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Nickelocene–Lithium Aluminum Hydride: A Versatile Desulfurization Reagent[1]

Man-Chor Chan, Kwok-Man Cheng, Kim Man Ho, Chi Tat Ng, Tsz Man Yam,
Betty S. L. Wang, and Tien-Yau Luh*

Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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A new homogeneous organonickel reagent prepared from nickelocene and $LiAlH_4$ has been shown to be effective for the reduction of the carbon–sulfur bonds of thiols, thioethers, sulfoxides, and sulfones to the corresponding carbon–hydrogen bonds. Functional groups such as isolated double bonds, esters, and carbonyls as well as halides remain intact under the reaction conditions. Preliminary studies on the nature of the reagent and the mechanism for the reaction have been carried out by employing deuterium labeling experiments and spectroscopic methods. Metal hydridic species may play an important role in these reactions. The reagent can also be used to reduce the carbon–carbon double bond of conjugate enones and to catalyze hydrogenation of carbon–carbon multiple bonds. A comparison of the reaction behavior of this newly developed nickel reagent with that of Raney nickel is discussed.

Raney nickel is widely used as the reagent for the reductive cleavage of the carbon–sulfur bond.[2] The mechanism for this important reaction is, however, not well established. Some kind of interaction between the sulfur moiety and nickel metal followed by the transfer of interstitial hydrogen from the metal surface has been suggested.[3] Mechanistic principles developed with homogeneous systems may sometimes apply to heterogeneous catalysis, for which much less mechanistic information is available.[4] Accordingly, organometallic reagent promoted reduction of carbon–sulfur bonds has recently received much attention.[5-19] To illustrate this, a Ni(0) complex has been employed to convert dibenzothiophene into biphenyl.[13] Certain transition-metal hydridic species have also been useful for desulfurization reactions.[14] Even secondary Grignard reagents in the presence of nickel catalyst, on the other hand, were found to be active for the reduction of the carbon–sulfur bond.[15] In this case, a metal hydridic species may be formed by β-elimination of nickel

Chart I

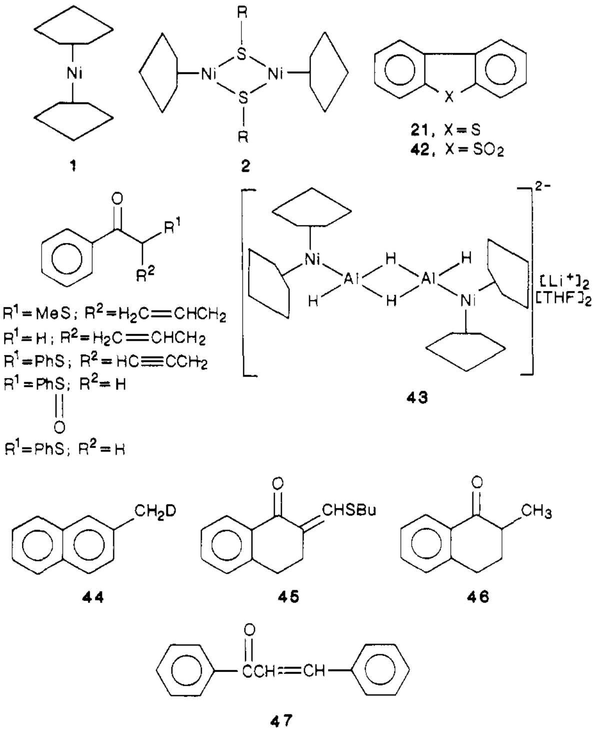

Table I. Desulfurization of Thiols with 3

substrate	product; % yield
2-naphthylmethanethiol (**4**)	2-methylnaphthalene (**12**); 80
1-naphthylmethanethiol (**5**)	1-methylnaphthalene (**13**); 83
2-naphthalenethiol (**6**)	naphthalene (**14**); 74
1-decanethiol (**7**)	decane (**15**); 41
1-adamantanethiol (**8**)	adamantane (**16**); 46
(3-(trifluoromethyl)phenyl) methanethiol (**9**)	α,α,α-trifluoro-*m*-xylene (**17**); 34
(4-methoxyphenyl)methanethiol (**10**)	4-methylanisole (**18**); 36
(4-(methoxycarbonyl)-phenyl) methanethiol (**11**)	4-(methoxycarbonyl)toluene (**19**); 40

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[1] Part 19 of the series "Transition-Metal-Promoted Reactions".

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Table II. Desulfurization of Thioethers with 3

substrate	product; % yield
bis(2-naphthylmethyl) sulfide (**20**)	2-methylnaphthalene (**12**); 67
dibenzothiophene (**21**)	biphenyl (**27**); 70
α-(methylthio)acetophenone (**22**)	acetophenone (28); 74
α-(methylthio)-α-allylacetophenone (**23**)	5-phenyl-5-oxopent-1-ene (**29**); 78
9,9-(ethylenedithio)fluorene (**24**)	fluorene (**30**); 55
9,9-(ethylenedithio)-2-nitrofluorenone (**25**)	2-aminofluorene (**31**); 40
2,2-(ethylenedithio)-adamantane, (**26**)	adamantane (**16**); 42

alkyls.[15,20] As a metal hydride can readily be formed by the reduction of metal halide with complexed metal hydride,[21] it has been reported that, in the presence of certain transition-metal halides, $LiAlH_4$ or $NaBH_4$ is effective for the reduction of the carbon–sulfur bond.[16-19]

Nickelocene (1; Chart I) readily reacts with mercaptans to give the corresponding dinuclear complexes, **2**.[22] We recently reported that the carbon–sulfur bond of such a complex is activated and can be readily reduced with lithium aluminum hydride.[23] A metal hydride intermediate was proposed.[23] In view of this interesting finding we felt that nickelocene itself might be used with complexed metal hydride to serve as an effective reducing agent for the desulfurization reaction. We now wish to report the details on the versatility of this newly developed reagent, especially for the reduction of various carbon–sulfur bonds.[24]

Results and Discussion

The reagent 3 was prepared by admixing an equimolar amount of 1 and $LiAlH_4$ in THF solution. The mixture turned from deep green to dark brown. The reaction was very vigorous, and 1 molar equiv of hydrogen was evolved from the reaction mixture. The reagent 3 is indefinitely stable under a nitrogen atmosphere at room temperature. After stirring at room temperature for 15–30 min, the solution was then treated with organosulfur compounds at ambient temperature, unless otherwise specified.

Desulfurization of Thiols and Thioethers. In general, 1 equiv of 3 was used for the desulfurization of mercaptans while 2 equiv of 3 was employed for the reduction of thioethers. After workup, the corresponding reduced products were obtained. Tables I and II summarize the desulfurization results with thiols and thioethers, respectively. It is interesting to note that thiols reacted vigorously upon mixing with 3, and 1 equiv of hydrogen was formed. This observation has implications for the mechanism of the reaction, which will be discussed later.

From Tables I and II, various carbon–sulfur bonds were reduced in moderate to good yields. α-Acyl-substituted, benzylic, or aryl carbon–sulfur bonds were found to be cleaved easily under the reaction conditions. On the other hand, more vigorous conditions were required for the simple C_{sp^3}–S bond. Hence, 1-decanethiol (**7**) was reduced to decane in 41% yield under refluxing conditions. Bridgehead thiol could also be reduced under similar conditions. Thus, adamantane was obtained in 46% yield from the reaction of 1-adamantanethiol (**8**). The fact that the aryl–sulfur bond is more reactive than the alkyl–sulfur bond is somewhat striking. It is noted that the aryl carbon–sulfur bond of alkyl aryl sulfide is selectively cleaved with $Os_3(CO)_{12}$,[7] and the facile oxidative addition across the aryl carbon–sulfur bond has recently been reported.[25]

Table III. Reaction of Sulfoxides and Sulfones with 3

substrate	product; % yield
bis(2-naphthylmethyl) sulfoxide (**34**)	2-methylnaphthalene (**12**); 47
decyl phenyl sulfoxide (**35**)	decane (**15**); 35
1-naphthylmethyl phenyl sulfoxide (**36**)	1-methylnaphthalene (**13**); 58
bis(2-naphthylmethyl) sulfone (**37**)	2-methylnaphthalene (**12**); 38
ethyl 2-naphthylmethyl sulfone (**38**)	2-methylnaphthalene (**12**); 54
α-(phenylsulfonyl)acetophenone (**39**)	acetophenone (**28**); 63

As shown in Tables I and II, various functional groups are stable under the reaction conditions. Halogen, methoxy, trifluoromethyl, carbonyl, and ester groups remain intact during the course of the reaction. Thioketals were reduced smoothly. However, a large excess of 3 was employed in order to give a satisfactory yield. Thus, fluorene was obtained in 55% yield when **24** was treated with 8 equiv of 3. The nitro group was found to be unstable under the reaction conditions. Hence, 2-aminofluorene (**31**) was obtained in 40% yield from 2-nitrofluorenone thioketal (**25**). It is worth mentioning that the nitro group can also be reduced by Raney nickel.[2]

An isolated double bond was found to be stable under the reaction conditions. As an illustration, the reduction of α-(methylthio)-α-allylacetophenone (**23**) gave **29** in 78% yield. It is noteworthy that the double bond in **23** was neither reduced nor caused to rearrange. The terminal alkyne, on the other hand, is unstable toward 3. Thus, **32** decomposed under the reaction conditions. It is noted that organonickel compounds can catalyze oligomerization reactions of alkynes.[26] Attempts to reduce ethyl thiobenzoate (**33**) were unsuccessful, and only starting material was recovered.

Several other conditions have been tested for the desulfurization reaction. The reagent prepared from bis(pentamethylcyclopentadienyl)nickel and $LiAlH_4$ was less reactive than 3. Other reducing agents, such as sodium amalgam or sodium borohydride reacted with nickelocene to give dark brown mixtures that were inert toward dibenzothiophene. A mixture of nickel bromide and $LiAlH_4$, on the other hand, was inactive under similar conditions, and $LiAlH_4$ alone did not promote reductive desulfurization.

Desulfurization of Sulfoxides and Sulfones. Since sulfoxides or sulfones can also readily be desulfurized by Raney nickel,[2] it was interesting to investigate the reactivity of 3 toward these substrates. Indeed, reactions of sulfoxides or sulfones with 2 equiv of 3 afforded the corresponding reduced products (Table III).

In general, the reaction required more time than the desulfurization of thioethers under similar conditions. It

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is interesting to note that a significant amount of thioether was obtained when the mixture was quenched before the reaction was complete. For example, thioether **41** and acetophenone were obtained in 20% and 25% yields, respectively, when the mixture of sulfoxide **40** and **3** was quenched before completion of the reaction. In a similar manner, dibenzothiophene (**21**) was isolated in 70% yield when sulfone **42** was treated with 1 equiv of **3**. In both reactions, the corresponding deoxygenated products were obtained in significant yields. Consequently, it is reasonable to suggest that the reaction may first involve a reduction of the sulfur–oxygen bond followed by the desulfurization process. The latter step may occur in the same manner as in the reduction of thioethers. It is noteworthy that the sulfur–oxygen bond can be reduced by a number of reducing agents.[27,28]

Nature of the Reagent 3. As described above, the nickel reagent, **3**, is apparently widely applicable for the reduction of various carbon–sulfur bonds. It was accordingly intriguing to investigate the nature of the reagent, which could provide useful information on the mechanism of the reaction. The THF solution of **1** and $LiAlH_4$ showed no signal in the ESR spectrum. Since **1** is paramagnetic and exhibits ESR absorption, this result suggests that all nickelocene was consumed upon treatment with $LiAlH_4$. Furthermore, there is no absorption between 1600 and 2200 cm^{-1} in the infrared region, while $LiAlH_4$ in THF absorbs at 1693 and 1644 (sh) cm^{-1}.[23,29] This finding indicates that all $LiAlH_4$ has been consumed.

The ^{13}C NMR spectrum for **3** in THF-d_8 exhibited only one absorption at δ 104.6 over the range of -100 to $+240$ ppm. The spectrum remained unchanged from -80 °C to ambient temperature. This absorption is characteristic for the symmetrically coordinated η^5-cyclopentadienyl ring.[30] This observation indicates that there is only one kind of cyclopentadienyl ring in the system and the cyclopentadienyl moiety remains symmetrically attached to some kind of metallic species during the course of the preparation of the reagent. It is noted that the starting material nickelocene is a 20-electron paramagnetic species. Reduction of this species is usually accompanied by the release of a cyclopentadienyl ring.[31] However, in this study we observed no signals other than those of the cyclopentadienyl moiety in the ^{13}C NMR spectrum. This observation suggests that both cyclopentadienyls may be still equivalently bonded, presumably to the nickel atom, on the NMR time scale. In other words, the cyclopentadienyl ligand in nickelocene may not be liberated upon reacting with $LiAlH_4$.

The ^1H NMR spectrum also showed a singlet at δ 5.80 (10 H), attributed to the absorption of the η^5-cyclopentadienyl ring. In addition, two broad singlets at δ 1.90 (1 H) and 2.40 (1 H) are assigned to the absorption of some kind of metal hydride. Again the NMR spectrum was not temperature dependent. These latter two signals disappeared when $LiAlD_4$ was employed as the reducing agent. Moreover, no absorption due to $LiAlH_4$ was observed.[23,29] The active reagent **3** contains ionic lithium because it showed a sharp singlet at δ -6.70 with reference to external LiCl in the ^7Li NMR.[32]

The chemistry of transition-metal aluminum hydride complexes has recently received much attention.[33] The IR bands for these complexes are sometimes very difficult to assign because of serious overlapping of different stretch frequencies.[33] It is noted that both terminal Al–H and bridged Al(μ-H)Al resonate in the NMR spectrum at lower field, while hydrides attached to transition metals normally emerge at much higher field.[33,34] As mentioned earlier, 1 equiv of hydrogen molecule was liberated during the course of the preparation of **3**. The stoichiometry of **3** would be $Cp_2NiAlH_2Li\cdot THF$ as revealed by the NMR study as well as by nickel analysis. One of the metal hydridic species might be the terminal aluminum hydride, and the other, the bridged one. Accordingly, structure **43**, which is consistent with the spectroscopic properties, is proposed for the active species **3**.[35] Attempts to obtain a single crystal of the active reagent for X-ray analysis were unsuccessful. It is noted that the composition of **3** is quite similar to that of Eisch's reagent, $LiAlH_2\cdot Ni\cdot(bpy)$, prepared from (2,2′-bipyridyl)(1,5-cyclooctadiene)nickel and lithium aluminum hydride.[13c]

Deuterium Labeling Studies. Since the reaction involves the reduction of the carbon–sulfur bond to the corresponding carbon–hydrogen bond, our main concern will be the origin of hydrogen. Our normal workup procedure involves quenching the reaction mixture with water. However, a nonaqueous workup procedure afforded, from the reaction of **4**, **12** in 82% yield. Furthermore, the use of D_2O instead of H_2O in the normal workup procedure using the same substrate yielded **12** (80%) without deuterium incorporation. These findings rule out water to be the possible hydrogen source.

From Table II, thioethers were successfully reduced to the corresponding hydrocarbons in good yields. Furthermore, compounds such as **6–8**, **21**, **24–26**, and **35**, which have no benzylic hydrogen(s), were smoothly desulfurized under the reaction conditions. These results suggest that activated hydrogen(s) may not be involved in the hydrogen atom transfer process.

When **4** was treated with the reagent prepared from $LiAlD_4$, at least 80% deuterium incorporation was found in the product 2-methylnaphthalene (**44**). This experiment demonstrates that the hydrogen source is indeed from the reducing agent.

Organosulfur compounds can form various kinds of complexes with transition metals.[37,38] The carbon–sulfur bonds are activated in certain thiolato complexes and, hence, readily cleaved by thermolysis[39] or by reducing agent.[23] Accordingly, it seems reasonable that, during the course of desulfurization, some kind of complex may first be formed. It is noted that the carbon–sulfur bond can undergo an oxidative addition reaction with a Ni(0) com-

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plex to give the corresponding carbon–nickel bond.[25] Such a process may be important for the reductive cleavage of carbon–sulfur bonds. As mentioned above, **3** contains metal hydridic functions. Consequently, direct abstraction of hydrogen from this hydridic moiety may occur to give the corresponding reduced product. It is noted that the thermolysis of the nickel complexes having hydrido and arylthiolato ligands caused cleavage of the C–S bond to evolve Ar–H.[40] Alternatively, electron transfer could also occur, leading to the cleavage of the carbon–sulfur bond,[13] and the intermediate thus obtained might undergo hydrogen abstraction from the nickel reagent.

Reduction of Enones. As discussed above, functional groups such as carbonyl and ester as well as the isolated double bond are stable under the reaction conditions. It is noted that 2-(alkylthio)methylene ketones are readily reduced by Raney nickel to the corresponding methyl ketones.[2] In this reaction, both the carbon–sulfur bond and the carbon–carbon double bond are reduced. We have carried out a similar reaction with our nickel reagent for comparison. Thus, 2-((butylthio)methylene)tetralone (**45**) was allowed to react with **3** to give 2-methyltetralone (**46**). We have extended our investigation to other conjugated enones and have found that our nickel reagent can serve as a general reagent to reduce the carbon–carbon double bond of these substrates. To illustrate this, cyclohexenone was reduced to cyclohexanone. Benzalacetophenone (**47**) behaved similarly. Although the yields in these reactions, in general, are not satisfactory, the similarity between our nickel reagent mediated reactions and those promoted by Raney nickel is of interest.

Catalytic Hydrogenation. It is noted that Raney nickel is an active catalyst for the hydrogenation reaction. Our reagent has also been shown to be a homogeneous catalyst for hydrogenation.[41] Various disubstituted double bonds were found to be reduced in excellent yields at ambient temperature and atmospheric pressure of hydrogen. This observation further demonstrates the similarity between Raney nickel and our nickel reagent.

Conclusion

In summary, we have depicted a new homogeneous organonickel reagent **3** for the reductive cleavage of various carbon–sulfur bonds and for the reduction of double bonds. The reaction behavior is very similar to that of Raney nickel and to Eisch's nickel reagent.[13c] Hence, this reagent **3** may serve as a homogeneous model for the study of the mechanism of the reaction promoted by Raney nickel or other heterogeneous hydrodesulfurization catalysts.

Experimental Section

All melting and boiling points are uncorrected. Infrared spectra were recorded on a Nicolet 20SX FT-IR spectrophotometer or on a Perkin-Elmer 283 spectrophotometer. NMR spectra were taken on a Bruker WM250 NMR spectrometer or on a JEOL PMX-60 NMR spectrometer. The ^1H or ^{13}C chemical shifts are reported on the δ scale in parts per million with reference to internal Me_4Si unless otherwise specified. The ^7Li NMR spectra were obtained at 97.2 MHz on a Bruker WM250 NMR spectrometer, and their chemical shifts are recorded on the δ scale in parts per million with reference to external LiCl in D_2O. The ^2H NMR spectra were measured at 38.4 MHz on a Bruker WM250 instrument. Chemical shifts are expressed on the δ scale relative to perdeuterio Me_4Si. In practice, internal C_6D_6 (δ 6.90) was used as reference. Mass spectra (EI) were measured on a VG7070F mass spectrometer. ESR spectra were recorded on a JEOL JES-FE3X spectrometer.

All reactions involving air-sensitive organometallic compounds were conducted under a nitrogen atmosphere according to standard procedures.[42] Solvents were purified according to standard procedures.[43] Commercial THF-d_8 was dried with sodium and stored under nitrogen without further purification. Nickelocene (**1**) was synthesized following the known procedure.[44] Mercaptans,[45] thioethers,[46] thioacetals,[47] sulfoxides,[27] and sulfones[28] were synthesized according to literature procedures.

α-(Methylthio)-α-allylacetophenone (23). Sodium hydride (80%, 0.80 g, 0.027 mol) in a three-necked round-bottom flask was first washed with petroleum ether 3 times under a nitrogen atmosphere. THF (150 mL) was introduced and the mixture was cooled to ca. −78 °C. Compound **22** (4.2 g, 0.025 mol) was then added dropwise, and the mixture was gradually warmed to room temperature. A solution of allyl bromide (4.5 g, 0.037 mol) in THF (30 mL) was then added, and the reaction mixture was stirred overnight under nitrogen, poured into water (100 mL), and extracted with ether (4 × 20 mL). The ethereal solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated in vacuo to give a residue, which was distilled to afford **23** (4.5 g, 86%): bp 78–82 °C at 0.08 mm; ^1H NMR ($CDCl_3$) δ 1.90 (3 H, s), 2.30–2.90 (2 H, m), 4.22 (1 H, t, J = 7.5 Hz), 4.90–5.35 (2 H, m), 5.40–6.30 (1 H, m), 7.10–8.00 (5 H, m); ν_{max} 1687 cm^{-1}; m/e 206.0743 (calcd for $C_{12}H_{14}OS$, 206.0762).

α-(Phenylthio)-α-propargylacetophenone (32). In a similar manner as described for the preparation of **23**, a mixture of sodium hydride (80%, 0.50 g, 0.017 mol), α-(phenylthio)acetophenone (3.0 g, 0.013 mol), and propargyl bromide (1.6 g, 0.013 mol) was transformed into **32** (2.6 g, 74%): mp 104–106 °C; ν_{max} 2110, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.00–2.20 (1 H, bs), 2.70–2.90 (2 H, m), 4.70 (1 H, t, J = 7.5 Hz), 7.4–8.3 (9 H, m); m/e 266.0743 (calcd for $C_{17}H_{14}OS$, 266.0776).

2,2-(Ethylenedithio)adamantane (26). A mixture of adamantanone (6.0 g, 0.04 mol), 1,2-ethanedithiol (10 mL, 0.12 mol), and boron trifluoride etherate (10 mL, 0.08 mol) in acetic acid (150 mL) was heated under reflux for 2 h. The mixture was cooled and let stand for crystallization. After filtration, the solid was recrystallized from chloroform–acetone, affording **26** as colorless leaflets (4.2 g, 46%): mp 56–57 °C (lit.[48] mp 55–56 °C); ^1H NMR ($CDCl_3$) δ 1.50–2.30 (14 H, m), 3.20 (4 H, s).

9,9-(Ethylenedithio)-2-nitrofluorene (25). In a similar way as described for the preparation of **26**, a mixture of 2-nitrofluorenone (2.0 g, 9.0 mmol), 1,2-ethanedithiol (5.0 mL, 60 mmol), and boron trifluoride etherate (2.0 mL, 16 mmol) was transformed into **25** (1.9 g, 70%): mp 231–234 °C; ^1H NMR ($CDCl_3$) δ 3.82 (4 H, s), 7.28–7.50 (2 H, m), 7.65–7.78 (3 H, m), 8.23 (1 H, d, J = 10 Hz), 8.52 (1 H, d, J = 3.8 Hz); m/e 301.0229 (calcd for $C_{15}H_{11}NO_2S_2$, 301.0231).

General Procedure for Desulfurization of Mercaptans. A THF solution (ca. 50 mL) of **1** (1.0 g, 5.3 mmol) was added dropwise to an equimolar amount of $LiAlH_4$ (0.20 g, 5.3 mmol) in THF (20 mL). The mixture was stirred at room temperature for 15 min to give a deep dark brown solution. A THF solution (30 mL) of an equimolar amount of mercaptan (5.3 mmol) was then added dropwise to the above mixture. After 24–48 h of stirring at room temperature under a nitrogen atmosphere, the reaction was quenched with water (10 mL). The mixture was filtered through Celite, and the filtrate was extracted with ether. The organic solution was dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to give a residue, which was chromatographed on silica gel.

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Desulfurization of 2-Naphthylmethanethiol (4). According to the general procedure described above, **4** (0.90 g, 5.0 mmol) was transformed to **12** (0.59 g, 80%), which showed the same properties as those of an authentic sample.

Desulfurization of 1-Naphthylmethanethiol (5). According to the general procedure, **5** (0.74 g, 4.3 mmol) was converted to **13** (0.50 g, 83%), which exhibited properties identical with those of an authentic sample.

Desulfurization of 2-Naphthalenethiol (6). According to the general procedure, **6** (0.83 g, 5.2 mmol) was transformed to **14** (0.66 g, 74%), which showed the same physical properties as those of an authentic sample.

Desulfurization of 1-Decanethiol (7). A mixture of **1** (2.3 g, 12 mmol) and $LiAlH_4$ (0.54 g, 14 mmol) in THF (50 mL) was treated with **7** (1.0 g, 6.0 mmol) in THF (ca. 150 mL) according to the general procedure except that the mixture was refluxed for 16 h to afford **15** (0.17 g, 41%), which exhibited properties identical with those of an authentic sample.

Desulfurization of 1-Adamantanethiol (8). Following the procedure for the reaction with **7**, a mixture of **1** (0.65 g, 3.4 mmol), $LiAlH_4$ (0.13 g, 3.4 mmol), and **8** (0.26 g, 1.5 mmol) in THF (50 mL) was heated under reflux for 16 h followed by normal workup procedure to give **16** (0.097 g, 46%), which showed the same physical properties as those of an authentic sample.

Desulfurization of (3-(Trifluoromethyl)phenyl)methanethiol (9). According to the general procedure, **9** (0.76 g, 4.0 mmol) was transformed to **17** (0.22 g, 35%), which exhibited the same physical properties as those of an authentic sample.

Desulfurization of (4-Methoxyphenyl)methanethiol (10). By the general procedure, a mixture of **1** (0.98 g, 5.2 mmol) and $LiAlH_4$ (0.19 g, 5.2 mmol) in THF (50 mL) and **10** (0.57 g, 3.7 mmol) was converted to **18** (0.16 g, 36%), which was characterized by comparing its spectroscopic properties with those of an authentic sample.

Desulfurization of (4-(Methoxycarbonyl)phenyl)methanethiol (11). According to the general procedure a mixture of **1** (0.52 g, 2.8 mmol), $LiAlH_4$ (0.11 g, 2.9 mmol), and **11** (0.45 g, 2.5 mmol) was transformed to **19** (0.14 g, 40%), which showed spectroscopic properties identical with those of an authentic sample.

General Procedure for the Desulfurization of Thioether. The procedure is essentially the same as that for the desulfurization of thiols except that 2 equiv of the reagent, **3**, was employed in the reaction.

Desulfurization of Dibenzothiophene (21). By reacting with **3** prepared from **1** (2.1 g, 11 mmol) and $LiAlH_4$ (0.41 g, 11 mmol) as described in the general procedure, **21** (1.0 g, 5.4 mmol) was transformed to **27** (0.59 g, 70%), which exhibited the same spectroscopic properties as those of an authentic sample.

Desulfurization of Bis(2-naphthylmethyl) Sulfide (20). According to the general procedure, **20** (1.2 g, 3.8 mmol) was treated with **3** prepared from **1** (1.5 g, 7.6 mmol) and $LiAlH_4$ (0.29 g, 7.6 mmol) to give **12** (0.73 g, 67%), which showed the same physical properties as those of an authentic sample.

Desulfurization of α-(Methylthio)acetophenone (22). According to the general procedure described above, a mixture of **1** (2.3 g, 12 mmol), $LiAlH_4$ (0.46 g, 12 mmol) in THF (50 mL) and **22** (0.84 g, 5.1 mmol) was transformed into **28** (0.45 g, 74%), which was characterized by comparing its spectroscopic properties with those of an authentic sample.

Desulfurization of α-(Methylthio)-α-allylacetophenone (23). By the general procedure, a mixture of **1** (0.98 g, 5.2 mmol), $LiAlH_4$ (0.20 g, 5.3 mmol), and **14** (0.40 g, 2.0 mmol) was transformed into 5-phenyl-5-oxopent-1-ene (**29**) (0.25 g, 78%): ^{1}H NMR ($CDCl_3$) δ 2.2–2.70 (2 H, m), 2.70–3.20 (2 H, m), 4.75–5.35 (2 H, m), 5.40–6.30 (1 H, m), 7.10–8.00 (5 H, m); ν_{max} 1680 cm^{-1}; m/e 160.0873 (calcd for $C_{11}H_{12}O$, 160.0885).

Desulfurization of 9,9-(Ethylenedithio)fluorene (24). By the general procedure, a mixture of **1** (3.0 g, 16 mmol), $LiAlH_4$ (0.61 g, 16 mmol), and **24** (0.51 g, 2.0 mmol) in THF (50 mL) was transformed into **30** (0.18 g, 55%): mp 112–115 °C (lit.[49] mp 115–116 °C).

Desulfurization of 9,9-(Ethylenedithio)-2-nitrofluorene (25). According to the general procedure, **25** (0.25 g, 0.83 mmol) was reduced to **31** (0.06 g, 40%): mp 125–128 °C (lit.[50] mp 129 °C).

Desulfurization of 2,2-(Ethylenedithio)adamantane (26). Following the general procedure, a mixture of **1** (0.87 g, 4.6 mmol) and $LiAlH_4$ (0.17 g, 4.6 mmol) in THF (30 mL) was mixed with **26** (0.26 g, 1.2 mmol) in THF (50 mL), and the mixture was heated under reflux for 16 h followed by normal workup to give **16** (0.068 g, 42%).

Desulfurization of 2-((Butylthio)methylene)tetralone (45). According to the general procedure, **45** (0.49 g, 2.0 mmol) was allowed to react with **3** prepared from **1** (0.75 g, 4 mmol) and $LiAlH_4$ (0.16 g, 4.2 mmol) to afford **46** (0.12 g, 38%), which showed the same physical properties as those of an authentic sample.

Desulfurization of Ethyl Thiobenzoate (33). Following the general procedure, **33** (0.86 g, 5.2 mmol) was treated with 2 equiv of **3**. After normal workup, only starting material was recovered (0.82 g, 95%).

General Procedure for the Desulfurization of Sulfoxide or Sulfone. Nickelocene (1–2 mmol) in THF (ca. 20 mL) was mixed with $LiAlH_4$ (1 equiv), and the solution was stirred at room temperature for 15 min. Sulfoxide (0.5 equiv) or sulfone (0.5 equiv) in THF (5–10 mL) was then added, and the mixture was stirred overnight at room temperature. Water was then introduced and after stirring for ca. 20 min, the mixture was filtered and filtrate was extracted with ether. The combined organic solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated in vacuo to give a residue, which was chromatographed on silica gel to give the corresponding desulfurized product.

Desulfurization of Bis(2-naphthylmethyl) Sulfoxide (34). According to the general procedure, **34** (0.35 g, 1.1 mmol) was treated with **3** prepared from **1** (0.39 g, 2.0 mmol) and $LiAlH_4$ (0.08 g, 2.1 mmol) to give **12** (0.15 g, 47%), which exhibited properties identical with those of an authentic sample.

Desulfurization of Decyl Phenyl Sulfoxide (35). Sulfoxide **35** (0.32 g, 1.2 mmol) was treated with **1** (0.45 g, 2.4 mmol) and $LiAlH_4$ (0.094 g, 2.5 mmol) according to the general procedure to yield decane (0.06 g, 35%), which showed the same physical properties as those of an authentic sample.

Desulfurization of 1-Naphthylmethyl Phenyl Sulfoxide (36). In a similar manner as described in the general procedure, sulfoxide **36** (0.16 g, 0.60 mmol) was treated with **1** (0.23 g, 1.2 mmol) and $LiAlH_4$ (0.046 g, 1.2 mmol) to afford **13** (0.049 g, 58%), which had the same physical properties as those of an authentic sample.

Desulfurization of Bis(2-naphthylmethyl) Sulfone (37). As described in the general procedure, sulfone **37** (0.21 g, 0.61 mmol) was allowed to react with **1** (0.23 g, 1.2 mmol) and $LiAlH_4$ (0.046 g, 1.2 mmol) to give **12** (0.065 g, 38%).

Desulfurization of Ethyl 2-Naphthylmethyl Sulfone (38). According to the general procedure, sulfone **38** (0.14 g, 0.61 mmol) was treated with **1** (0.23 g, 1.2 mmol) and $LiAlH_4$ (0.046 g, 1.2 mmol) to afford **12** (0.046 g, 54%).

Desulfurization of α-(Phenylsulfonyl)acetophenone (39). Substrate **39** (0.22 g, 0.86 mmol) was treated with **1** (0.32 g, 1.7 mmol) and $LiAlH_4$ (0.065 g, 1.7 mmol) following the same method as described in the general procedure to yield **28** (0.065 g, 63%), which exhibited properties identical with those of an authentic sample.

Reduction of Benzalacetophenone (47). Compound **47** (0.70 g, 3.4 mmol) was mixed with **3** prepared from **1** (0.63 g, 3.4 mmol) and $LiAlH_4$ (0.13 g, 3.4 mmol) in THF (25 mL), and the mixture was stirred at room temperature for 48 h. Water (10 mL) was then added and the mixture was filtered through Celite. The filtrate was extracted with ether. The combined organic solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel to give **48** (0.20 g, 29%), which exhibited the same physical properties as those of an authentic sample.

Reduction of Cyclohexenone. In a similar manner as described for **47**, cyclohexenone (0.67 g, 7.0 mmol) was allowed to

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react with **3** prepared from **1** (1.32 g, 7.0 mmol) and $LiAlH_4$ (0.27 g, 7.1 mmol) to give cyclohexanone (0.21 g, 30%) in addition to an unidentified mixture (0.26 g).

Desulfurization of 4 by Nonaqueous Workup Procedure. According to the general procedure, **4** (0.95 g, 5.5 mmol) was allowed to react with **3** prepared from **1** (1.03 g, 5.5 mmol) and $LiAlH_4$ (0.21 g, 5.5 mmol) overnight. The mixture was filtered through Celite, and the filtrate was evaporated in vacuo to give a residue, which was chromatographed on silica gel to give **12** (0.64 g, 82%), which exhibited the same physical properties as those of an authentic sample.

Desulfurization of 4 Using D_2O in the Workup Procedure. The reaction was conducted in a similar manner as the general procedure except that D_2O was used instead of H_2O to quench the reaction mixture. Thus, **4** (0.78 g, 4.5 mmol) was allowed to react with **3** obtained from **1** (0.85 g, 4.5 mmol) and $LiAlH_4$ (0.17 g, 4.5 mmol). The mixture was treated with D_2O (2 mL) for 2 h to quench the reaction. The mixture was then filtered through Celite, and the filtrate was extracted with ether. The organic solution was dried over anhydrous magnesium sulfate and filtered, and the filtrate was evaporated in vacuo to give a residue, which was chromatographed on silica gel to yield **12** (0.54 g, 85%): *m/e* 142.

Desulfurization of 4 Using $LiAlD_4$. The reaction was carried out in the manner described in the general procedure except that $LiAlD_4$ was used instead to $LiAlH_4$. Thus, **4** (0.61 g, 3.5 mmol) was transformed to (deuteriomethyl)naphthalene, **44** (0.40 g, 80%): ^1H NMR ($CDCl_3$) δ 2.50 (s, 2.2 H),[51] 7.2–8.0 (m, 7 H); ^2H NMR ($CHCl_3$) δ 2.10 (t, $J = 4.0$ Hz); *m/e* 143.

NMR Study of 3 in THF-d_8. Under a nitrogen atmosphere, a THF-d_8 solution (2.0 mL) of **1** (34 mg, 0.18 mmol) was added to $LiAlH_4$ (6.8 mg, 0.18 mmol) in THF-d_8 (1.0 mL) in an NMR tube. The mixture was shaken for 15 min at room temperature. The NMR tube was then sealed and subjected to NMR analysis. The sample was $LiAlD_4$ was prepared similarly. The results for both experiments were described in detail in the text.

Stoichiometry of 3. Under a nitrogen atmosphere, a THF solution (10 mL) of **1** (0.3819 g, 2.023 mmol) was added to a THF solution of $LiAlH_4$ (1.015 M, 2.00 mL, 2.030 mmol). After the initial exothermic reaction subsided, the solution was stirred for an additional 30 min. The solvent was then removed under vacuum to give a residue (0.5818 g),[52] to which water (10 mL) was carefully added. The pale green solution was mixed with concentrated HNO_3 (20 mL) and concentrated HCl (20 mL), and the mixture was allowed to boil for 1 h. After filtration the solution was diluted to 500 mL and divided into five 100-mL portions. Each portion was subjected to nickel analysis.[53] To a 100-mL portion was added dimethylglyoxime (15 mL of 1% EtOH solution) at 60 °C. The mixture was made basic with NH_4OH (25%), allowed to stand for 1 h, and then filtered through a weighed no. 3 sintered glass crucible. The precipitate was thoroughly washed with cold water until free from chloride. The crucible was dried at 120 °C until a constant weight was obtained. Anal. Calcd for $C_{14}H_{20}AlLiNiO$: Ni, 19.8%. Found: Ni, 19.8 ± 0.1%.

Gas Evolution Studies. A two-necked 100-mL round-bottom flask fitted with a rubber septum was connected to a calibrated mercury-filled gas buret. The system was flushed with nitrogen. A THF solution of **1** (5.0 mL, 0.04 M) was placed in the flask to which an equimolar amount of $LiAlH_4$ in THF (ca. 1.0 M) was slowly introduced through the septum with a gastight syringe. The evolved gas was subjected to mass spectral analysis and was found to be hydrogen. The vapor pressure of THF was corrected for,[54] and the molar equivalent of hydrogen gas evolved was 0.99 ± 0.03 molar equivalent from an average of three runs.

To the above mixture was added water (2 mL) to liberate 1.95 ± 0.04 molar equivalents of hydrogen from an average of three runs. When 1 equiv of thiophenol was introduced to the above mixture of **1** and $LiAlH_4$, 1.00 ± 0.04 molar equivalent (three runs) of hydrogen gas was obtained.

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Registry No. **1**, 1271-28-9; **4**, 1076-67-1; **5**, 5254-86-4; **6**, 91-60-1; **7**, 143-10-2; **8**, 34301-54-7; **9**, 25697-55-6; **10**, 6258-60-2; **11**, 102203-61-2; **12**, 91-57-6; **13**, 90-12-0; **14**, 91-20-3; **15**, 124-18-5; **16**, 281-23-2; **17**, 401-79-6; **18**, 104-93-8; **19**, 99-75-2; **20**, 613-81-0; **21**, 132-65-0; **22**, 5398-93-6; **23**, 72731-11-4; **24**, 7049-31-2; **25**, 115464-98-7; **26**, 19557-70-1; **27**, 92-52-4; **28**, 98-86-2; **29**, 3240-29-7; **30**, 86-73-7; **31**, 153-78-6; **32**, 115464-99-8; **33**, 1484-17-9; **34**, 115465-00-4; **35**, 17712-09-3; **36**, 115465-01-5; **37**, 115465-02-6; **38**, 115465-03-7; **39**, 3406-03-9; **40**, 6099-23-6; **41**, 16222-10-9; **42**, 1016-05-3; **44**, 82101-70-0; **45**, 40014-89-9; **46**, 1590-08-5; **47**, 94-41-7; **48**, 1083-30-3; $LiAlD_4$, 14128-54-2; $LiAlH_4$, 16853-85-3; allyl bromide, 106-95-6; α-(phenylthio)acetophenone, 16222-10-9; propargyl bromide, 106-96-7; adamantanone, 700-58-3; 1,2-ethanedithiol, 540-63-6; 2-nitrofluorenone, 115465-04-8; cyclohexenone, 25512-62-3; cyclohexanone, 108-94-1.

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(51) The integration has been calibrated with a standard mixture of methylnaphthalene-α-d and methylnaphthalene.

(52) This solid was extremely air sensitive and inflammable upon contact with air. This solid can be redissolved in THF, and the solution can be used as the desulfurization reagent.

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