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A Novel Approach to the Practical Synthesis of Sulfides: An $InBr_3$–Et_3SiH Catalytic System Promoted the Direct Reductive Sulfidation of Acetals with Disulfides

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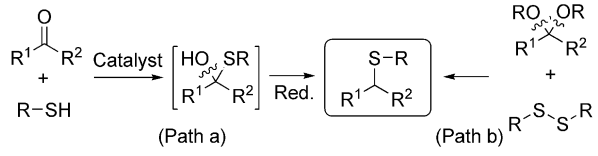
We have demonstrated a facile and direct synthesis of sulfide derivatives using acetals and ketals, derived from aromatic/conjugated aldehydes and aromatic ketones, with disulfides and the $InBr_3$–Et_3SiH reducing system. We also succeeded in developing an unprecedented one-pot preparation of an aliphatic sulfide from a disulfide and an aliphatic acetal.

Introduction

As sulfide skeletons are ubiquitous in natural products and in biologically active substances,[1] there have been numerous attempts to prepare them in a facile and practical way.[2] Typical approaches have included the reduction of sulfones or sulfoxides,[3] a Williamson-type thioether synthesis from thiols and alcohols in the presence of a base,[4] and an Ullmann-type reaction of thiols with organic halides using metals such as copper,[5] palladium,[6] and nickel.[7] In this context, for the last two decades, extensive work has been dedicated to developing a direct reductive preparation of sulfides from thiols and either aldehydes or ketones using a combined method with an appropriate catalyst and a reducing reagent (Path a, Scheme 1). For example, Kikugawa reported the preparation of sulfides from either aldehydes or ketones with thiols in CF_3CO_2H using a pyridine–BH_3 reducing system.[8] Also, Olah and co-workers demonstrated the synthesis of sulfides from carbonyl compounds via an *O*,*S*-acetal intermediate using a $BF_3{\cdot}H_2O$–Et_3SiH reducing system.[9] However, these contributions generally have several disadvantages, including harsh reaction conditions owing to the use of a strong acid, a flammable reagent, and a thiol that has an unpleasant odor. There have also been reports of the use of more than a stoichiometric amount of catalyst. Therefore, the development of a convenient, efficient, and easy-to-handle preparation of sulfides from carbonyl compounds is a priority.



Scheme 1.

Previously, we reported that an $InBr_3$–Et_3SiH reducing system effectively promotes the reduction of the acetyl group of propargylic acetates, as well as the direct and selective reduction of the carbonyl group in esters and amides, which directly produces the corresponding ethers and amines, respectively.[10,11] During ongoing studies on the selective reduction of carbonyl compounds and related compounds using our standard $InBr_3$–Et_3SiH reducing system, a member of our group found that this reducing catalytic system promoted a new C–S bond formation in acetals (ketals), which were relatively inactive in common organic reactions, with fewer odorous disulfides than found when using thiols, and which led to the direct formation of sulfide derivatives. As far as can be ascertained, a direct skeletal transformation from acetals and disulfides to a sulfide skeleton accompanied by the cleavage of two C–O bonds has not been reported (Path b, Scheme 1). Herein, we detail the results of a novel method for the synthesis of sulfide derivatives using the $InBr_3$–Et_3SiH catalytic system.

Results and Discussion

To find the optimal sulfidation conditions, the use of other solvents and 2 equiv. of the silane was first investigated using benzaldehyde dimethyl acetal (**1a**) and diphenyl disulfide (**2a**) as the model reaction. The results are listed

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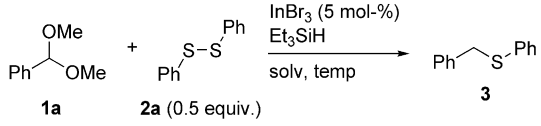
in Table 1. For example, the use of polar solvents such as THF, MeCN, and DMF did not produce desired sulfide product **3** (Table 1, runs 2–4). On the other hand, a nonpolar solvent, toluene, had a relatively good effect (Table 1, run 5). When the reaction temperature was raised to 100 °C, the yield slightly increased and the reduction was completed within 1 h (Table 1, run 6). Moreover, when the amount of Et_3SiH was increased to four equivalents with respect to disulfide **2**, the yield improved dramatically to 83% (Table 1, run 7). Needless to say, without $InBr_3$, the desired reductive sulfidation did not take place, but led to the recovery of the starting materials (Table 1, run 8). Thus, we found that heating the reagents at 100 °C in a toluene solution with 5 mol-% of $InBr_3$ and 4 equiv. of Et_3SiH per acetal in the presence of a disulfide were the optimal conditions.

Table 1. Optimization of the conditions for sulfidation.

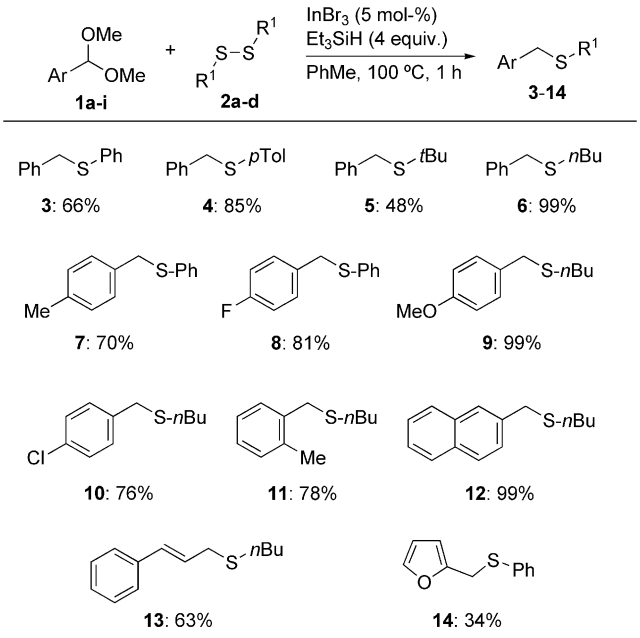


Run	Et_3SiH [equiv.]	Solvent	Temperature [°C]	Time [h]	Yield[a] [%]
1	2	$CHCl_3$	60	18	63
2	2	THF	60	18	n.d.
3	2	MeCN	60	18	trace
4	2	DMF	60	18	n.d.
5	2	PhMe	60	18	50
6	2	PhMe	100	1	61
7	4	PhMe	100	1	83
8[b]	2	PhMe	100	1	n.r.

[a] NMR yield. [b] Reaction was carried out without $InBr_3$.

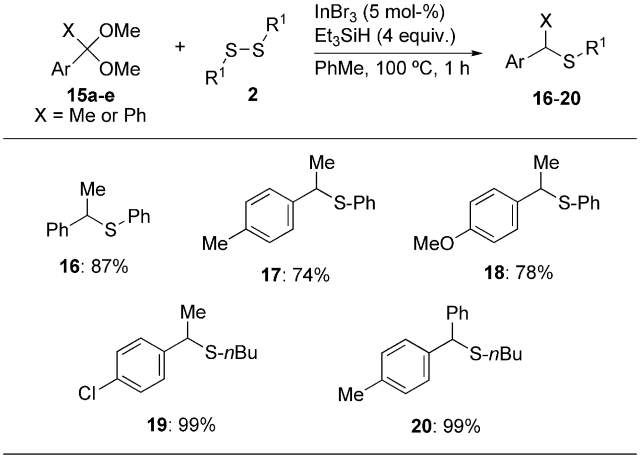
By using the optimal reaction conditions we investigated the scope and limitation of the reductive sulfidation of a variety of acetals **1a**–**i**. The results are listed in Table 2. For example, when sulfidation of benzaldehyde dimethyl acetal with aromatic disulfides, such as diphenyl disulfide (**2a**) and di-*p*-tolyl disulfide (**2b**) was performed under the optimal conditions, the corresponding sulfide derivatives **3** and **4** were obtained in good yields. On the other hand, employment of di-*tert*-butyl disulfide (**2c**) produced expected sulfide **5** in only a 48% yield, which seemed to be caused by the steric effect of the bulky *tert*-butyl groups. When di-*n*-butyl disulfide (**2d**) was used as the starting material, desired sulfide **6** was produced in a moderate yield. In general, reactions of benzaldehyde dimethyl acetal derivatives **1b**–**g** with either an electron-donating substituent, such as a methyl or methoxy group, or with an electron-withdrawing substituent, such as a fluorine or chlorine atom, produced expected sulfides **7**–**12** in good-to-excellent yields. The reaction of acetal **1h** derived from the conjugated aldehyde, cinnamaldehyde also produced sulfide **13** in a practical yield. The reaction of acetal **1i** bearing a furan moiety with di-*n*-butyl disulfide gave sulfide **14** in only 34% yield.

Table 2. Synthesis of sulfide derivatives **3**–**14** from acetals and disulfides.

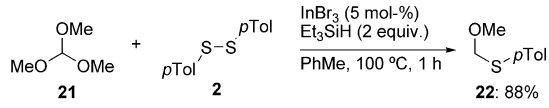


The reactions of ketal derivatives **15a**–**e** with disulfides **2** also gave the desired aryl or alkyl benzyl sulfides **16**–**20** in excellent yields (Table 3). Neither the type of substituent on the benzene ring of ketal **15** nor the substituted group on the disulfide had any effect on the product yields. In addition, the reaction could be applied to the sulfidation of trimethyl orthoformate (**21**), which produced *O*,*S*-acetal **22** in 88% yield (Scheme 2).

Table 3. Synthesis of sulfide derivatives **16**–**20** from ketals and disulfides.

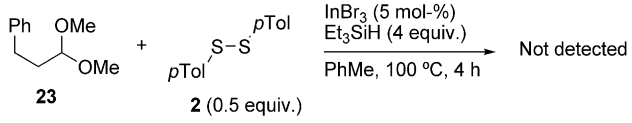


Unfortunately, with the exception of a benzyl-type acetal, the expected formation of an aliphatic aromatic sulfide did not occur when the reaction was applied to the sulfidation of aliphatic acetal **23**. Instead, the disappearance of both starting materials and the formation of unknown compli-

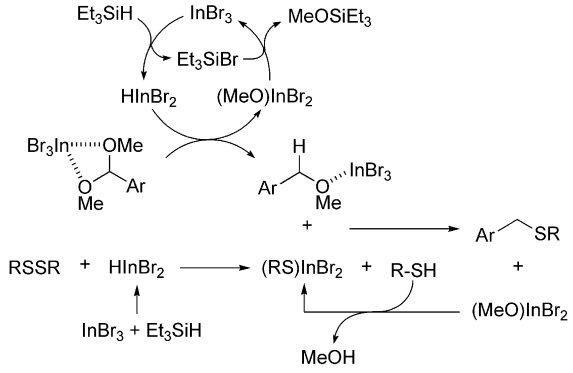


Scheme 2. Sulfidation of orthoformate derivative **21**.

cated products were observed (Scheme 3). Hence, when the sulfidation path for the reaction of aromatic acetal **1** and di-*p*-tolyl disulfide (**2b**) was reinvestigated in detail, the formation of both benzyl methyl ether (64% NMR yield) and *p*-toluenethiol (84% GC yield) was confirmed under our conditions.[12] Moreover, when a mixture of benzyl methyl ether with *p*-toluenethiol was treated with the reducing reagents, expected sulfide **4** was obtained in 67% yield (see Table 2).[13] Consequently, as the results show in Scheme 4, with an aromatic acetal and a disulfide, sulfidation proceeds entirely by trans-sulfidation of the benzyl methyl ether derivative and the thiol generated in situ by the $InBr_3$–Et_3SiH reducing system.

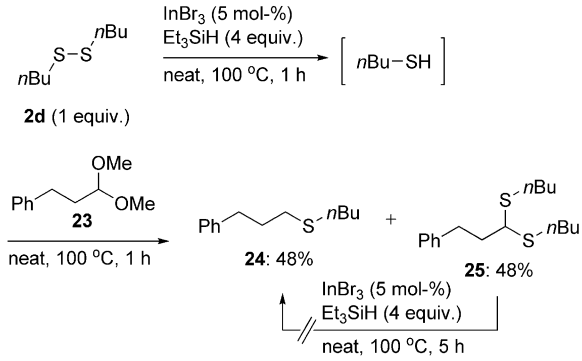


Scheme 3. Attempt at the direct sulfidation of an aliphatic acetal.



Scheme 4. Reaction path for sulfidation using a benzylic acetal and a disulfide.

Therefore, our original plan, the direct synthesis of a thioether from the corresponding aliphatic acetal, had to be shifted to the development of a stepwise procedure. After a great deal of experimentation, we managed to succeed in the development of a novel stepwise procedure as follows. A mixture of di-*n*-butyl disulfide (**2d**), $InBr_3$, and Et_3SiH was initially heated without a solvent at 100 °C for 1 h. Aliphatic acetal **23** was then added to the resultant solution containing the in situ generated thiol with further heating at 60 °C for 1 h, which finally produced desired dialkyl sulfide **24** in 48% yield along with thioacetal **25** (Scheme 5).[14] To confirm the sulfidation path, isolated dithioacetal **25** was treated with the standard $InBr_3$/Et_3SiH reducing system but unfortunately it did not form expected dialkyl thioether **24**.[15] This result suggests the existence of another reaction path involving the reductive deoxygenation of an *S*,*O*-acetal with a silane, as proposed by several other groups.[9c,16]



Scheme 5. One-pot preparation of a dialkyl sulfide.

Conclusions

We have demonstrated the facile reductive synthesis of a variety of sulfide derivatives from acetals (or ketals), which were derived from aromatic or conjugated aldehydes and relatively easy-to-handle disulfides using the $InBr_3$–Et_3SiH reduction system. In particular, we found that this reaction occurs by the trans-sulfidation of a benzyl methyl ether with an in situ formed thiol. We have also developed an unprecedented preparation of a dialkyl sulfide from a linear aliphatic acetal and an aliphatic disulfide.

Experimental Section

General Methods: Chloroform and MeCN were distilled from P_2O_5. THF and PhMe were distilled from sodium benzophenone. Other organic solvents were dried and distilled prior to use. $InBr_3$ and triethylsilane were commercially available and were used without further purification. All reactions were carried out under an atmosphere of nitrogen unless otherwise noted. ^1H NMR spectra were measured at 500 and 300 MHz using tetramethylsilane as an internal standard. ^{13}C NMR spectra were measured at 125 and 75 MHz using the center peak of chloroform (δ =77.0 ppm) as the internal standard. High-resolution mass spectra were measured by using NBA (3-nitrobenzyl alcohol) as the matrix. Benzaldehyde dimethyl acetal (**1a**), diphenyl disulfide (**2a**), di-*n*-butyl disulfide (**2d**), and trimethoxymethane (**21**) were commercially available and used without further purification. Other acetals were prepared from the corresponding aldehydes or ketones and alcohols according to a previously reported procedure, and were identified by their ^1H and ^{13}C NMR (JEOL ECP-500) and mass spectra (JEOL MS-700 MStation).

General Procedure for the Preparation of Acetals

Method A:[17a] A methanol solution (10 mL) of trimethyl orthoformate (2.1 g, 20 mmol) and $Yb(OTf)_3$ (62 mg, 0.10 mmol) was stirred at room temperature under N_2, followed by the addition of an aldehyde (10 mmol). After stirring at room temperature for 2 h, the reaction mixture was poured into a mixture of saturated $NaHCO_3$ aqueous solution (5 mL) and diethyl ether (15 mL). The

ether layer was extracted, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was distilled under reduced pressure with a bulb-to-bulb distillation apparatus to give the corresponding acetal.

Method B:[17b] A CH_2Cl_2 solution (40 mL) of an aldehyde (10 mmol) and trimethyl orthoformate (2.1 g, 20 mmol) was stirred at room temperature under N_2, followed by the addition of $In(OTf)_3$ (28 mg, 0.050 mmol). After stirring at room temperature for 3 min, a further portion of $In(OTf)_3$ (28 mg, 0.050 mmol) was added, and the reaction mixture was stirred for another 30 min. The reaction mixture was then poured into a mixture of a saturated $NaHCO_3$ aqueous solution (5 mL) and diethyl ether (15 mL). The ether layer was extracted, dried with anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was distilled under reduced pressure with a bulb-to-bulb distillation apparatus to give the corresponding acetal.

4-Methylbenzophenone Dimethyl Acetal (15e). Method A: Yield: 1.45 g (60%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H, Ar-CH_3), 3.11 (s, 6 H, O-CH_3), 7.09 (d, J = 7.8 Hz, 2 H, Ar-*H*), 7.17–7.22 (m, 1 H, Ar-*H*), 7.25–7.30 (m, 2 H, Ar-*H*), 7.37 (d, J = 7.8 Hz, 2 H, Ar-*H*), 7.47–7.51 (m, 2 H, Ar-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1, 49.2, 102.9, 126.7, 126.8, 127.3, 127.9, 128.7, 137.0, 139.5, 142.6 ppm. MS (EI): *m*/*z* (%)= 242 211 (100) $[M]^+$. $C_{16}H_{18}O_2$ (242.31): calcd. C 79.31, H 7.49; found C 79.05, H 7.80.

General Procedure for the Synthesis of Sulfides: A magnetic stirrer bar, acetal (0.50 mmol), disulfide (0.25 mmol), $InBr_3$ (8.9 mg, 0.0025 mmol), and Et_3SiH (330 μL, 2.0 mmol) were successively added to a freshly distilled toluene solution (0.5 mL) in a screw-capped vial under N_2. The vial was sealed with a cap containing a PTFE septum. The reaction mixture was stirred at 100 °C (bath temperature) and monitored by TLC until the starting disulfide was consumed. Saturated $NaHCO_3$ aqueous solution (3 mL) was then added to quench the reaction. The aqueous layer was extracted with CH_2Cl_2 (15 mL) and the combined organic phases were dried with anhydrous Na_2SO_4, filtered, and then evaporated under reduced pressure. The crude product was purified by preparative TLC (SiO_2/hexane) to give the corresponding sulfide.

1-[(Butylthio)methyl]naphthalene (12): Yield: 114 mg (99%), yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (t, J = 7.5 Hz, 3 H, CH_3-CH$_2$), 1.37 (sext., J = 7.5 Hz, 2 H, CH_2), 1.57 (quint., J = 7.5 Hz, 2 H, CH_2), 2.47 (t, J = 7.5 Hz, 2 H, CH_2), 4.15 (s, 2H Ar-CH_2-S), 7.36–7.37 (m, 2 H, Ar-*H*), 7.48 (t, J = 7.5 Hz, 1 H, Ar-*H*), 7.53 (t, J = 7.5 Hz, 1 H, Ar-*H*), 7.75 (m, 1 H, Ar-*H*), 7.84 (d, J = 8.5 Hz, 1 H, Ar-*H*), 8.15 (d, J = 8.5 Hz, 1 H, Ar-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.7, 22.0, 31.4, 31.8, 34.1, 124.0, 125.0, 125.7, 126.0, 126.9, 127.9, 128.7, 131.4, 134.0, 134.1 ppm. MS (EI): *m*/*z* (%) = 230 (100) $[M]^+$. HRMS (FAB): calcd. for $C_{15}H_{19}S$ $[M + H]^+$ 231.1207; found 231.1236.

1-Chloro-4-[1-(butylthio)ethyl]benzene (19): Yield: 113 mg (99%), colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.87 (t, J = 7.2 Hz, 3 H, CH_3-CH$_2$), 1.27–1.36 (m, 2 H, CH_2), 1.42–1.50 (m, 2 H, CH_2), 1.53 (d, J = 7.2 Hz, 3 H, CH_3), 2.29 (q, J = 7.2 Hz, 2 H, CH_2), 3.91 (q, J = 7.2 Hz, 1 H, CH$_3$-C*H*-S), 7.26–7.27 (m, 4 H, Ar-*H*) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6, 22.0, 22.6, 31.0, 31.3, 43.4, 128.5, 128.6, 132.5, 142.8 ppm. MS (EI): *m*/*z* (%) = 228 (100) $[M]^+$. HRMS (FAB): calcd. for $C_{12}H_{18}ClS$ $[M + H]^+$ 229.0818; found 229.0800.

1-Methyl-4-[phenyl(butylthio)methyl]benzene (20): Yield: 133 mg (99%), colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.85 (t, J = 7.5 Hz, 3 H, CH_3-CH$_2$), 1.35 (sext., J = 7.5 Hz, 2 H, CH_2), 1.53 (quint., J = 7.5 Hz, 2 H, CH_2), 2.31 (s, 3 H, Ar-CH_3), 2.38 (t, J = 7.5 Hz, 2 H, CH_2), 5.11 (s, 1 H, Ph-C*H*-S), 7.10 (t, J = 8 Hz, 2 H, Ar-*H*), 7.20 (t, J = 8 Hz, 1 H, Ar-*H*), 7.25–7.31 (m, 4 H, Ar-*H*), 7.41 (d, J = 7.5 Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6, 20.9, 22.0, 31.1, 31.9, 53.8, 126.9, 128.1, 128.2, 128.4, 129.1, 136.6, 138.6, 141.8 ppm. MS (EI): *m*/*z* (%) = 270 $[M]^+$, 181 (100). $C_{18}H_{22}S$ (270.43): calcd. C 79.94, H 8.20; found C 80.18, H 8.46.

Procedure for the Stepwise Synthesis of Dialkyl Sulfide 24: Di-*n*-butyl disulfide (**2d**; 0.3 mmol), $InBr_3$ (10.6 mg, 0.0030 mmol), and Et_3SiH (200 μL, 2.0 mmol) were successively added to a screw-capped vial under N_2. The vial was sealed with a cap containing a PTFE septum. During heating of the reaction mixture at 100 °C (bath temperature) the reaction was monitored by TLC until consumption of the starting disulfide. After 1 h, 3-phenylpropylaldehyde dimethyl acetal (**23**; 0.3 mmol) was added to the resulting mixture, and the vial was reheated at 100 °C for 1 h. The reaction was monitored by TLC until consumption of the substrates. A saturated $NaHCO_3$ aqueous solution (3 mL) was then added to quench the reaction. The aqueous layer was extracted with CH_2Cl_2 (15 mL) and the combined organic phases were dried with anhydrous Na_2SO_4, filtered, and then evaporated under reduced pressure. The crude product was purified by a preparative TLC (SiO_2/hexane) and a further GPC separation ($CHCl_3$) to give the corresponding sulfide **24** and thioacetal **25**.

Supporting Information (see footnote on the first page of this article): Details of experimental procedures and spectroscopic data for the known compounds.

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[1] a) G. Liu, J. R. Huth, E. T. Olejniczak, R. Mendoza, P. DeVries, S. Leitza, E. B. Reilly, G. F. Okasinski, S. W. Fesik, T. W. von Geldern, *J. Med. Chem.* **2001**, *44*, 1202–1210; b) S. F. Nielsen, E. O. Nielsen, G. M. Olsen, T. Liljefors, D. Peters, *J. Med. Chem.* **2000**, *43*, 2217–2226.

[2] For selected reviews, see: a) I. Koval, *Russ. J. Org. Chem.* **2007**, *43*, 319–346; b) D. J. Procter, *J. Chem. Soc. Perkin Trans. 1* **1999**, 641–668; c) C. P. Baird, C. M. Rayner, *J. Chem. Soc. Perkin Trans. 1* **1998**, 1973–2004; d) C. M. Rayner, *Contemp. Org. Synth.* **1996**, *3*, 499–533.

[3] For selected recent papers on the reduction of sulfones or sulfoxides, see: a) G. Hua, J. D. Woollins, *Tetrahedron Lett.* **2007**, *48*, 3677–3679; b) K. Bahrami, M. M. Khodaei, M. Khedri, *Chem. Lett.* **2007**, *36*, 1324–1325; c) J. M. Khurana, V. Sharma, S. A. Chacko, *Tetrahedron* **2006**, *63*, 966–969; d) B. R. Raju, G. Devi, Y. S. Nongpluh, A. K. Saikia, *Synlett* **2005**, 358–360; e) N. Iranpoor, H. Firouzabadi, A. Jamalian, *Synlett* **2005**, 1447–1449; f) N. Iranpoor, H. Firouzabadi, H. R. Shaterian, *J. Org. Chem.* **2002**, *67*, 2826–2830; g) K. C. Nicolaou, A. E. Koumbis, S. A. Snyder, K. B. Simonsen, *Angew. Chem. Int. Ed.* **2000**, *39*, 2529–2533; h) N. Somasundaram, K. Pitchumani, C. Srinivasan, *J. Chem. Soc., Chem. Commun.* **1994**, 1473–1474.

[4] a) Y. Guindon, R. Frenette, R. Fortin, J. Rokach, *J. Org. Chem.* **1983**, *48*, 1357–1359; b) L. Zervas, I. Photaki, J. Taylor-Papadimitriou, C. Sakarellos, P. Mazarakis, *J. Chem. Soc. C* **1970**,

2683–2687; c) R. G. Hiskey, J. B. Adams, *J. Org. Chem.* **1965**, *30*, 1340–1340.
[5] For selected recent papers on Cu-catalyzed reactions, see: a) L. Rout, P. Saha, S. Jammi, T. Punniyamurthy, *Eur. J. Org. Chem.* **2008**, 640–643; b) A. K. Verma, J. Singh, R. Chaudhary, *Tetrahedron Lett.* **2007**, *48*, 7199–7202; c) L. Rout, T. K. Sen, T. Punniyamurthy, *Angew. Chem. Int. Ed.* **2007**, *46*, 5583–5586; d) X. Lv, W. Bao, *J. Org. Chem.* **2007**, *72*, 3863–3867; e) D. Zhu, L. Xu, F. Wu, B. Wan, *Tetrahedron Lett.* **2006**, *47*, 5781–5784; f) Y. J. Chen, H. H. Chen, *Org. Lett.* **2006**, *8*, 5609–5612; g) C. G. Bates, P. Saejueng, M. Q. Doherty, D. Venkataraman, *Org. Lett.* **2004**, *6*, 5005–5008.
[6] For selected recent papers on Pd-catalyzed reactions, see: a) M. A. Fernandez-Rodriguez, Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 2180–2181; b) C. Mispelaere-Canivet, J.-F. Spindler, S. Perrio, P. Beslin, *Tetrahedron* **2005**, *61*, 5253–5259; c) M. Murata, S. L. Buchwald, *Tetrahedron* **2004**, *60*, 7397–7403; d) T. Itoh, T. Mase, *Org. Lett.* **2004**, *6*, 4587–4590; e) K. J. Miller, M. M. Abu-Omar, *Eur. J. Org. Chem.* **2003**, 1294–1299.
[7] For selected recent papers on Ni-catalyzed reactions, see: a) S. Jammi, P. Barua, L. Rout, P. Saha, T. Punniyamurthy, *Tetrahedron Lett.* **2008**, *49*, 1484–1487; b) Y. Yatsumonji, O. Okada, A. Tsubouchi, T. Takeda, *Tetrahedron* **2006**, *62*, 9981–9987.
[8] Y. Kikugawa, *Chem. Lett.* **1981**, *10*, 1157–1158.
[9] a) Q. Wang, X.-y. Li, G. K. S. Prakash, G. A. Olah, D. P. Loker, K. B. Loker, *ARKIVOC* **2001**, 116–128; b) G. Olah, Q. Wang, N. Trivedi, G. K. Surya Prakash, *Synthesis* **1992**, 465–466; c) M. B. Sassaman, G. K. S. Prakash, G. A. Olah, *Tetrahedron* **1988**, *44*, 3771–3780; for an example with esters and carboxylic acids, see: S. Kim, S. S. Kim, *Tetrahedron Lett.* **1987**, *28*, 1913–1916.
[10] a) N. Sakai, T. Moriya, K. Fujii, T. Konakahara, *Synthesis* **2008**, 3533–3536; b) N. Sakai, K. Fujii, T. Konakahara, *Tetrahedron Lett.* **2008**, *49*, 6873–6875; c) N. Sakai, T. Moriya, T. Konakahara, *J. Org. Chem.* **2007**, *72*, 5920–5922; d) N. Sakai, M. Hirasawa, T. Konakahara, *Tetrahedron Lett.* **2005**, *46*, 6407–6409.
[11] For selected recent papers on reductive reactions with the In^{III}–R_3SiH reducing system, see: a) M.-S. Yang, L.-W. Xu, H.-Y. Qiu, G.-Q. Lai, J.-X. Jiang, *Tetrahedron Lett.* **2008**, *49*, 253–256; b) K. Miura, M. Tomita, Y. Yamada, A. Hosomi, *J. Org. Chem.* **2007**, *72*, 787–792; c) M. Yasuda, T. Saito, M. Ueba, A. Baba, *Angew. Chem. Int. Ed.* **2004**, *43*, 1414–1416; d) K. Miura, Y. Yamada, M. Tomita, A. Hosomi, *Synlett* **2004**, 1985–1989; e) N. Hayashi, I. Shibata, A. Baba, *Org. Lett.* **2004**, *6*, 4981–4983; f) M. Yasuda, Y. Onishi, M. Ueba, T. Miyai, A. Baba, *J. Org. Chem.* **2001**, *66*, 7741–7744; g) T. Miyai, M. Ueba, A. Baba, *Synlett* **1999**, 182–184.
[12] In^{I} salts reductively cleave disulfides to produce the corresponding thiolate anions, see: a) B. C. Ranu, T. Mandal, *Can. J. Chem.* **2006**, *84*, 762; b) B. C. Ranu, T. Mandal, *Synlett* **2004**, 1239–1242.
[13] For microwave-assisted sulfidation of benzylic ethers with thiols, see: B. C. Ranu, S. Samanta, A. Hajra, *Synlett* **2002**, 987–989.
[14] When the reaction of acetals with thiols was carried out with $MgBr_2$ in the absence of an appropriate reducing reagent, selective conversion from acetals to dithioacetals occurred, see: J. H. Park, S. Kim, *Chem. Lett.* **1989**, 629–632.
[15] Group 13 metals/1,4-cyclohexadiene have promoted the reductive cleavage of dithioacetals to produce sulfide derivatives, but these examples are limited to cleavage at the benzyl position, see: K. Ikeshita, N. Kihara, M. Sonoda, A. Ogawa, *Tetrahedron Lett.* **2007**, *48*, 3025–3028.
[16] a) D. Nakata, C. Kusaka, S. Tani, M. Kunishima, *Tetrahedron Lett.* **2001**, *42*, 415–418; b) T. Mukaiyama, T. Ohno, T. Nishimura, J. S. Han, S. Kobayashi, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2524–2527; c) S. Kim, J. Ho Park, S. Lee, *Tetrahedron Lett.* **1989**, *30*, 6697–6700.
[17] a) T. Okano, T. Michihashi, J. Kiji, *Appl. Organomet. Chem.* **1995**, *9*, 473–478; b) R. Kumar, A. K. Chakraborti, *Tetrahedron Lett.* **2005**, *46*, 8319–8323.

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