ated in aqueous solution, *p*-nitrobenzyl carbanions readily "eject" electrons. In addition, we have recently established[7] that even non-nitro-substituted carbanions, when generated in aqueous solution, can also "eject" electrons provided that there is a good electron acceptor in solution. Furthermore, nitroarenes in general are known to be oxidants of carbanions in strongly basic solution.[8] These observations coupled with the above results indicate that the mechanism of reaction of 4-NA in aqueous NaOH probably involves initial electron transfer from its enolate ion to the unionized substrate (Scheme I). It is known that 4-NA is an excellent electron acceptor[4] and its radical anion has a lifetime of several minutes in aqueous base. However, in order to reduce 4-NA to 4-AA, a total of six electrons is required. This implies that sequential transfer of electrons to 4-NA and its subsequently derived partially reduced products from the enolate ions is involved. The details of the mechanism beyond the initial electron-transfer step are probably complicated. However, a reasonable pathway (Scheme I) is attack of the radical **1** by hydroxide ion in the medium, to give a new radical anion **2**, which transfers its electron to 4-NA, resulting in 2-hydroxy-4′-nitroacetophenone (**3**). The enolate ion of **3** can now undergo a similar series of steps, which eventually oxidizes the carbonyl moiety to carboxyl (with loss of the extra carbon in the form of carbon dioxide). When an authentic sample of **3** was dissolved in aqueous NaOH and allowed to react over 3 h, 4-NBA was formed in ≈65% yield. However, the expected reduction product in this case (2-hydroxy-4′-aminoacetophenone) was not observed. In hindsight, this was not unexpected since 2-hydroxy-4′-nitroacetophenone would be expected to be oxidized by nitro compounds in basic solution due to its readily ionizable α-methylenes. The identity of the reduced products has not been completely determined, but the isolation of a good yield of 4-NBA in the reaction is consistent with the mechanism proposed in Scheme I.

Experimental Section

^{1}H NMR spectra were recorded at 90 MHz in $CDCl_3$. IR spectra were recorded by using NaCl plates. ESR spectra were recorded on a Bruker E200TT spectrometer in quartz flat cells. Solutions were transferred to the cell via a syringe and purged with argon prior to study. All reactions were carried at 22 ± 2 °C.

All the compounds used in this study were commercially available, with the exception of 2-hydroxy-4′-nitroacetophenone (**3**), which was prepared by refluxing 2-bromo-4′-nitroacetophenone in aqueous solution in the presence of $AgNO_3$. The purity of all the compounds used was >95%, as determined from their ^{1}H NMR spectra.

2-Bromo-4′-nitroacetophenone. To a cooled (ice bath) and stirred solution of 5 g (30 mmol) of 4-nitroacetophenone (Aldrich) in 200 mL of glacial acetic acid was added dropwise 5.1 g (32 mmol) of reagent grade bromine. After addition (≈30 min), the solution was poured into ice water, which gave a mass of precipitate. The solid was collected on a funnel and air-dried, to give crude 2-bromo-4′-nitroacetophenone (6 g; 82%; mp 92 °C, lit.[13] mp 98 °C).

2-Hydroxy-4′-nitroacetophenone (3). A solution of 5 g (20.6 mmol) of 2-bromo-4′-nitroacetophenone and 5 g (30 mmol) of $AgNO_3$ in 250 mL of H_2O and 150 mL of acetone was refluxed for 4 h with stirring. After cooling, the solution was filtered to remove insoluble material, and the filtrate was extracted twice with 150-mL portions of CH_2Cl_2. The crude solid obtained was recrystallized twice from 50% EtOH, to give 2 g (54%) of pure **3** (mp 118-120 °C; lit.[13] mp 121 °C).

Disproportionation Reaction of 4-NA. In a typical run, 100 mg (0.61 mmol) of 4-NA was dissolved in 50 mL of reagent grade CH_3CN and added with stirring to 200 mL of 0.5 M NaOH (100 mmol), which was continuously purged with a stream of argon. After several minutes, the solution turned yellow and became successively darker in color over the period of the reaction. The solution was kept away from light. After 3 h at 22 °C, the solution developed a deep orange color. It was extracted twice with 100-mL portions of CH_2Cl_2, which on evaporation gave ≈47 mg (57%) of pure 4-AA (mp 103 °C, lit.[14] mp 105-107 °C; identical with an authentic sample by ^{1}H NMR, IR, and MS). The aqueous layer was acidified with 10% HCl and extracted twice with 100-mL portions of CH_2Cl_2, which on evaporation gave ≈37 mg (37%) of pure 4-NBA (mp 235-237 °C, lit.[14] mp 239-241 °C; identical with an authentic sample by ^{1}H NMR, IR, and MS).

When oxygen was used in place of argon, the solution never took on the dark orange color observed above over the period of the reaction. Direct extraction of the solution with CH_2Cl_2 gave no observable product by ^{1}H NMR. Extraction of the acidified solution gave only 4-NBA (≈75 mg; 74%). The pH dependence of the reaction shown in Figure 1 was determined by carrying out the reaction in different pH's for 3 h and analyzing the ratio of products and substrate by integration of ^{1}H NMR spectra.

Disproportionation of 2-Hydroxy-4′-nitroacetophenone (3). A solution of 100 mg (0.55 mmol) of **3** in 50 mL of CH_3CN was mixed with 150 mL of 0.5 M NaOH with stirring and continuous purging with a stream of argon. The solution was allowed to stand for 3 h under argon, which was then diluted with 100 mL of distilled H_2O and acidified to pH ≈ 1 with 10% HCl. Extraction of this solution with CH_2Cl_2 followed by evaporation of the solvent gave ≈60 mg (65%) of 4-NBA. The ^{1}H NMR spectrum of the material obtained after complete removal of the water of the aqueous portion proved to be complex and was not studied further.

Acknowledgment. We thank the National Sciences and Engineering Research Council (NSERC) of Canada for support of this work. We also thank Dr. S. Muralidharan for help with the ESR studies.

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Nickel(II)-Lithium Aluminum Hydride Mediated Reduction of Carbon-Sulfur Bonds[†,1]

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A number of organonickel compounds are thiophilic, and several systems are known to be active desulfurization agents.[3,4] To illustrate this, $LiAlH_4$ in the presence of Ni(COD)(bpy) reduces dibenzothiophene and related compounds into desulfurized products.[4] We recently re-

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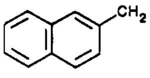
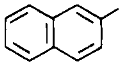
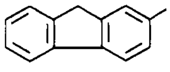
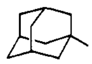
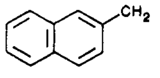
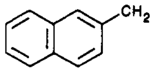
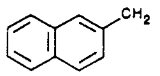
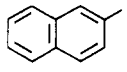
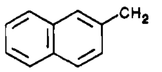
[†] Dedicated to Professor Kung Tsung Wang on the occasion of his 60th birthday.

0022-3263/89/1954-4474$01.50/0

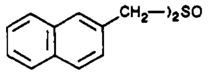
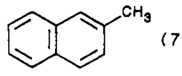
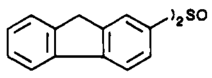
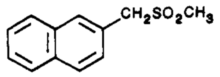
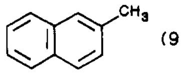
Table I. Reduction of Mercaptans and Thioethers with $NiBr_2 \cdot DME$, Ph_3P, and $LiAlH_4$

$RSR' \rightarrow RH + R'H$

R	R′	% yield RH	% yield R′H
	H	80	
	H	50	
	H	83	
n-$C_{10}H_{21}$-	H	60	
	H	52	
		72	
	Ph	64	
	CH_3	53	
		45	70

ported that nickelocene can promote the reduction of various organosulfur compounds with $LiAlH_4$.[3] It is noted that secondary Grignard reagents in the presence of $NiCl_2(PPh_3)_2$ can smoothly reduce C_{sp^2}–S bonds.[4] A metal hydridic moiety may be the active species for this reduction.[5] As metal hydride can be formed readily by the reduction of metal halide with complex metal hydride,[6] we felt the nickel hydridic species generated in situ from the reduction of nickel halide complex(es) could be a useful desulfurization agent. As part of our continuing interest in the transition metal mediated C–S bond cleavage reactions,[3,7] we describe here a useful nickel reagent to mediate the reduction of C–S bond.

Table II. Reduction of Sulfoxides and Sulfone with $NiBr_2 \cdot DME$, Ph_3P, and $LiAlH_4$

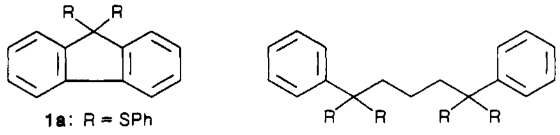
substrate	product (% yield)
	 (70)
	**1b** (70)
$C_{10}H_{21}SOPh$	$C_{10}H_{22}$ (55)
	 (92)

Results and Discussion

A THF solution of $NiBr_2 \cdot DME$ and 2 equiv of Ph_3P was treated with 1 equiv of $LiAlH_4$ to give a dark brown solution, which was allowed to react with the organosulfur substrate at room temperature. In general, 1 equiv of the nickel reagent was employed for each carbon–sulfur bond to be reduced. Hence, 2 equiv of the nickel reagent were used for the reduction of thioethers. The results are tabulated in Table I.

As shown in Table I, mercaptans of different nature were smoothly reduced under the reaction conditions. It is noteworthy that bridgehead adamantanethiol afforded adamantane in satisfactory yield. Thioethers behaved similarly (Table I). To illustrate this, adamantane and 2-methylnaphthalene were obtained in 45% and 70% yields, respectively, from the reduction of the corresponding thioether.

The reaction with dithioacetals also proceeded smoothly. Thus, fluorenone dithioacetal **1a** was reduced to fluorene **1b** in 84% yield. The bisdithioacetal **2a** was also converted to the corresponding hydrocarbon **2b** in 58% yield.



1a: R = SPh
b: R = H

2a: R R = $S(CH_2)_2S$
b: R = H

Sulfoxides and sulfones can also be reduced under the same conditions (Table II). Excess amount of the nickel reagent, however, was required in these reactions. Presumably these substrates were first reduced to thioethers,[9] which were further converted to hydrocarbons.

When 2-naphthylmethanethiol was treated with the nickel reagent prepared from $LiAlD_4$, 2-methylnaphthalene-α-d_1 was obtained in 45% yield with at least 90% of deuterium incorporation.

In conclusion, we have demonstrated a convenient desulfurization reagent for the reductive cleavage of various carbon–sulfur bonds.

Experimental Section

NMR spectra were taken on a Bruker WM250 NMR spectrometer. The ^1H chemical shifts are reported on the δ scale in parts per million with reference to internal Me_4Si unless otherwise specified. Mass spectra (EI) were measured on a VG7070F mass spectrometer. All reactions involving air-sensitive organometallic compounds were conducted under nitrogen atmosphere according to standard procedures.[10] Solvents were purified according to standard procedures.[11] Mercaptans,[12] thioethers,[13] thioacetals,[14]

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(1) Part 27 of the series "Transition Metal Promoted Reactions".

(2) (a) The Chinese University of Hong Kong. (b) National Taiwan University. (c) To whom correspondence should be addressed at NTU.

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(8) Phosphine and phosphite have been shown to be active desulfurization agent under photochemical or thermolytic conditions. (e.g. Hoffmann, F. W.; Ess, R. J.; Simmons, T. C.; Hanzel, R. S. *J. Am. Chem. Soc.* **1956**, *78*, 6414.) However, under our mild reaction conditions, no desulfurization reaction was observed without nickel.

(9) It is known that complex hydride can reduce sulfoxide to sulfide. See: Chasar, D. W. *J. Org. Chem.* **1971**, *36*, 613. Kano, S.; Tanaka, Y.; Sugino, E.; Hibino, S. *Synthesis* **1980**, 695.

(10) Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

sulfoxides,[15] and sulfones[16] were synthesized according to literature procedures.

General Procedure for Desulfurization. The nickel reagent was prepared by mixing $NiBr_2$·DME with 2 equiv of Ph_3P and 2 equiv of $LiAlH_4$ in THF (ca. 30 mL) under nitrogen atmosphere. After the initial exothermic reaction subsided, the dark brown solution was stirred at room temperature for 30 min. Organosulfur compound was then syringed into 1-10 equiv (depending on the nature of the organosulfur substrate) of the nickel reagent described above. The mixture was stirred at room temperature for 1 day, quenched with saturated ammonium chloride solution (10 mL), and extracted with ether (3 × 25 mL). The combined organic solution was washed with brine solution, dried over anhydrous magnesium sulfate, and filtered. The filtrate was evaporated in vacuo to afford the residue, which was chromatographed on silica gel and eluted with hexane.

Desulfurization of 2-Naphthalenemethanethiol. According to the general procedure described above, the substrate (0.76 g, 4.4 mmol) was allowed to react with the nickel reagent prepared from $NiBr_2$·DME (0.97 g, 4.4 mmol), Ph_3P (2.4 g, 9.2 mmol), and $LiAlH_4$ (0.21 g, 5.5 mmol) to yield 2-methylnaphthalene (0.50 g, 80%), which showed the same physical properties as those of the authentic sample.

Desulfurization of 2-Naphthalenemethanethiol with the Nickel Reagent Prepared from $LiAlD_4$. According to the general procedure described above, the substrate (0.32 g, 1.8 mmol) was treated with the nickel reagent prepared from $NiBr_2$·DME (0.58 g, 1.9 mmol), Ph_3P (1.0 g, 3.8 mmol), and $LiAlD_4$ (77 mg, 1.8 mmol) to give 2-methylnaphthalene-α-d_1 (0.12 g, 45%): ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 2.1 H), 7.2-8.0 (m, 7 H); ^{2}H NMR ($CHCl_3$) δ 2.10 (t, *J* = 4.0 Hz); *m/e* 143.

Desulfurization of 2-Naphthalenethiol. According to the general procedure, the substrate (0.30 g, 1.9 mmol) was treated with the nickel reagent prepared from $NiBr_2$·DME (0.40 g, 1.8 mmol), Ph_3P (0.97 g, 3.7 mmol), and $LiAlH_4$ (73 mg, 1.9 mmol) to give naphthalene (0.12 g, 50%), which exhibited properties identical with those of the authentic sample.

Desulfurization of 1-Decanethiol. Via the same method described above, the mercaptan (0.61 g, 3.5 mmol) was reduced by the nickel reagent prepared from $NiBr_2$·DME (0.76 g, 3.5 mmol), Ph_3P (1.9 g, 7.2 mmol), and $LiAlH_4$ (0.14 g, 3.6 mmol) to afford *n*-decane (60%, GC yield[17]).

Desulfurization of 1-Adamantanethiol. By use of the general procedure, the sulfur compound (0.19 g, 1.1 mmol) was allowed to react with the nickel reagent prepared from $NiBr_2$·DME (0.39 g, 1.3 mmol), Ph_3P (0.61 g, 2.3 mmol), and $LiAlH_4$ (47 mg 1.2 mmol) to afford adamantane (52% GC yield[17]).

Desulfurization of 9,9-Bis(phenylthio)fluorene (1a). Via the general procedure, **1a** (0.38 g, 1.0 mmol) was allowed to react with the nickel reagent prepared from $NiBr_2$·DME (0.62 g, 2.0 mmol), Ph_3P (1.1 g, 4.0 mmol), and $LiAlH_4$ (76 mg, 2.0 mmol) to afford **1b** (0.14 g, 84%).

Desulfurization of 1,5-Diphenylpentane-1,5-dione Bis(dithioacetal) (2a). According to the general procedure depicted above, **2a** (0.40 g, 1.0 mmol) was treated with the nickel reagent prepared from $NiBr_2(Ph_3P)_2$ (7.4 g, 10 mmol) and $LiAlH_4$ (0.38 g, 10 mmol) to yield **2b** (0.13 g, 58%), which exhibited the same physical properties as those of the authentic sample.

Desulfurization of Bis(2-naphthylmethyl) Sulfoxide. Via the general procedure, the sulfoxide (0.19 g, 0.58 mmol) was treated with the nickel reagent prepared from $NiBr_2$·DME (0.79 g, 2.6 mmol), Ph_3P (1.3 g, 5.1 mmol), and $LiAlH_4$ (0.10 g, 2.7 mmol) to afford 2-methylnaphthalene (0.12 g, 70%).

Desulfurization of Ethyl 2-Naphthylmethyl Sulfone. According to the general procedure, a mixture of the sulfone (0.22 g, 0.94 mmol) and the nickel reagent prepared from $NiBr_2$·DME (1.9 g, 6.0 mmol), Ph_3P (3.2 g, 12 mmol), and $LiAlH_4$ (0.23 g, 6.0 mmol) to give 2-methylnaphthalene (0.12 g, 92%).

Acknowledgment. We thank the Croucher Foundation of Hong Kong for generous support and National Science Council of Republic of China for partial support.

Supplementary Material Available: Experimental procedures of the desulfurization of certain thiols, thioethers, and sulfoxides are available (2 pages). Ordering information is given on any current masthead page.

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(15) Oae, S. In *Organic Chemistry of Sulfur*; Oae, S., Ed.; Plenum: New York, 1977; Chapter 8.

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(17) GC yield was obtained by the integration of the peak on the chromatogram. Authentic sample was used for calibration.

Use of Polysorbate 80 (Tween 80) as a Phase-Transfer Catalyst[1a]

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Mary Korpusik, and Donald F. Slish

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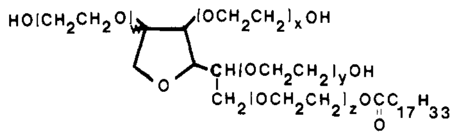
Polysorbate 80, also known as Tween 80 (1), has found extensive use as a surfactant and solubilizing agent, not only in chemical, biochemical, pharmacological, and medical research, but also in the food, cosmetics, and pharmaceutical industries. Recently,[2] its properties as an ionophore have been documented.



1

(w + x + y + z = 20)

Many ionophores, particularly the crown ethers which are so structurally similar to Polysorbate 80, have been found to be very effective phase-transfer catalysts.[3] The present work was initiated to determine whether Polysorbate 80 could also be used as an effective phase-transfer catalyst. Three reactions were studied: the cyanation of alkyl halides, the Williamson synthesis of ethers, and the base-catalyzed dehydrobromination of an alkyl halide.

Results and Discussion

Cyanation of Alkyl Halides (2). Cyanation of a series of alkyl halides and dihalides (2) was carried out by the method of Liotta et al.[4] as described in Starks and Liotta.[3a] This involves a solid-liquid system, in which solid KCN is acted upon by a solution of substrate and catalyst in acetonitrile at reflux for a set period of time: 1.5 h (Scheme Ia). The purpose was to compare our results using Polysorbate 80 to those reported by them using 18-crown-6 as a catalyst. Our results are summarized in Table I.

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(1) (a) Taken in part from the undergraduate theses of T.D.H. (1985), M.H. (1987), M.K. (1987), and D.F.S. (1985), University of Scranton. A preliminary report of this work was given at the 15th MARM of the ACS, Stockton State University, Pomona, NJ, May 1987. (b) Present address: Philadelphia College of Pharmacy and Science, Philadelphia, PA 19104.

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