 12 from 13. A hexane solution of *n*-BuLi (401 μL, 0.992 mmol, 1.5 equiv) was added dropwise to a solution of 2-propanethiol (94 μL, 0.99 mmol, 1.5 equiv) in THF (10.0 mL) at –78 °C under an atmosphere of nitrogen. After 30 min at the same temperature, *trans*-β-nitrostyrene (**13**, 101 mg, 0.662 mmol, 1.0 equiv) in THF (1.0 mL) was added. The solution was stirred at room temperature for 3 h. Hexamethyldisilathiane (214 μL, 0.992 mmol, 1.5 equiv) was then added and the flask was surrounded with aluminum foil to avoid light. The reaction was stirred at room temperature for 24 h and then refluxed for 48 h. After workup and purification by use of gravity column chromatography (40% EtOAc in hexanes as eluant), thiohydroxamic acid **12** was obtained as a yellow oil in 50% yield (80 mg, 0.33 mmol).

Standard Procedure for the Preparation of Thiohydroximates. A hexane solution of *n*-BuLi was added dropwise to a flask containing a nitro compound in THF at 0 °C under an atmosphere of nitrogen. After 30 min of stirring at the same temperature, (methylthio)trimethylsilane or (phenylthio)trimethylsilane was added and stirring was continued at room temperature. The reaction mixture was diluted with water at 0 °C, neutralized with 10% aqueous HCl, and extracted with Et_2O (10 mL x 3). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was chromatographed to give the desired thiohydroximate.

***E*- and *Z*-*S*-Methyl Acetothiohydroximates (14).** The standard procedure was followed using *n*-BuLi (665 μL, 1.66 mmol, 1.2 equiv), nitroethane (**1**, 101 μL, 1.39 mmol, 1.0 equiv), (methylthio)trimethylsilane (299 μL, 2.08 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was

stirred at room temperature for 60 h. After workup and purification by use of a chromatotron (40% EtOAc in hexanes as eluant), a mixture of *E*- and *Z*-*S*-methyl acetothiohydroximates (*E*-**14**:*Z*-**14** = 1:1.9) was obtained as a white crystal in 78% yield (117 mg, 1.08 mmol). The mixture was recrystallized with hexanes to give the pure *Z*-**14** as a white crystal with mp 91.0–92.0 °C (lit. mp 88.0–90.0 °C).[17,28] The hexanes portion was condensed to give the *E*-**14** as a white crystal with mp 50.5–52.5 °C (lit. mp 50.0–52.0 °C).[17] The *E*-isomer gradually reverted to the *Z*-isomer at room temperature over several days.

For *E*-**14**: GC (column program: initial temperature 50 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 3.84 min; TLC R_f 0.67 (40% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.06 (s, 3 H, CCH_3), 2.31 (s, 3 H, SCH_3), 8.60 (s, 1 H, OH); IR ($CHCl_3$) 3563 (m, OH), 3200 (s, OH), 2980 (s), 2920 (s), 1612 (s, C=N), 1543 (w), 1430 (s), 1372 (s), 1335 (m), 1317 (m), 1015 (m), 972 (m), 916 (s), 620 (m) cm^{-1}; exact mass calcd for C_3H_7NOS 105.0248, found 105.0250. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[17]

For *Z*-**14**: GC (column program: initial temperature 50 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 5.58 min; TLC R_f 0.35 (40% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.15 (s, 3 H, CCH_3), 2.35 (s, 3 H, SCH_3), 8.60 (s, 1 H, OH); IR ($CHCl_3$) 3563 (m, OH), 3200 (s, OH), 2980 (s), 2920 (s), 1612 (s, C=N), 1543 (w), 1430 (s), 1372 (s), 1335 (m), 1317 (m), 1015 (m), 972 (m), 916 (s), 620 (m) cm^{-1}; exact mass calcd for C_3H_7NOS 105.0248, found 105.0250. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[17,28]

***E*-*S*-Phenyl Acetothiohydroximate (15).** The standard procedure was followed using *n*-BuLi (665 μL, 1.66 mmol, 1.2 equiv), nitroethane (**1**, 101 μL, 1.39 mmol, 1.0 equiv), (phenylthio)trimethylsilane (405 μL, 2.08 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 60 h. After workup, the crude product was purified by use of a chromatotron (20% EtOAc in hexanes as eluant) and then by recrystallization with hexanes. Pure thiohydroximate **15** was obtained as a white crystal with mp 120.5–122.5 °C[9] in 62% yield (144 mg, 0.859 mmol): GC (column program: initial temperature 80 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 9.78 min; TLC R_f 0.21 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.79 (s, 3 H, CH_3), 7.15–7.70 (m, 5 H, C_6H_5), 9.05–9.10 (br, 1 H, OH); IR ($CHCl_3$) 3560 (m, OH), 3160 (s, OH), 2978 (s), 2820 (s), 1618 (s, C=N), 1581 (m), 1468 (s, C=C), 1433 (m), 1370 (s), 1327 (m), 1015 (s), 935 (s), 915 (s) cm^{-1}; exact mass calcd for C_8H_9NOS 167.0405, found 167.0408.

***Z*-*S*-Methyl Hexanothiohydroximate (16).** The standard procedure was followed using *n*-BuLi (337 μL, 0.843 mmol, 1.2 equiv), 1-nitrohexane (**3**, 101 μL, 0.702 mmol, 1.0 equiv), (methylthio)trimethylsilane (157 μL, 1.05 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 48 h. After workup and purification by use of a chromatotron (20% EtOAc in hexanes as eluant), thiohydroximate **16** was obtained as a white crystal with mp 63.5–64.0 °C in 61% yield (69 mg, 0.43 mmol): GC (column program: initial temperature 80 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 6.59 min; TLC R_f 0.30 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.90 (t, J = 6.0 Hz, 3 H, CH_3), 1.08–1.74 (m, 6 H, 3 x CH_2), 2.35 (s, 3 H, SCH_3), 2.44 (t, J = 8.0 Hz, 2 H, CH_2C=N), 8.01 (s, 1 H, OH); IR ($CHCl_3$) 3589 (w, OH), 3260 (m, OH), 2954 (s), 2919 (s), 2860 (m), 1608 (m, C=N), 1461 (m), 1431 (m), 1378 (w) cm^{-1}; exact mass calcd for $C_7H_{15}NOS$ 161.0874, found 161.0877.

***Z*-*S*-Methyl Phenylacetothiohydroximate (17).** The standard procedure was followed using *n*-

BuLi (360 μL, 0.897 mmol, 1.2 equiv), (2-nitroethyl)benzene (**9**, 113 mg, 0.748 mmol, 1.0 equiv), (methylthio)trimethylsilane (168 μL, 1.12 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 48 h. After workup and purification by use of a chromatotron (10% EtOAc in hexanes as eluant), thiohydroximate **17** was obtained as a white crystal with mp 122.0–122.5 °C in 63% yield (86 mg, 0.47 mmol): GC (column program: initial temperature 80 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 8.61 min; TLC R_f 0.49 (40% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.19 (s, 3 H, CH_3), 3.83 (s, 2 H, CH_2), 7.28 (s, 5 H, C_6H_5), 8.47–8.50 (br, 1 H, OH); IR ($CHCl_3$) 3577 (s, OH), 3272 (m, OH), 3013 (s, =C–H), 2919 (w), 1596 (m, C=N), 1490 (m), 1449 (m, C=C), 1208 (s), 967 (s) cm^{-1}; exact mass calcd for $C_9H_{11}NOS$ 181.0561, found 181.0565.

Standard Procedure for the Preparation of Oximes. In a one-necked, round-bottomed flask equipped with a stirring bar and a rubber septum, KH was washed with hexanes (3 x 5 mL). Hexanes were then removed to give KH as a white powder. A nitro compound and THF or 1,4-dioxane were added. After 1.0 h of stirring at room temperature under an atmosphere of nitrogen, hexamethyldisilathiane or (methylthio)trimethylsilane was added. Stirring was continued at room temperature and then the mixture was heated if necessary. The reaction mixture was diluted with water at 0 °C, neutralized with 10% aqueous HCl, and extracted with Et_2O (10 mL x 3). The combined organic layers were washed with saturated aqueous NaCl, dried over $MgSO_4$(s), filtered, and concentrated under reduced pressure. The residue was chromatographed to give the desired oxime.

***E*- and *Z*-2-Heptanone Oximes (19).** The standard procedure was followed using KH (30 mg, 0.76 mmol, 1.1 equiv), 2-nitroheptane (**18**, 101 mg, 0.689 mmol, 1.0 equiv), hexamethyldisilathiane (163 μL, 0.758 mmol, 1.1 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 24 h and then refluxed for 24 h. After workup and purification by use of a chromatotron (5% EtOAc in hexanes as eluant), oxime **19** was obtained as a yellow oil in 96% yield (85 mg, 0.66 mmol): GC (column program: initial temperature 80 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 3.60 min; TLC R_f 0.34 (10% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.89 (t, J = 4.5 Hz, 3 H, CH_3), 1.19–1.75 (m, 6 H, 3 x CH_2), 1.89, 2.02 (two s, 3 H, *E* and Z CH_3), 2.20 (t, J = 7.6 Hz, 2 H, CH_2C=N), 7.86–8.21 (br, 1 H, OH); IR (CCl_4) 3587 (m, OH), 3225 (br, OH), 2958 (m), 2924 (m), 2859 (m), 1550 (s, C=N), 1461 (w), 1372 (w), 1266 (m), 1215 (w), 1009 (m), 979 (m), 912 (w) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with data in the literature.[29]

Cyclohexanone Oxime (21). Method A. The standard procedure was followed using KH (35 mg, 0.88 mmol, 1.1 equiv), 1-nitrocyclohexane (**20**, 101 μL, 0.798 mmol, 1.0 equiv), hexamethyldisilathiane (189 μL, 0.876 mmol, 1.1 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 24 h and then refluxed for 20 h. After workup and purification by use of a chromatotron (20% EtOAc in hexanes as eluant), oxime **21** was obtained as a white solid with mp 86.5–87.5 °C (lit. mp 88.0 °C)[30] in 83% yield (75 mg, 0.66 mmol): GC (column temperature 80 °C) t_R 3.26 min; TLC R_f 0.16 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.42–1.85 (br, 6 H, 3 x CH_2), 3.22 (t, J = 5.9 Hz, 2 H, CH_2C=N), 3.50 (t, J = 5.8 Hz, 2 H, CH_2C=N), 9.03–9.30 (br, 1 H, OH); IR (CCl_4) 3584 (m, OH), 3250 (br, OH), 2921 (s), 2844 (m), 1541 (s, C=N), 1445 (m), 1312 (w), 1248 (m), 1217 (m), 1100 (w), 985 (m), 945 (w), 886 (w) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with those of an authentic sample.[27b]

Method B. The standard procedure was followed using KH (35 mg, 0.88 mmol, 1.1 equiv), 1-nitrocyclohexane (**20**, 101 μL, 0.798 mmol, 1.0 equiv), (methylthio)trimethylsilane (127 μL, 0.876 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 48 h.

After workup and purification by use of a chromatotron (20% EtOAc in hexanes as eluant), oxime **21** was obtained as a white solid in 69% yield (62 mg, 0.55 mmol).

***E*- and *Z*-2-Methylcyclohexanone Oximes (23).** The standard procedure was followed using KH (32 mg, 0.81 mmol, 1.1 equiv), 2-methyl-1-nitrocyclohexane (**22**, 99 mg, 0.73 mmol, 1.0 equiv), hexamethyldisilathiane (173 μL, 0.802 mmol, 1.1 equiv), and 1,4-dioxane (10.0 mL). The mixture was heated at 90–95 °C for 40 h. After workup and purification by use of a chromatotron (10% EtOAc in hexanes as eluant), oxime **23** was obtained as a white solid with mp 41.0–42.0 °C (lit. mp 43.0 °C)[30] in 81% yield (71 mg, 0.59 mmol): GC (column program: initial temperature 70 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 4.50 min; TLC R_f 0.14, 0.27 for *E*- and *Z*-isomers (10% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.11 (d, J = 6.6 Hz, 3 H, CH_3), 1.14–1.81 (m, 6 H, 3 x CH_2), 1.81–2.43 (m, 2 H, CH_2C=N), 2.79–3.25 (m, 1 H, CHC=N), 8.24–8.55 (br, 1 H, OH); IR (CCl_4) 3592 (m, OH), 3260 (br, OH), 2969 (m), 2930 (s), 2858 (m), 1545 (s, C=N), 1447 (m), 1389 (w), 1244 (m), 1004 (m), 977 (m), 948 (s), 920 (m) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[31]

Camphor Oxime (25). The standard procedure was followed using KH (29 mg, 0.72 mmol, 1.1 equiv), 1,7,7-trimethyl-2-nitrobicyclo[2.2.1]heptane (**24**, 120 mg, 0.655 mmol, 1.0 equiv), hexamethyldisilathiane (155 μL, 0.721 mmol, 1.1 equiv), and 1,4-dioxane (10.0 mL). The mixture was heated at 90–95 °C for 40 h. After workup and purification by use of a chromatotron (10% EtOAc in hexanes as eluant), oxime **25** was obtained as a white solid with mp 115.0–116.0 °C (lit. mp 117.0 °C)[32] in 80% yield (93 mg, 0.52 mmol): GC (column program: initial temperature 70 °C, duration 2.00 min; increment rate 15 °C/min; final temperature 250 °C) t_R 6.66 min; TLC R_f 0.20 (10% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 0.81 (s, 3 H, CH_3), 0.92 (s, 3 H, CH_3), 1.01 (s, 3 H, CH_3), 1.08–1.91 (m, 5 H, 2 x CH_2 + CH), 2.46 (dd, J = 2.9, 16.0 Hz, 1 H, CHC=N), 2.68 (dd, J = 3.1, 16.0 Hz, 1 H, CHC=N), 7.76–8.20 (br, 1 H, OH); IR (CCl_4) 3595 (w, OH), 3280 (br, OH), 2957 (s), 2923 (s), 2871 (m), 1549 (s, C=N), 1460 (w), 1391 (w), 1375 (w), 1250 (m), 1219 (m), 1005 (m), 980 (m), 931 (w), 912 (m) cm^{-1}. Its physical properties and spectroscopic characteristics are consistent with data reported in the literature.[32]

Acetophenone Oxime (27). The standard procedure was followed using KH (29 mg, 0.73 mmol, 1.1 equiv), (1-nitroethyl)benzene (**26**, 101 mg, 0.663 mmol, 1.0 equiv), hexamethyldisilathiane (157 μL, 0.728 mmol, 1.1 equiv), and 1,4-dioxane (10.0 mL). The mixture was heated at 90–95 °C for 4 days. After workup and purification by use of a chromatotron (5% EtOAc in hexanes as eluant), oxime **27** was obtained as a white solid with mp 57.0–58.0 °C (lit. mp 59.0 °C)[30] in 81% yield (72 mg, 0.54 mmol): GC (column program: initial temperature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 7.44 min; TLC R_f 0.15 (5% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 2.31 (s, 3 H, CH_3), 7.26–7.72 (m, 5 H, C_6H_5), 8.65–8.83 (br, 1 H, OH); IR (CCl_4) 3563 (m, OH), 3240 (br, OH), 3041 (m, =C–H), 2885 (w), 1535 (s, C=N), 1438 (m, C=C), 1359 (m), 1270 (m), 1241 (m), 1206 (w), 995 (s), 921 (s), 907 (m), 678 (s, =C–H) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[33]

***E*- and *Z*-4-Phenyl-2-butanone Oximes (29).** The standard procedure was followed using KH (31 mg, 0.74 mmol, 1.1 equiv), (3-nitrobutyl)benzene (**28**, 121 mg, 0.671 mmol, 1.0 equiv), hexamethyldisilathiane (159 μL, 0.737 mmol, 1.1 equiv), and 1,4-dioxane (10.0 mL). The mixture was heated at 90–95 °C for 4 days. After workup and purification by use of a chromatotron (10% EtOAc in hexanes as eluant), oxime **29** was obtained as a white solid with mp 86.5–87.0 °C (lit. mp 86.0 °C)[34] in 83% yield (91 mg, 0.56 mmol): GC (column program: initial temperature 70 °C, duration 2.00 min; increment rate 10 °C/min; final temperature 250 °C) t_R 8.99, 9.26 min for *E*- and *Z*-isomers; TLC R_f 0.36 (20% EtOAc in hexanes as eluant); ^{1}H NMR ($CDCl_3$, 80 MHz) δ 1.90 (s,

3 H, CH_3), 2.31–2.57 (m, 2 H, CH_2), 2.61–2.94 (m, 2 H, CH_2), 7.23 (s, 5 H, C_6H_5), 8.11–8.62 (br, 1 H, OH); IR (CCl_4) 3589 (m, OH), 3284 (br, OH), 3081 (m, =C–H), 3062 (m, =C–H), 3025 (s, =C–H), 2922 (s), 2856 (w), 1601 (w, C=C), 1491 (m, C=N), 1450 (s, C=C), 1362 (m), 1159 (w), 1077 (w), 1031 (m), 943 (m), 797 (s), 781 (s), 752 (s), 698 (s, =C–H) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with data reported in the literature.[22]

Acetone Oxime (31). The standard procedure was followed using KH (47 mg, 1.18 mmol, 1.1 equiv), 2-nitropropane (**30**, 101 μL, 1.068 mmol, 1.0 equiv), (methylthio)trimethylsilane (232 μL, 1.602 mmol, 1.5 equiv), and THF (10.0 mL). The mixture was stirred at room temperature for 48 h. After workup and purification by use of a chromatotron (20% EtOAc in hexanes as eluant), oxime **31** was obtained as a white solid with mp 61.0–62.0 °C (lit. mp 60.0–63.0 °C)[27c] in 68% yield (53 mg, 0.73 mmol): TLC R_f 0.16 (20% EtOAc in hexanes as eluant); ^1H NMR ($CDCl_3$, 80 MHz) δ 1.89 (s, 6 H, 2 x CH_3), 8.33–8.85 (br, 1 H, OH); IR (CCl_4) 3585 (s, OH), 3228 (br, OH), 2960 (m), 1545 (s, C=N), 1460 (m), 1375 (s), 1268 (s), 1062 (s), 935 (s) cm^{-1}. Its physical properties and spectroscopic characteristics were consistent with those of an authentic sample.[27c]

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