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A Novel Approach to Catalytic Desulfurization of Coal

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Abstract. The reactions of dialkyl mono- and disulfides and functionalized alkylthio compounds with sodium in refluxing hydrocarbon solvent (tetradecane, mesitylene or toluene) resulted in sulfur-free products in very high yields. Greater than 95% sulfur removal was observed when dialkyl mono or polysulfides were treated with Na in liquid ammonia. Polycyclic aromatic sulfur heterocycles were only moderately desulfurized under these conditions while phenylthio derivatives gave thiophenol as the major product and dithiophenols as the minor products.

Project Objectives

A. Optimize the coal desulfurization reaction with respect to time, temperature, coal type and

$$\text{Coal(S)} + \text{excess } PR_3 \longrightarrow \text{Coal} + S{=}PR_3/PBu_3 \qquad (1)$$

the R groups (including R = H), and also on extraction, impregnation and sonication conditions.

B. Optimize the conditions for the HDS reaction

$$H_2 + S{=}PR_3 \rightleftharpoons H_2S + PR_3 \qquad (2)$$

(which allows the PR_3 to function as an HDS catalyst for coal) with respect to R group, temperature, pressure, H_2 gas flow rate and inert solvent presence.

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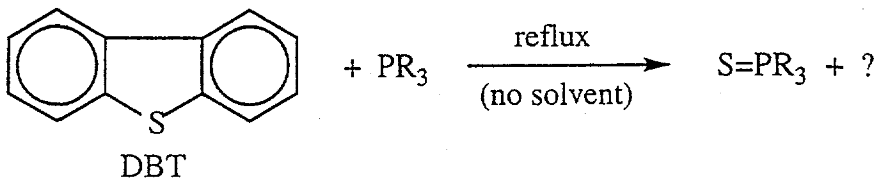
C. Determine the product(s) and the pathway of the novel redox reaction that appears to



(3)

quantitatively remove sulfur from dibenzothiophene (DBT) when R = Bu when $FeCl_3$ is used as a catalyst.

D. Impregnate sulfur-laden coals with Fe^{3+} to ascertain if the PR_3 desulfurization rate increases.

E. Determine the nature of the presently unextractable phosphorus compounds formed in solid coals by PR_3.

F. Explore the efficacy of PR_3/Fe^{3+} in removing sulfur from petroleum feedstocks, heavy ends (whether solid or liquid), coal tar and discarded tire rubber.

G. Explore the possibility of using water-soluble PR_3 compounds and Fe^{3+} to remove sulfur from petroleum feedstocks and heavy ends in order to remove the SPR_3 (and Fe^{3+} catalyst) by water extraction (for subsequent HDS of the SPR_3).

H. Explore the possibility of using solid-supported PR_3 compounds (plus Fe^{3+} catalyst) to remove sulfur from petroleum feedstocks and heavy ends in order to keep the oil and the SPR_3 (formed in the reaction) in easily separable phases.

Results

In this report we conclude our studies on the desulfurization of organosulfur compounds using sodium. We demonstrate that sodium efficiently desulfurizes a variety of dialkyl sulfides, alkyl-aryl sulfides and alkylthiol compounds under relatively mild conditions:

$$RSR' + 2Na \xrightarrow{110\text{-}254^\circ} \text{hydrocarbon} + Na_2S \qquad (4)$$

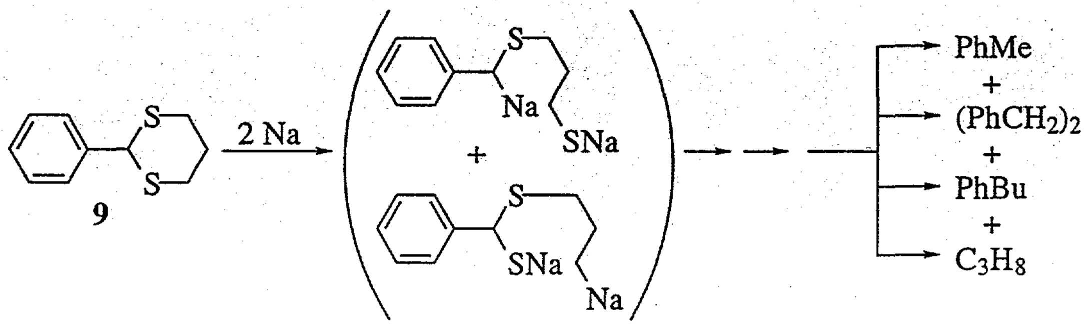
On the other hand, Birch reduction is only moderately successful for desulfurizing polycyclic aromatic compounds, but it is quite efficient for dialkyl mono or polysulfides, dialkyl sulfones, and pentavalent phosphine sulfides. This procedure is not successful for phenylthio substrates, however.

$$RS_xR' + 2xNa \xrightarrow{\text{liq } NH_3} RR' + 2xNa_2S \qquad (5)$$

Mild and Efficient Desulfurization of Alkyl Sulfides with Sodium. Chemical removal of sulfur from liquid fossil fuels and coals has received much attention because conventional hydrodesulfurization (HDS) can not effectively desulfurize polycyclic aromatic sulfur compounds, such as benzo[*b*]thiophene (BT), dibenzo[*b*,*d*]thiophene (DBT) and their derivatives. Among the chemical approaches directed to desulfurization of organosulfur compounds, reductive desulfurization has been considered to possess potential. Unfortunately, procedures involving $LiAlH_4$ in refluxing ethanol[1] and Li in refluxing dioxane[2] were found difficult to repeat.[3] Procedures using sodium at 350 °C and pressures of 200-1200 psi in the presence of hydrogen gave 51-99% sulfur removal from DBT with 45.6-93.2% yields of biphenyl.[4] Nickel boride was reported to desulfurize DBT to biphenyl in 83% of yield.[5] Trivalent organophosphorus compounds are known to desulfurize acylic dialkyl trisulfides to disulfides, and disulfides to monosulfides in moderate yields.[6-9] In the previous semi-annual report we showed that Li and Na efficiently desulfurize BT and DBT and their derivatives at relatively modest temperatures (110-254 °C) somewhat exceeding the melting points of the metals, in inert hydrocarbon solvents at atmospheric pressure.[3] In this report we show that this method is quite general and efficient for a variety of dialkyl and alkyl-aryl organosulfur compounds.

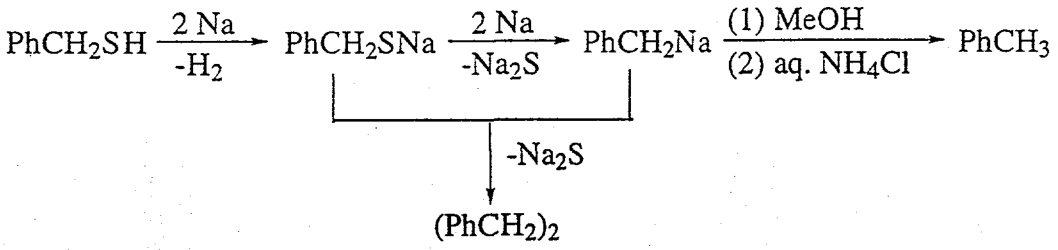
Although alkyl sulfides **1-3** did not desulfurize at 110 °C or 164 °C, at 254 °C, the corresponding alkanes were formed in high yields along with only small amounts of the corresponding alkylmercaptans (Table 1). The reactions of cyclohexene sulfide (**4**) and propylene sulfide (**5**) in refluxing toluene gave essentially quantitative yields of cyclohexene and propylene, respectively. Benzyl methyl sulfide (**6**) and disulfide (**7**) were efficiently desulfurized to toluene, ethylbenzene, and/or bibenzyl. Raising the reaction temperature improved the desulfurization of benzyl phenyl sulfide (**8**) because at lower temperature Bz-S bond cleavage by sodium was the predominant process (Table 1). The complete desulfurization of 2-phenyl-1,3-dithiane (**9**) can be envisioned to occur *via* the pathway indicated in Scheme 1. Changing the temperature results in an altered product distribution (Table 1).

Functionalized alkyl sulfides **10-13** were desulfurized without destruction of their remaining functionalities, and without the formation of desulfurized coupling products. For example, pyrrolidine (from **12**) and THF (from **13**) were not detected by GC analysis (Table 2).



Scheme 1

Compound **14** in the presence of sodium in toluene or mesitylene at room temperature produced an orange precipitate. That the precipitate is the corresponding enolate is indicated by the recovery of the starting material when the reaction mixture was treated with MeOH followed by aqueous NH_4Cl. This enolate intermediate was efficiently desulfurized to propiophenone in mesitylene at a relatively low temperature (164 °C). Interestingly, benzylmercaptan (**15**) was desulfurized to toluene and bibenzyl in 85.2% conversion within 13.5 hours, presumably according to Scheme 2. Substrate **16** underwent a similar reaction to generate triphenylmethane and hexaphenylethane. The reaction of benzyl thiocyanate (**17**) gave the PhC-S bond cleavage product PhMe and the desulfurized intramolecular coupling product bibenzyl, but benzyl cyanide was not detected. The reaction of alkenyl sulfone **18** occurred predominantly *via* CH-S bond cleavage resulting in styrene as the major product and thiophenol as the minor product (Table 2).



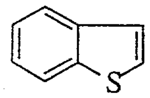
$$PhCH_2SH \xrightarrow[-H_2]{2\,Na} PhCH_2SNa \xrightarrow[-Na_2S]{2\,Na} PhCH_2Na \xrightarrow[(2)\ aq.\ NH_4Cl]{(1)\ MeOH} PhCH_3$$

$$\xrightarrow{-Na_2S} (PhCH_2)_2$$

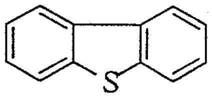
Scheme 2

Reductive Desulfurization of Organosulfur Compounds with Sodium in Liquid Ammonia. Birch reduction is known to reduce a variety of functional groups,[17] and here we report the results of our investigation of the application of this reaction to a range of organosulfur compounds.

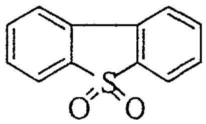
Treatment of BT (**19**) with Na/liq. NH_3 gave 2-ethylthiophenol in 99% yield and a small amount of ethylbenzene (Table 3). Although similar treatment of DBT (**20**) and DBT sulfone (**21**) produced moderate amounts of the desulfurized product biphenyl, DBT gave a black residue with a sulfur content of 1.81%, and the overall sulfur removal based on the sulfur content of the starting material was an impressive 92.3%. In the case of **21**, 2-phenylthiophenol was the major product. Thiophenols, the only products from the reduction of thianthrene (**22**), may well be



19
(BT)



20
(DBT)



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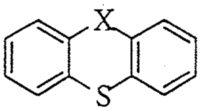
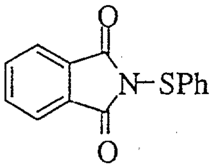


22, X = S; **23**, X = NH; **24**, X = O



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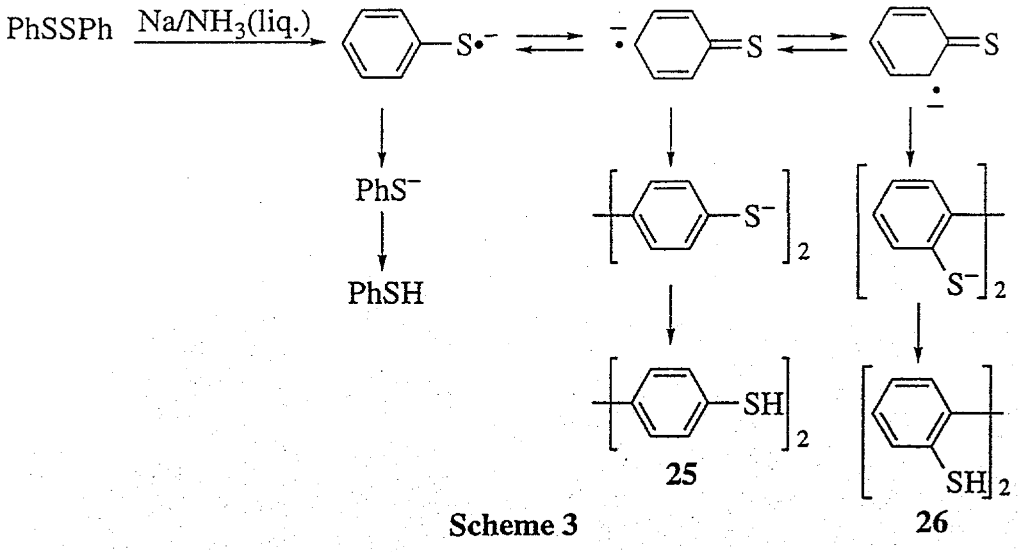
formed via a pathway resembling that shown in Scheme 3. Here formation of the phenylthio radical anion leads to the 4,4'-dithiophenol (**25**) and the 2,2'-dithiophenol (**26**) after the reaction is quenched by methanol and aqueous NH_4Cl. For the polycyclic aromatics **23** and **24** (Table 3), only a small amount of identifiable product was detected in each case, but reasonable desulfurization was observed from the sulfur analysis of the reaction residue (Table 3).



Scheme 3

Conclusions

Alkyl sulfides and disulfides are efficiently desulfurized in the presence of sodium between 110 and 254 °C in hydrocarbon solvents to give hydrocarbons and Na_2S. Thiol formation is generally not a problem except in the case of $PhCH_2SPh$ (**8**) for which 22% PhSH is observed. Alkyl sulfides such as **10-13** are selectively desulfurized but, interestingly, the oxygen and nitrogen functionalities remain intact. Using sodium in liquid ammonia, it is curious that benzothiophene (**19**) is virtually completely converted to 2-ethylthiophenol while dibenzothiophene (**20**) and DBT sulfone (**21**) give substantial amounts of the completely desulfurized product biphenyl (21-35%) under these mild conditions. It is also curious that even though the residue from the DBT Birch reduction was intractable, its sulfur content suggested that overall, 92% of the sulfur had been removed under the mild conditions employed here. Although we would like to pursue this chemistry further, we plan to return to the main objectives of the proposal with the remaining resources and time.

Experimental Section

Gas chromatographic analyses were carried out on a Hewlett-Packard 6980 GC system with a 25 m 200 μ diameter HP fused silica capillary column coated with HP-1 cross-linked methyl silicone (0.33 μm). Column chromatography was performed on silica gel. Solvents were dried over 4A molecular sieves. All the products were identified by comparison of their GC traces with those of authentic samples. Quantitation of the desulfurized products listed in the tables was accomplished by comparison of peak areas with those of authentic samples obtained in separate GC runs. NMR-pure biphenyl and bibenzyl were isolated by column chromatography in several cases.

Mild and Efficient Desulfurization of Alkyl Sulfides with Sodium. Under argon, sodium (10.0 mmol), organosulfur substrate (1.0 mmol) and solvent (3 mL of tetradecane or 5 mL of toluene or mesitylene) was added to a 50 mL Schlenk bottle fitted with a condenser connected at the top to an argon line. The reaction mixture was vigorously stirred at the temperatures and times indicated in Tables 1 and 2. After cooling the reaction mixture to room temperature, unreacted sodium was destroyed with methanol (5 mL) at 0 °C under argon. Saturated aqueous NH_4Cl (40 mL) was then added to the mixture followed by extraction with Et_2O (3×80 mL). The organic phase was dried over $MgSO_4$, filtered and then used directly for product analysis by GC. For the reaction involving **10**, the extraction solvent was THF while for **13** it was *n*-hexane.

Reductive Desulfurization of Organosulfur Compounds with Sodium in Liquid Ammonia. To a 150 mL two-necked Schlenk bottle charged with organosulfur substrate (1.0 mmol) and 40 mL of liquid ammonia, 0.69 g (30 mmol) of Na was added in portions and the mixture was vigorously stirred at –78 °C for 3 h under argon. Then ammonia was evaporated by slowly warming the reaction mixture to room temperature. Methanol (10 mL) was added at 0 °C followed by 40 mL of saturated NH_4Cl. Ether extracts (3 × 70 mL) of the mixture were dried over $MgSO_4$, filtered and concentrated by rotary evaporation for GC analysis. While this procedure was in progress, the residues indicated in Table 1 were collected and washed alternately with Et_2O and H_2O and then dried in vacuo. In the cases of BT (Table 1) and dibenzyl sulfide, disulfide, trisulfide and sulfone (Table 2), the organic phases were used directly for the analysis of the products.

References

1. Blicke, F. F.; Sheets, D. G. *J. Am. Chem. Soc.* **1948**, *70*, 3768-3770; **1949**, *71*, 4010-4011.
2. Gilman H.; Esmay, D. L. *J. Am. Chem. Soc.* **1953**, *75*, 2947-2949.
3. Yu, Z.; Verkade, J. G., submitted.
4. Sternberg, H. W.; Delle Donne, C. L.; Markby, R. E.; Friedman, S. *Ind. Eng. Chem., Process Des. Dev.* 1974, *13*, 433-436.
5. Back, T. G.; Yang, K.; Krouse, H. R. *J. Org. Chem.* **1992**, *57*, 1986-1990.
6. (a) Rastetter, W. H.; Spero, D. M.; Adams, J. *J. Org. Chem.*, **1982**, *47*, 2785-2787. (b) Harpp, D. N.; Smith, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 6045-6053 and references therein.
7. (a) Field, L. D.; Wilkinson, M. P. *Tetrahedron Lett.* **1997**, *38*, 2779-2782. (b) Verkade, J. G.; Mohan, T. *US Patent* 5,509,945, **1996**. (c) Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem.*

Soc. **1992**,*114*, 1926-1927. (d) Touchard, D.; Fillaut, J. L.; Dixneuf, P. H.; Toupet, L. *J. Organomet. Chem.* **1986**, *317*, 291-299.

8. Holand, S.; Ricard, L.; Mathey, F. *J. Org. Chem.* **1991**, *56*, 4031-4035.

9. (a) Harrp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1980**, *45*, 5155-5160. (b) Harpp, D. N.; Vines, S. M. *J. Org. Chem.* **1974**, *39*, 647-651. (c) Harp, D. N.; Orwig, B. A. *Tetrahedron Lett.* **1970**, *31*, 2691-2694. (d) Harpp, D. N.; Gleason, J. G. *J. Am. Chem. Soc.* **1968**, *90*, 4181-4182.

10. Yu, Z.; Verkade, J. G. ms in progress.

11. For a general review of the Birch reduction see: (a) L. N. Mander, in "Comprehensive Organic Synthesis", B. M. Trost and I. Flemming (Ed), Pergamon, **8**, 489 (1991). (b) Z. Lin, J. Chen and Z. Valenta, *Tetrahedron Lett.*, **38**, 3863 (1997). (c) T. J. Donohoe, R. Garg and C. A. Stevenson, *Tetrahedron Asym.*, **7**, 317 (1996).

Table 1. Desulfurization of alkyl sulfides with sodium.

substrate		solvent	temp/time (°C/h)	product[a] yield (%)
$(n\text{-}C_6H_{13})_2S$	1	tetradecane	254/8	$n\text{-}C_6H_{14}$ (90.0), $n\text{-}C_6H_{13}SH$ (5.0)
$(n\text{-}C_8H_{17})_2S$	2	tetradecane	254/8	$n\text{-}C_8H_{18}$ (97.5), $n\text{-}C_8H_{17}SH$ (< 2.0)
$(n\text{-}C_{12}H_{25})_2S$	3	tetradecane	254/23.5	$n\text{-}C_{12}H_{26}$ (> 99.0)
$(C_6H_{10})S$[b]	4	toluene	110/7	cyclohexene (> 99.0), cyclohexane (< 0.1)
$(C_3H_6)S$[c]	5	toluene	110/4	$CH_3CH=CH_2$ (> 99.0)[d]
$PhCH_2SMe$	6	mesitylene	164/4	PhMe (89.0), PhEt (10.9)
$PhCH_2SMe$	6	tetradecane	254/4	PhMe (72.1), PhEt (27.4)
$PhCH_2SSMe$	7	mesitylene	164/4	PhMe (16.6), PhEt (3.4), $(PhCH_2)_2$ (50.9)[e]
$PhCH_2SSMe$	7	tetradecane	254/4	PhMe (44.3), PhEt (5.8), $(PhCH_2)_2$ (48.4)[e]
$PhCH_2SPh$	8	toluene	110/5.5[f]	PhMe (24.0), PhSH (22.0), $(PhCH_2)_2$ (0.7)[g]
$PhCH_2SPh$	8	tetradecane	254/5.5	PhMe (95.0), PhSH (1.0), Ph_2CH_2 (1.1), $(PhCH_2)_2$ (0.6)[g]
$C_{10}H_{12}S_2$[h]	9	tetradecane	140/5.5	PhMe (21.6), Ph-Bu (< 1.0), $(PhCH_2)_2$ (75.0)[i]
$C_{10}H_{12}S_2$[h]	9	tetradecane	254/5.5	PhMe (49.2), Ph-Bu (< 0.5), $(PhCH_2)_2$ (50.0)[i]

[a] GC analysis, 100% conversion. [b] $(C_6H_{10})S$ = cyclohexene sulfide. [c] $(C_3H_6)S$ = propylene sulfide, 3.2 mmol. [d] Conversion > 99.0%. [e] Methane is presumably produced. [f] 25.5% conversion. [g] PhH was detected but not quantitated owing to its volatility. [h] $C_{10}H_{12}S_2$ = 2-phenyl-1,3-dithiane. [i] Propane is presumably produced.

Table 2. Desulfurization of alkylthio compounds with sodium.

substrate		temp/time[a] (°C/h)	conversion (%)	product yield (%)
$S(CH_2CH_2OH)_2$	**10**	254/4	100	CH_3CH_2OH (95.5)
$S(CH_2CH_2CH_2OH)_2$	**11**	254/5	100	$CH_3CH_2CH_2OH$ (90.0)
thiomorpholine	**12**	254/7.5	100	Et_2NH (> 95.0)
1,4-thioxane	**13**	254/8	100	Et_2O (> 95.0)
thiochroma-4-one	**14**	164/5.5[b]	100	$PhCOC_2H_5$ (> 99.0)
$PhCH_2SH$	**15**	254/13.5	85.2	PhMe (64.5), $(PhCH_2)_2$ (20.5)
Ph_3CSH	**16**	254/18	100	Ph_3CH (69.9), $(Ph_3C)_2$ (27.3)
$PhCH_2SCN$	**17**	140/5	100	PhMe (6.4), $(PhCH_2)_2$ (90.0)
$PhCH_2SCN$	**17**	254/5	100	PhMe (21.1), $(PhCH_2)_2$ (76.5)
$PhSO_2CH{=}CHPh$	**18**	110/6[c]	100	$PhCH{=}CH_2$ (95.0), PhSH (< 1.0)[d]
$PhSO_2CH{=}CHPh$	**18**	254/6	100	$PhCH{=}CH_2$ (95.0), PhSH (11.5)[d]

[a] Unless otherwise stated the solvent is tetradecane. [b] Mesitylene. [c] Toluene. [d] The $PhSO_2$ moiety is presumably transformed to other unidentified compounds plus PhH which was detected but not quantitated owing to its volatility.

Table 3. Birch reductions of polycyclic aromatic organosulfur compounds

substrate	conversion (%)[a]	product (%)[a]
19	100	2- ethylthiophenol (99.0), $PhCH_2CH_3$ (0.9)
20[b]	99.2	Ph-Ph (20.9), residue (70 mg, 1.81%S)[c]
21	100	Ph-Ph (35.3), 2-phenylthiophenol (58.4)
22	100	PhSH (47.9), **25** (51.0), **26** (0.8)
23	96.8	PhSH (5.6), Ph_2NH (1.4), carbazole (0.1) residue (125 mg, 6.00% S)[d]
24	100	PhOH (1.2), 2-phenylphenol (2.4) residue (130 mg, 5.75%S)[e]

[a] According to GC analysis. The products were identified by GC/MS and by comparing their GC traces with those of the authentic samples. [b] **20** (95 mg, 0.5 mmol) was used and 0.5 mL Bu_3P was added. [c] Sulfur removal, 92.3%. [d] Sulfur removal, 76.6%. [e] Sulfur removal, 80.2%.

Table 4. Birch reductions of non-polycyclic organosulfur compounds[a]

substrate	product (%)
PhSPh	PhSH (99.6), Ph-Ph (0.1), **7** (0.2)[b]
PhSSPh	PhSH (84.1), **25** (11.4), **26** (4.1)
$PhS(CH_2)_3SPh$	PhSH (94.2), **25** (3.0), **26** (2.7)
$(PhS)_2CH_2$	PhSH (85.0), **25** (9.9), **26** (5.0)
$(PhS)_3CH$	PhSH (77.3), **25** (10.3), **26** (12.3)
27	PhSH (30.9), phthalimide (18.0), **7** (65.0), **26** (2.0)
$PhCH_2SCH_2Ph$	PhMe (95.4), $(PhCH_2)_2$ (4.1)[c]
$PhCH_2SSCH_2Ph$	PhMe (98.0), $(PhCH_2)_2$ (0.6)[c]
$PhCH_2SSSCH_2Ph$	PhMe (91.0), $(PhCH_2)_2$ (7.7)[c]
$(PhCH_2)_2SO_2$	PhMe (90.7), $(PhCH_2)_2$ (9.2)
$Bu_3P{=}S$	Bu_3P (100)[d]
$Ph_3P{=}S$	Ph_2PH (>99.0)

[a] 100% conversion. [b] PhH was detected by GC analysis but not quantified owing to its volatility in the work up. [c] $PhCH_2SH$ (< 1%) was also detected by GC/MS. [d] Partly oxidized to $Bu_3P{=}O$ by air exposure.