In a control experiment, dimethyl maleate was irradiated as above in the absence of diphenyl diselenide. It was recovered unchanged in 90% yield.

Registry No. **1a**, 114221-61-3; **1b**, 114221-62-4; **2a**, 114221-64-6; **2b**, 114221-65-7; **3**, 114221-63-5; **4a**, 114221-67-9; **4b**, 114221-68-0; **5**, 114221-69-1; **6a**, 114221-66-8; **6b**, 114249-90-0; **7b**, 114221-70-4; **8**, 114221-71-5; DMAD, 762-42-5; PhSeSePh, 1666-13-3; methyl propiolate, 922-67-8; dimesityl diselenide, 71518-92-8; dimethyl maleate, 624-48-6; dimethyl fumarate, 624-49-7.

$W(CO)_6$ Mediated C–S Bond Cleavage Reactions[1]

Chi Tat Ng, Xiaojun Wang,[2] and Tien-Yau Luh*

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

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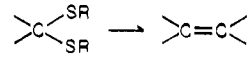
$W(CO)_6$-mediated reactions of thioethers in refluxing chlorobenzene yield mainly the corresponding dimers. Optically active thioethers give the respective racemic products. Mercaptans, on the other hand, predominantly afford the corresponding reduced products. A deuterium labeling experiment suggests that the SH group is the hydrogen source in the latter reduction reactions. A free-radical mechanism is suggested.

The reductive cleavage of the carbon–sulfur bond is important in organic synthesis[3] as well as in the hydrodesulfurization process of fossil fuels.[4] Homogeneous organometallic reagents have been investigated extensively in these applications.[5-7] Metal carbonyls have been shown to be useful to promote cleavage reactions of the carbon–sulfur bond.[5,6] Group 6 metal carbonyls are particularly thiophilic, and certain reactive C–S bonds in mercaptans and thioethers are selectively reduced with $Mo(CO)_6$ in ethereal solvents such as THF[5l] or dioxane.[5m] Although the actual mode of these reactions is not clear, it has been envisaged that the latter reactions may proceed via a radical mechanism.[5l] Accordingly, active hydrogen(s) in solvent molecules or in the substrates may be the hydrogen source for the radical abstraction reaction. Indeed, when chlorobenzene was employed as the solvent, dithioacetals underwent desulfurdimerization upon treatment with $Mo(CO)_6$ or $W(CO)_6$ (eq 1).[6] We felt that the extension



(1)

of this latter reaction to mercaptans as well as thioethers would be useful in synthesis and in understanding the mechanism of the metal carbonyl mediated C–S cleavage reactions and now wish to report our results.

Table I. $W(CO)_6$ Mediated Reaction of Thioethers

substrate	product (% yield)
methyl 2-naphthylmethyl sulfide (**1**)	1,2-di(2-naphthyl)ethane (**8**) (50) 2-methylnaphthalene (**9**) (34)
bis(2-naphthylmethyl) sulfide (**2**)	**8** (54) **9** (15)
1-naphthylmethyl phenyl sulfide (**3**)	1,2-di(1-naphthyl)ethane (**10**) (53) 1-methylnaphthalene (**11**) (5)
dibenzyl sulfide (**4**)	bibenzyl (**12**) (42)[a]
4-bromobenzyl phenyl sulfide (**5**)	1,2-bis(4-bromophenyl)ethane (**13**) (48) 4-bromotoluene (**14**) (4)
4-methoxybenzyl phenyl sulfide (**6**)	1,2-bis(4-methoxyphenyl)-ethane (**15**) (48) 4-methylanisole (**16**) (4)
methyl 2-phenyl-2-(phenylthio)-acetate (**7**)	dimethyl 2,3-diphenylsuccinate (**17**) (47) methyl phenylacetate (**18**) (3)

[a] The yield of toluene in this reaction was not determined.

Results and Discussion

Desulfurdimerization of Thioethers. A chlorobenzene solution[8] of thioether and 1 equiv of $W(CO)_6$ was heated under reflux for 24–72 h, and after workup, the corresponding product(s) was (were) obtained. The results are outlined in Table I.

(1) Part 21 of the series "Transition Metal Promoted Reactions".
(2) On leave from the Institute of Chemistry, Academia Sinica, Beijing.
(3) Magnus, P. D. *Tetrahedron* **1977**, *32*, 2019.
(4) Mithcell, P. C. H. *Catal. Rev.* **1970**, *4*, 245.
(5) (a) Alper, H. *J. Org. Chem.* **1975**, *40*, 2694. (b) Alper, H.; Paik, H.-N. *J. Org. Chem.* **1977**, *42*, 3522. (c) Ayral-Kalonstaan, S.; Agosta, W. C. *Synth. Commun.* **1981**, *11*, 1011. (d) Broadhurst, P. V.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R. *J. Am. Chem. Soc.* **1981**, *103*, 3198. (e) Alper, H.; Sibtain, F.; Haveling, J. *Tetrahedron Lett.* **1983**, *24*, 5329. (f) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235. (g) Alper, H. *J. Organomet. Chem.* **1974**, *73*, 359. (h) Shim, S. C.; Antebi, S.; Alper, H. *J. Org. Chem.* **1985**, *50*, 147. (i) Alper, H.; Shim, S. C.; Antebi, S. *Tetrahedron Lett.* **1985**, *26*, 1935. (j) Antebi, S.; Alper, H. *Organometallics* **1986**, *5*, 596. (k) Alper, H.; Blais, C. *J. Chem. Soc., Chem. Commun.* **1980**, 169. Alper, H.; Blais, C. *Fuel* **1980**, *59*, 670. (l) Luh, T.-Y.; Wong, C. S. *J. Org. Chem.* **1985**, *50*, 5413. (m) Masuyama, Y.; Yamada, K.; Kurusu, Y. *Tetrahedron Lett.* **1987**, *28*, 443.
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(8) Chlorobenzene was used as the solvent throughout this study for two reasons. First, it has no "active" hydrogen for the abstraction reactions. Secondly, the aromatic rings are deactivated and it is noteworthy that direct thermolysis of $W(CO)_6$ with aromatic compounds in general affords the cooresponding arene complexes in very low yield. Cf.: Davis, R.; Kane-McGuire, L. A. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, p 1321.

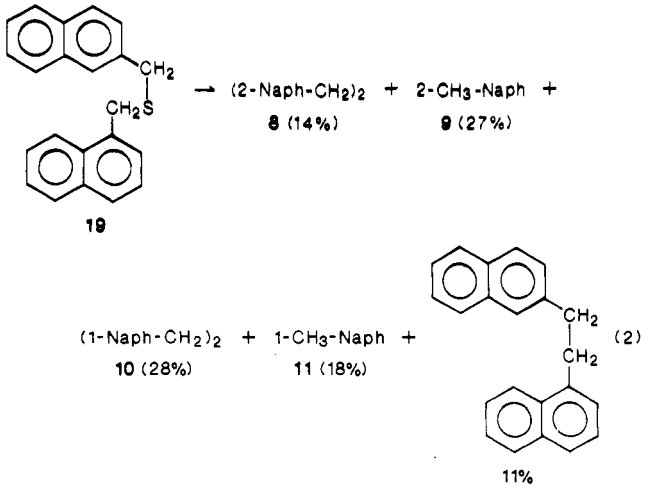
0022-3263/88/1953-2536$01.50/0

Table II. Reactions of Mercaptans with $W(CO)_6$ in Chlorobenzene

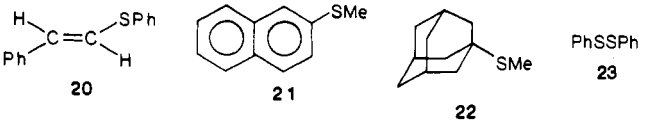
substrate	product (% yield)
2-naphthylmethanethiol (**24**)	**9** (59)
	8 (10)
(4-methoxyphenyl)methanethiol (**25**)	**16** (46)
	15 (5)
(4-bromophenyl)methanethiol (**26**)	**14** (48)
	13 (6)
triphenylmethanethiol (**27**)	triphenylmethane (**31**) (78)
2-naphthalenethiol (**28**)	naphthalene (**32**) (42)
	di(2-naphthyl) sulfide (**33**) (18)
	2,2′-binaphthyl (**34**) (trace)
1-adamantanethiol (**29**)	adamantane (**35**) (70)
8-phenoxyoctane-1-thiol (**30**)	1-phenoxyoctane (**36**) (65)

As shown in Table I, benzylic thioethers afforded the dimeric products in moderate yields. Functional groups such as halogen and ethereal linkages as well as esters remain intact under the reaction conditions. Interestingly, the corresponding reduced products were also isolated in significant amounts from these reactions. These results suggest that the reaction may proceed via free-radical mechanism. As the benzylic hydrogen is readily abstracted by organic radicals, these hydrogen atoms might be the hydrogen source for this reduction process.

Thermolysis of the thioether **19** with $W(CO)_6$ under our normal conditions yielded a mixture of coupling products in addition to the corresponding reduced products (eq 2). This observation again demonstrates that free-radical intermediates may be involved during the course of the reaction.



In those substrates having no benzylic hydrogens, the reactions were found to occur either extremely slowly or not at all. Thus, the thioether **20** gave *trans*-stilbene in

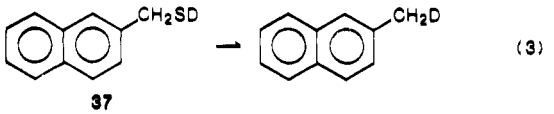


18% yield after 4 days under our normal conditions. Moreover, only starting materials were recovered from the reactions with **21–23**. It is noted that the C–S bonds in these thioethers are either C_{sp^2}–S or unactivated aliphatic C–S bonds.

Desulfurization of Mercaptans. The reactions with mercaptans under the same conditions have also been carried out for comparison. The results are tabulated in Table II. Interestingly, the C–S bonds in these mercaptans were reduced smoothly to afford the corresponding hydrocarbons in addition to a small amount of the dimeric product. In contrast to the observations with thioethers, various C–S bonds in these mercaptans are reactive under the reaction conditions. Hence, less reactive C–S bonds such as aryl–S or aliphatic C–S bonds were readily reduced in reasonable yields. This discrepancy is somewhat interesting.

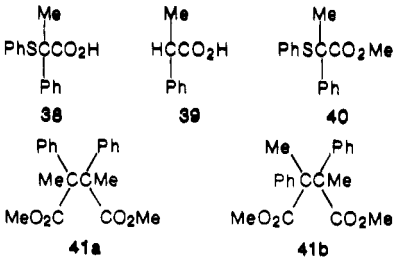
It is well-known that the S–H bonds are readily cleaved by transition metals to form the corresponding thiolato complexes[9] and the C–S bonds in these thiolato complexes are indeed activated and readily cleaved.[7m,10] It is likely that the ability of formation of the metal–sulfur complexes during the course of the reaction might play a prime role in the transition metal mediated C–S bond cleavage process. It is therefore understandable that the mercaptans are more reactive than thioethers under our reaction conditions.

As can be seen from Table II, substrates that do not contain benzylic hydrogen(s) were also reduced smoothly. In these substrates, the SH group may provide the hydrogen source for the reduction. Indeed, monodeuterio-2-methylnaphthalene was obtained when **37** was treated under our usual conditions (eq 3).



Stereochemistry of Desulfurization Reactions. As discussed above, active hydrogens such as the SH moiety in mercaptans as well as possibly benzylic hydrogens in thioethers may provide a hydrogen source to account for the corresponding reduced products. The SH group has long been known as a radical quencher.[11] In order to prove that the reaction may actually proceed via a radical mechanism, we carried out a detailed stereochemical investigation of this reaction.

Optically active carboxylic acid **38** was treated with $W(CO)_6$ in chlorobenzene in the same manner as described above to give the racemic mixture of **39** in 39% yield. No



dimerization product was obtained at all. Presumably, the acidic hydrogen in the carboxyl group in **38** provides the hydrogen source. In addition, the corresponding chiral methyl ester **40** was thermolyzed in the presence of $W(CO)_6$ under the same conditions to afford an equal amount of diastereomeric mixture of the dimers **41a** and **41b** which are optically inactive. Both of these experiments suggest a planar symmetrical intermediate which is likely to be a radical.

The reaction behavior of **42** is interesting. A mixture of disproportionation products **43**, **44**, and **45** was obtained in a ratio of 5:4:1. Apparently, the reaction pattern of the

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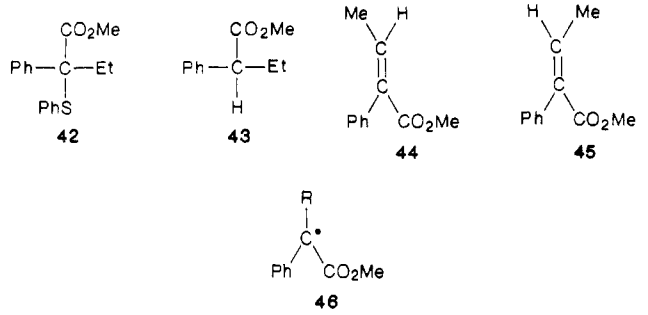
radical intermediate **46** is very much substituent dependent. When R is hydrogen or a methyl group, a coupling



reaction will be the predominant pathway. On the other hand, when R is an ethyl group, the steric environment around the radical center in **46** will not allow the coupling reaction to occur. Instead, intermolecular metathesis may proceed to give equal amounts of the reduced product **43** and the olefinic products **44** and **45**. The ratio of these stereoisomers can be understood within the framework of the steric requirements of this disproportionation reaction.

In summary, we have demonstrated the $W(CO)_6$ mediated C–S bond cleavage reactions of mercaptans and thioethers. Our result suggest that these reactions are consistent with a free-radical mechanism and imply that other metal carbonyl promoted C–S bond cleavage reactions may occur via similar pathways.

Experimental Section

All melting points are uncorrected. Infrared spectra were recorded 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 chemical shifts are reported on the δ scale in parts per million with reference to internal Me_4Si. Mass spectra were measured on a VG7070F mass spectrometer. Solvents were purified according to standard procedures.[12] Mercaptans[13] and thioethers[14] were synthesized according to literature methods.

General Procedure for the Desulfurization Reaction. A mixture of organosulfur compounds (1–2 mmol) and $W(CO)_6$ (1 equiv) in chlorobenzene (30–50 mL) was first flushed with nitrogen and then heated under reflux for 24–72 h. The blackish mixture was cooled to room temperature and filtered. The yellowish filtrate was evaporated in vacuo, and the residue was chromatographed on silica gel to give the products.

Desulfurization of Methyl 2-Naphthylmethyl Sulfide (1). According to the general procedure, a mixture of **1** (199 mg, 1.1 mmol) and $W(CO)_6$ (371 mg, 1.0 mmol) in chlorobenzene (5 mL) was transformed into **9** (51 mg, 34%) and the dimer **8** (75 mg, 50%); mp 182–183 °C (lit.[15] mp 183–184 °C).

Desulfurization of Bis(2-naphthylmethyl) Sulfide (2). By employing the same procedure described in the general procedure, we converted a chlorobenzene solution (6 mL) of **2** (239 mg, 0.8 mmol) and $W(CO)_6$ (245 mg, 0.7 mmol) into **9** (31 mg, 15%) and **8** (109 mg, 54%), which exhibited the same physical properties as the authentic samples.

Desulfurization of 1-Naphthylmethyl Phenyl Sulfide (3). Following the general procedure, we treated a mixture of **3** (250 mg, 1.0 mmol) and $W(CO)_6$ (349 mg, 1.0 mmol) in chlorobenzene (30 mL) for 72 h to give 1-methylnaphthalene (11 mg, 5%) and the dimer **10** (66 mg, 53%); mp 162–164 °C (lit.[15] mp 160–161 °C).

Desulfurization of Dibenzyl Sulfide (4). By using the method described in the general procedure, we transformed a mixture of **4** (475 mg, 2.2 mmol) and $W(CO)_6$ (711 mg, 2.0 mmol) into bibenzyl (160 mg, 42%), which showed identical physical properties with those of the authentic sample.

Desulfurization of 4-Bromobenzyl Phenyl Sulfide (5). According to the general procedure, **5** (225 mg, 0.75 mmol) and $W(CO)_6$ (383 mg, 1.1 mmol) in chlorobenzene were refluxed for 72 h. After chromatographic separation, bromotoluene (**14**) (5 mg, 4%) and the dimer **13** (64 mg, 48%), mp 113–116 °C (lit.[15] mp 114–115 °C), were obtained.

Desulfurization of 4-Methoxybenzyl Phenyl Sulfide (6). In accordance with the general procedure, a chlorobenzene solution (50 mL) of **6** (413 mg, 2.5 mmol) and $W(CO)_6$ (901 mg, 2.6 mmol) was refluxed for 48 h to give 4-methylanisole (**16**) (30 mg, 4%) and the dimer **15** (144 mg, 48%); mp 121–123 °C (lit.[16] mp 122–123 °C).

Desulfurization of Methyl 2-Phenyl-2-(phenylthio)acetate (7). By employing the general procedure, we refluxed a chlorobenzene solution (20 mL) of **7** (516 mg, 2.0 mmol) and $W(CO)_6$ (710 mg, 2.0 mmol) for 30 h. After workup, the mixture was chromatographed on silica gel and eluted with hexane–ethyl acetate (25:1) to give methyl phenylacetate (**18**) (10 mg, 3%) and a diastereomeric mixture of **17** (140 mg, 47%), which exhibited identical spectroscopic properties with those reported in the literature.[17]

Desulfurization of 2-Naphthylmethanethiol (24). According to the general procedure, a chlorobenzene solution (10 mL) of **24** (171 mg, 1.0 mmol) and $W(CO)_6$ (355 mg, 1.0 mmol) was heated under reflux for 72 h to afford 2-methylnaphthalene (**9**) (82 mg, 59%) and the dimer **8** (15 mg, 10%), which exhibited identical physical properties with those of the authentic samples.

Desulfurization of (4-Methoxyphenyl)methanethiol (25). A chlorobenzene solution (5 mL) of **25** (193 mg, 1.3 mmol) and $W(CO)_6$ (456 mg, 1.3 mmol) was allowed to react according to the general procedure described above to give **16** (70 mg, 46%) and the dimer **15** (8 mg, 5%), which showed the same physical properties as the authentic samples.

Desulfurization of (4-Bromophenyl)methanethiol (26). According to the general procedure, a mixture of **26** (268 mg, 1.3 mmol) and $W(CO)_6$ (457 mg, 1.3 mmol) in chlorobenzene (5 ml) afforded 4-bromotoluene (**14**) (107 mg, 48%) and the dimer **13** (13 mg, 6%), which showed the same physical properties as the authentic samples.

Desulfurization of Triphenylmethanethiol (27). A mixture of **27** (305 mg, 1.1 mmol) and $W(CO)_6$ (420 mg, 1.2 mmol) in chlorobenzene (30 mL) was treated according to the general procedure for 24 h to give triphenylmethane (**31**) (210 mg, 78%), mp 92–94 °C, which exhibited the same physical properties as the authetic sample.

Desulfurization of 2-Naphthalenethiol (28). By using the general procedure, we refluxed a mixture of **28** (206 mg, 1.3 mmol) and $W(CO)_6$ (452 mg, 1.3 mmol) in chlorobenzene (5 mL) for 35 h to give **32** (76 mg, 42%) and **33** (29 mg, 18%), which exhibited the same properties as the authentic samples, in addition to a trace amount of 2,2′-binaphthyl detected by GC/MS.

Desulfurization of 1-Adamantanethiol (29). A mixture of **29** (215 mg, 1.3 mmol) and $W(CO)_6$ (524 mg, 1.5 mmol) in chlorobenzene (5 mL) treated according to the general procedure yielded **35** (122 mg, 70%), which exhibited identical physical properties with those of the authentic sample.

Desulfurization of 8-Phenoxyoctane-1-thiol (30). According to the general procedure, a chlorobenzene solution (6 mL) of **30** (247 mg, 1.0 mmol) and $W(CO)_6$ (385 mg, 1.1 mmol) yielded 1-phenoxyoctane (127 mg, 65%) as a colorless oil: ^1H NMR δ 0.9–2.0 (m, 15 H), 3.9 (br t, 2 H), 6.8–7.5 (m, 5 H); MS, m/e 206 (M^+), 94 (base peak).

Desulfurization of (*R*)-(−)-2-Phenyl-2-(phenylthio)-propionic Acid (38). A mixture of **38**[18] (260 mg, 1 mmol) and $W(CO)_6$ (350 mg, 1 mmol) in chlorobenzene (20 mL) was refluxed for 30 h. After the mixture was cooled to room temperature, aqueous potassium carbonate was added. The mixture was washed

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with ether, and the aqueous layer was neutralized with dilute hydrochloric acid (10%). The aqueous solution was then extracted with ether three times. The combined organic solution was dried over anhydrous sodium sulfate and filtered, and the filtrate was evaporated in vacuo to give the oily product **39** (59 mg, 39%), which did not exhibit any optical rotation. The spectroscopic properties are consistent with the structure of **39**.[19]

Desulfurization of (*R*)-(−)-Methyl 2-Phenyl-2-(phenylthio)propionate (40). Accordiung to the general procedure, a mixture of **40**[18] (544 mg, 2.0 mmol) and $W(CO)_6$ (710 mg, 2.0 mmol) in chlorobenzene (20 mL) was heated under reflux for 30 h. After being cooled to room temperature, the mixture was filtered and the filter cake was washed with ether. The combined organic solution was evaporated in vacuo, and the residue was chromatographed on silica gel and eluted with hexane–ethyl acetate (20:1) to give the first portion, **41a** (138 mg, 43%): mp 113–115 °C; ^{1}H NMR δ 1.85 (s, 6 H), 3.60 (s, 6 H), 6.60–7.20 (m, 10 H); MS, *m/e* 326. The second portion was isolated as oil **41b** (115 mg, 35%): ^{1}H NMR δ 1.77 (s, 6 H), 3.67 (s, 6 H), 6.60–7.20 (m, 10 H); MS, *m/e* 326. The high-melting compound **41a** would be the more symmetric isomer or the meso form.

Desulfurization of Methyl 2-Phenyl-2-(phenylthio)-butyrate (42). A mixture of **42** (858 mg, 3 mmol) and $W(CO)_6$ (1.1 g, 3 mmol) in chlorobenzene (20 mL) was treated according to the general procedure described above to give a mixture of three products **43**, **44**, and **45** in a ratio of 5:4:1 based on the NMR spectrum of the crude mixture. After careful thromatography on silica gel using hexane–ethyl acetate (30:1) as eluent, **43** (120 mg, 23%) was obtained as the first portion: ^{1}H NMR δ 0.90 (t, 3 H), 2.04 (dq, 2 H), 3.70 (dd, 1 H), 3.77 (s, 3 H), 7.50 (m, 5 H).[20] The second portion was a mixture of **43**, **44**, and **45**. The third portion afforded pure **45** (100 mg, 19%): ^{1}H NMR δ 1.68 (d, 3 H), 3.67 (s, 3 H), 7.04 (m, embodied in the aromatic absorptions), 7.05–7.40 (m, 5 H). **44**: ^{1}H NMR δ 2.06 (d, 3 H), 3.60 (s, 3 H), 6.10 (q, 1 H), 7.00–7.30 (m, 5 H).[20]

Desulfurization of 1-Naphthylmethyl 2-Naphthylmethyl Sulfide (19). Following the same procedure as described above, we refluxed a mixture of **19** (507 mg, 1.6 mmol) and $W(CO)_6$ (616 mg, 1.7 mmol) in chlorobenzene (10 mL) for 48 h. After filtration and evaporation of the solvent, the residue was subject to NMR and GC/MS analyses. The yields of the products are as follows: **8** (14%), **9** (27%), **10** (28%), **11** (18%), and 1-(1-naphthyl)-2-(2-naphthyl)ethane (11%).

Desulfurization of 2-(Phenylthio)styrene (20). According to the general procedure, a chlorobenzene solution (10 mL) of **20** (639 mg, 3.0 mmol) and $W(CO)_6$ (1.81 g, 5.1 mmol) was allowed to react. After chromatographic separation, *trans*-stilbene (98 mg, 18%) was the only product which was identified by comparing its physical properties with those of an authentic sample.

Desulfurization of 2-Naphthylmethanethiol-*d* (37). A mixture of **37** (387 mg, 2.2 mmol) and $W(CO)_6$ (804 mg, 2.3 mmol) in chlorobenzene (5 mL) was allowed to react according to the general procedure to afford 2-methylnaphthalene-*d* (186 mg, 59%); MS, *m/e* 143.

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Registry No. **1**, 13183-61-4; **2**, 114132-36-4; **3**, 58948-52-0; **4**, 538-74-9; **5**, 75954-35-7; **6**, 5023-67-6; **7**, 51256-38-3; **8**, 21969-45-9; **9**, 91-57-6; **10**, 15374-45-5; **11**, 90-12-0; **12**, 103-29-7; **13**, 19829-56-2; **14**, 106-38-7; **15**, 1657-55-2; **16**, 104-93-8; **17**, 19020-59-8; **18**, 101-41-7; **19**, 114132-37-5; **20**, 7214-53-1; **24**, 1076-67-1; **25**, 6258-60-2; **26**, 19552-10-4; **27**, 3695-77-0; **28**, 91-60-1; **29**, 34301-54-7; **30**, 114132-38-6; **31**, 519-73-3; **32**, 91-20-3; **33**, 613-81-0; **34**, 612-78-2; **35**, 281-23-2; **36**, 1818-07-1; **37**, 114132-39-7; (*R*)-**38**, 14182-43-5; (±)-**39**, 2328-24-7; (*R*)-**40**, 13448-77-6; *meso*-**41a**, 84892-14-8; *d,l*-**41b**, 84892-15-9; **42**, 114132-40-0; **43**, 2294-71-5; **44**, 50415-84-4; **45**, 50415-85-5; $W(CO)_6$, 14040-11-0; 2-methylnaphthalene-*d*, 82101-70-0; *trans*-stilbene, 103-30-0; 1-(1-naphthyl)-2-(2-naphthyl)ethane, 83313-24-0.

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S_N2 Displacement on 2-(Alkylthio)ethyl Derivatives

M. R. Sedaghat-Herati, Samuel P. McManus,* and J. Milton Harris*

Department of Chemistry, University of Alabama in Huntsville, Huntsville, Alabama 35899

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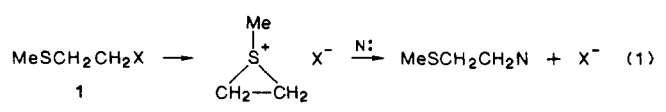
We have studied the reaction mechanism of various 2-(alkylthio)ethyl and 2-(arylthio)ethyl derivatives with strong nucleophiles in an attempt to overcome powerful neighboring sulfur participation and shift reaction to a direct displacement S_N2 mechanism. The 2,4-dinitrophenolate derivative of specifically deuteriated 2-(methylthio)ethanol reacts by an aromatic substitution mechanism (S_NAr) when exposed to amines in aprotic solvents. Use of sulfonate esters avoids competition from the S_NAr mechanism. The rate of reaction of these esters in dimethyl sulfoxide (DMSO) or acetonitrile is independent of concentration of added methylamine, thiourea, urea, or iodide, thus indicating continued S_N1 reaction with neighboring sulfur participation. As would be expected on this basis, but in contrast to previous mechanistic suggestions, the product for reaction with iodide in acetone shows complete scrambling of methylene groups. In contrast, reaction with thiophenolate ions in DMSO proceeds by direct nucleophilic displacement (an S_N2 mechanism), as shown by second-order kinetics and unrearranged product. This is the first demonstration of S_N2 displacement on a 2-(alkylthio)ethyl or 2-(arylthio)ethyl derivative.

Introduction

One of the prime concerns of physical organic chemistry has been to understand the processes whereby reactions shift from one mechanism to another.[1] We have been investigating this question using 2-(alkylthio)ethyl compounds, which may react with nucleophiles by neighboring-group participation, elimination, or direct nucleophilic substitution. Reaction of 2-(alkylthio)ethyl derivatives with several nucleophiles and bases under a variety of conditions has shown these substrates to be extremely resistant to direct nucleophilic displacement (an S_N2 mechanism) because of the dominant competition from powerful neighboring sulfur participation (k_Δ pathway), eq 1.[2-4] For example, solvolysis in water or alcohols



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