DOE/FE/95208-10

A NOVEL APPROACH TO CATALYTIC DESULFURIZATION OF COAL

Final Technical Progress Report

Reporting Period:
September 1, 1995 – August 31, 2000

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Date Issued: November, 2001

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Grant No.
DE-FG22-95PC95208

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ABSTRACT

A Novel Approach to Catalytic Desulfurization of Coal

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Column chromatographic separation of the S=PBu_3/PBu_3 product mixture followed by weighing the S=PBu_3, and by vacuum distillation of S=PBu_3/PBu_3mixture followed by gas chromatographic analysis are described. Effects of coal mesh size, pre-treatment with methanol

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

and sonication on sulfur removal by PBu_3 revealed that particle size was not observed to affect desulfurization efficiency in a consistent manner. Coal pretreatment with methanol to induce swelling or the addition of a filter aid such as Celite reduced desulfurization efficiency of the PBu_3 and sonication was no more effective than heating. A rationale is put forth for the lack of efficacy of methanol pretreatment of the coal in desulfurization runs with PBu_3. Coal desulfurization with PBu_3 was not improved in the presence of miniscule beads of molten lithium or sodium as a desulfurizing reagent for $SPBu_3$ in a strategy aimed at regenerating PBu_3 inside coal pores. Although desulfurization of coals did occur in sodium solutions in liquid ammonia, substantial loss of coal mass was also observed.

Of particular concern is the mass balance in the above reaction, a problem which is described in some detail. In an effort to solve this difficulty, a specially designed apparatus is described which we believe can solve this problem reasonably effectively.

Elemental sodium was found to remove sulfur quantitatively from a variety of polycyclic organosulfur compounds including dibenzothiophene and benzothiophene under relatively mild conditions (150 ^{0}C) in a hydrocarbon solvent *without requiring the addition of a hydrogen donor.* Lithium facilitates the same reaction at a higher temperature (254 ^{0}C). Mechanistic pathways are proposed for these transformations. Curiously, dibenzothiophene and its corresponding sulfone was virtually quantitatively desulfurized in sodium solutions in liquid ammonia at –33 ^{0}C, although the yield of biphenyl was only about 20 to 30%. On the other hand, benzothiophene gave a high yield of 2-ethylthiophenol under these conditions.

Although our superbase $P(MeNCH_2CH_2)_3N$, which is now commercially available, is a more effective desulfurizing agent for a variety of organophosphorus compounds than PPh_3 or its acyclic analogue $P(NMe)_3$, it does not desulfurize benzothiophene or dibenzothiophene.

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Project Objectives

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

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

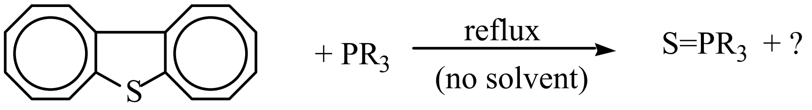
The R groups (including R = H), and also on extraction, impregnation and sonication conditions.

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.

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



DBT

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 feed stocks 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.

Background

For environmental reasons, many efforts aimed at efficient desulfurization of coals have been made over the past two decades. Sulfur present in coals can be removed by physical, chemical, or microbial methods.[1] The microbial process is slow but quite effective in removing all types of organic and inorganic sulfur simultaneously using a single type of bacterium. The simpler physical methods are currently more economical compared with processes that convert coal into liquid or gaseous fuels. Chemical processes developed in the past for the removal of both organically and inorganically bound sulfur from coal include the use of high-temperature alkaline solutions,[1] molten caustic at ca. 380ºC,[1d] alkoxides in refluxing alcohol,[1e] KOH in supercritical alcohols,[1f] oxidation with hydrogen peroxide[2] and peroxyacetic acid,[3] reductions involving hydrogenation,[1b] carboxylation,[4] zerovalent metal treatment,[5] reactions with single-electron transfer agents,[1c,6] and strong base.[7] Although these methods remove sulfur from coals to varying extents, other routes that improve coal desulfurization continue to be sought. Over the past decade, many organometallic systems have been investigated for their HDS properties and a substantial number of successful examples of C-S bond cleavage in benzothiophenes and dibenzothiophenes by such systems have been reported.[8] In a recent patent from laboratory,[9] data on the desulfurization of Illinois No. 6 coal with tributylphosphine under mild conditions were presented.

Results and Discussion

Speciation and Quantitation of $SPBu_3$ and PBu_3 in Reaction 1

A nagging and persistent problem with reaction 1 has been the determination of how much sulfur is actually removed from the coal. ^{31}P NMR analysis by integration of $SPBu_3$ and PBu_3 peaks indicated that up to 90% of the sulfur was removed in some reactions. Elemental analysis of the coal residues gave variable and often conflicting results owing to the fact that some of PBu_3 and $SPBu_3$ remains in the coal matrix, and also, a small amount of the coal is dissolved in the $SPBu_3$/PBu_3 product mixture. Further complicating the ^{31}P NMR integrations are the paramagnetic mineral materials extracted from the coal that broaden the peaks and interfere with quantitation of the peak areas. The analytical problem here is a non-trivial one because part of the coal dissolves in the $SPBu_3$/PBu_3 reagent mixture and part of this mixture is embedded in the coal residue.

At first, efforts were made to quantitatively separate the product $SPBu_3$ from the reaction by the obvious method of column chromatography. This failed, however, because $SPBu_3$ and PBu_3 do not elute separately very well owing to the large excess of PBu_3 used in the reaction. Attempts were then made to pass the mixture through a bed of $KHSO_4$ to achieve reaction 3 wherein the $HPBu_3^+$ was expected to remain

$$SPBu_3 + PBu_3 + KHSO_4 \longrightarrow SPBu_3 + \underline{HPBu_3^+K^+SO_4^{2-}} \qquad (3)$$

on the column. While the desired separation does occur to a large extent, the eluate is not pure $SPBu_3$, and further separation and purification must be carried out on a silica gel column. This procedure is not very satisfactory at best, since there are too many opportunities for loss and incomplete separation.

Gas chromatography is another possibility. A problem with this approach, however, is that we cannot inject the products of reaction 1 directly onto the column; not even a carefully centrifuged reaction mixture. Metal compounds (primarily iron species) are dissolved in the product mixture and such materials would damage the column. We therefore treated the centrifuged reaction mixture with aqueous base to precipitate the metal salts as their hydroxides and separated the aqueous and organic phases. The organic phase was to be subjected to GC and the centrifuged aqueous phase to elemental analysis for sulfur and phosphorus. We felt that it was likely that there would be negligible sulfur and phosphorus in the aqueous phase since $SPBu_3$ and PBu_3 are not very soluble in water. If these methods corroborated our ^{31}P NMR results, we would use this approach wherever appropriate, since it is more convenient. This methodology turns out to be unworkable for a variety of reasons, including retention of metal species in the organic phase as complexes ligated by PBu_3.

We then developed another technique. After the coal sample is refluxed in PBu_3, we vacuum distilled the $SPBu_3$, PBu_3 and other volatile organics into a separate vessel, leaving the non-volatile metal salts and coal residue behind. In carrying out this procedure with an Illinois No. 6 coal-derived pyrite sample we were able to remove 52% of its sulfur content as indicated by our gas chromatographic analysis. This was encouraging since the calculated amount removable by our method is 50% according to reaction 4. In other words, PBu_3 is not expected to remove sulfur from the FeS product of this reaction and this was demonstrated in an identical reaction with FeS.

$$\underset{\substack{\text{iron}\\\text{pyrite}}}{FeS_2} + PBu_3 \longrightarrow FeS + SPBu_3 \qquad (4)$$

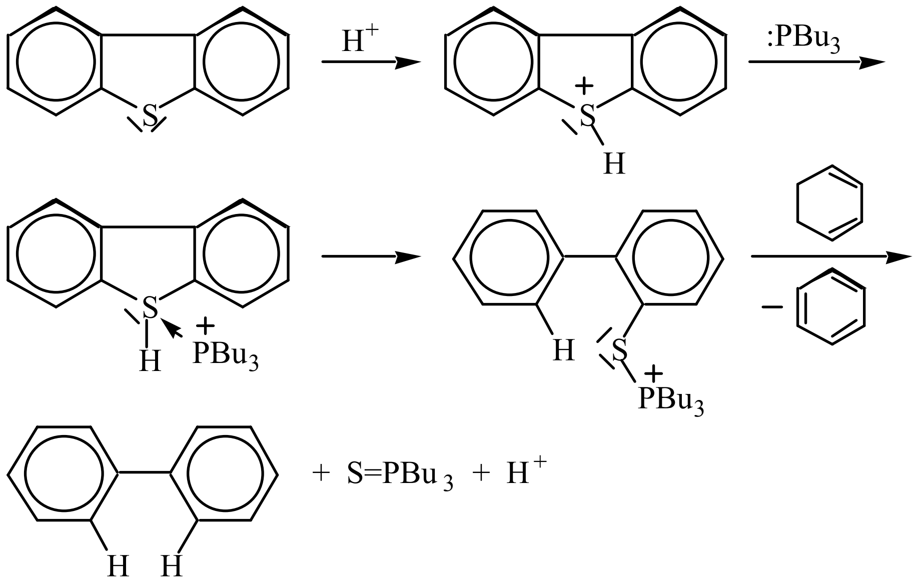
The above approach to our analytical problem has an additional advantage in that virtually all the coal (except its small amount of unextracted sulfur content) will be left after the vacuum distillation. Thus elemental analyses for residual sulfur content will be more informative in telling us how much sulfur that remains is as original sulfur and how much has become incorporated as $SPBu_3$.

Using ^{31}P NMR peak integration methods (which we do not yet regard as definitive) we analyzed the sulfur removal from DBT. This reaction, which is run at 70 ºC over 28 hours in acetonitrile results in less than 10% of the sulfur being removed when phenol is used as a catalyst, but with 1,4-cyclohexadiene present as a hydrogen donor, 39% sulfur removal is realized. Interestingly, when para-chloro phenol is used in place of phenol in this reaction, 62% sulfur appears to be removed after 24 hours. We find this result remarkable since DBT has never given up so much sulfur so easily under any conditions found in the literature. We did these reactions with phenol and para-chloro phenol present because we had evidence from research carried out under the previous grant that phenolics in coal aided sulfur removal by PBu_3. These results suggest that nucleophilic attack of PBu_3 on sulfur in DBT is facilitated by sulfur protonation as shown in Scheme 1. Here the proton may act as a catalyst since it is regenerated. Why para-chloro phenol is apparently more effective in this reaction than phenol itself is not clear. Thus an acid stronger than para-chloro phenol (e.g. HO_2CCF_3) does not work in this reaction

Effect of particle size, liquid NH_3 pretreatment, and sonication

Moderate desulfurization (*ca.* 61 % sulfur removal) was observed in the reactions of 20 or 80 mesh Illinois No. 6 coal with tributylphosphine, while greater desulfurization (76.2%) was realized with 100 mesh Illinois No. 6 coal (Table 1). The particle size of the coal was not observed to affect desulfurization efficiency in a consistent manner. Coal pretreatment with liquid ammonia at –78 ºC for 3 h to induce swelling or the addition of Celite to improve dispersion and filtration of the coal residue actually reduced desulfurization efficiency. Sonication instead of heating was also disappointing (Table 1).

Scheme 1



The desulfurization reaction in this work occurs as shown in eqn 1 in which the sulfur present in coal is predominantly converted to tributylphosphine sulfide. We observed in CPMAS ^{31}P NMR studies that the phosphorus species incorporated into the coal residue from this reaction can include Bu_3P, $Bu_3P{=}S$, $Bu_3P{=}O$, Bu_3PH^+ and a phosphate ester that can be written as $(Coal\text{-}O)_3P{=}O$. After the desulfurization coal residue was washed with ethyl ether and/or methylene chloride eight times for all entries in Table 1, only $Bu_3P{=}O$ could be detected in the filtrate by GC analysis. The >100% mass recovery and the relatively high phosphorus content of the residue in entry 7 suggest that any loss of starting mass by sulfur removal and coal solubility is overcompensated by phosphorus incorporation.

Effect of methanol pretreatment

Methanol treatment did not enhance the desulfurization of Illinois No. 6 coal with Bu_3P (Table 2). Not unexpectedly, methanol by itself did not extract a detectable amount of sulfur from Illinois No. 6 coal at 65 ºC. Pretreatment of coal with methanol in a variety of ways prior to its reaction with Bu_3P at 250 ºC only decreased the desulfurization efficiency of Bu_3P used by itself. It is plausible that the greater polarity and smaller bulk of methanol molecules compared with those of Bu_3P allowed methanol molecules to hydrogen bond within the coal pore, thus blocking penetration of the larger Bu_3P molecules.

Effect of alkali metal presence

It is reasonable to expect better desulfurization efficiency if the $Bu_3P{=}S$ generated in reaction 1 could be removed as it was formed, in order to inhibit accumulation of this compound in the coal pores, thereby reducing further access of Bu_3P to the coal matrix. We found that alkali metals (i.e., sodium and lithium) efficiently desulfurize polycyclic aromatic sulfur compounds and a variety of phenylthio and alkylthio compounds (see later). Addition of sodium to the Bu_3P under the same conditions as those used for Bu_3P by itself in the treatment of 100 mesh Illinois

No. 6 coal (Table 3) resulted in decreased desulfurization by a few percent to 74.7 %, albeit with less incorporation of phosphorus (Table 3). However, the mass recovery was also substantially less. The addition of lithium appears to interfere with sulfur removal from Illinois No. 6 coal for reasons that are presently obscure (Table 3). GC analysis of the extract after workup of the reaction mixture indicated that a small amount of $Bu_3P{=}S$ was still present in the washings of the residue. These observations demonstrate that although sodium or lithium can desulfurize the $Bu_3P{=}S$ generated from coal during the reaction, few if any of the miniscule beads of molten metal that formed were apparently small enough to penetrate the coal pores for reaction with the $Bu_3P{=}S$ that had become trapped in the pores.

Although Na and Li remove sulfur from a variety of organosulfur compounds (including thiophenes) in hydrocarbon solvents at temperatures above the melting points of the metal (see later), these metals displayed only poor to moderate efficiencies for desulfurizing coal in refluxing hydrocarbon solvents, such as tetradecane, mesitylene and toluene (Table 4).

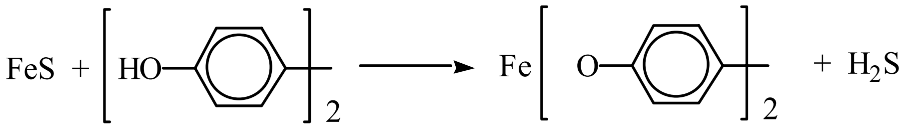
Effect of coal/PR_3 ratio

By using half the amount of Illinois No. 6 coal (0.500 g instead of the 1.000 g used in Table 1, entry 2), up to 92.3 % apparent sulfur removal was realized using Bu_3P by itself (Table 5). A temperature of 250ºC (the boiling point of Bu_3P) and a time of 48 h appears to be optimal for Illinois No. 6 coal. The higher desulfurization efficiencies may be attributed to the greater dilution of the $Bu_3P{=}S$ generated by Bu_3P during the reaction. Here the addition of Celite again only reduced desulfurization efficiency (entries 4 and 6 in Table 5).

Other coals and coal materials

The conditions in entry 4 of Table 5 were then applied to the desulfurization of a series of low-sulfur coals (Table 6). Where two mesh sizes of coals were employed, the desulfurization efficiencies were similar except in the cases of entries 1a, b and 4a, b. Interestingly, 70-90% desulfurization was achieved in most cases, with the Illinois No. 6, Pittsburgh No. 8 and Blind Canyon coal samples releasing approximately 90% of their sulfur.

Coal-derived pyrite, pyrite and FeS were also subjected to the same desulfurization conditions (Table 7). According to the atomic S/Fe ratios obtained from elemental analyses of the reaction residues in entries 3 (0.89) and 4 (0.90) it would appear that the FeS generated from FeS_2 was partially desulfurized. By assuming that the phosphorus content is present as Bu_3P, however, the amount of the available sulfur removed was 52.65 and 51.05%, respectively, which is close to the 50% value expected since FeS is very stable. By making the same corrections for the phosphorus contents of the coal-derived pyrites in entries 1 and 2, the quantities of the available sulfur removed were 47.13 and 55.13%, respectively. The latter somewhat high value may be due to the reaction in eqn 5 which stems from the presence of acidic biphenol. The $HPBu_3^+$ cation, which readily forms from PBu_3 in phenols, may also be involved in hydrogen transfer to the sulfidic sulfur. The sulfur removal from FeS in Table 7 is 11% (entry 5). The percent sulfur removed from the demineralized coal sample in Table 7 is only 31% (entry 7).



(5)

The nature of our sulfur removal process

Because virtually all of the inorganic sulfur in Illinois No. 6 is pyritic and since FeS does not appear to be appreciably desulfurized under our conditions, only about half of the ~ 3% inorganic sulfur in Illinois No. 6 is removed by Bu_3P. This would indicate that virtually all of the approximately 2% organic sulfur in this coal is removed (entry 4, Table 5). Since almost all of the organic sulfur in Illinois No. 6 is thiophenic sulfur, all of this type of sulfur is apparently removed under our conditions.

It could be suggested that thiophenic compounds merely dissolve out of the coal into the extract and are not chemically attached by the Bu_3P. Although this conjecture receives support from our observations that Bu_3P does not react with dibenzo[*b,d*]thiophene or benozo[b]thiophene to any detectable extent at 250 ºC for several days (see later), neither of these compounds was detected in the ^{13}C NMR spectra of the extracts. Earlier we showed that $HPBu_3^+$ (observed by ^{31}P NMR spectroscopy in Illinois No. 6 treated with Bu_3P) can be formed from phenolic (or carboxylic acid) protons present in the coals. We also showed that desulfurization of this coal with Bu_3P was negligible when the acidic protons were replaced with alkyl groups or Na^+ ions, thus leading to the conclusion that labile protons in coal facilitate desulfurization. It is interesting that the elemental analyses of the residues were consistent with incorporation of biphenol to the solid matrix (Table 7) when biphenol was added. Such incorporation could occur as a result of the reaction of biphenol with Bu_3P to form Bu_3PH^+ and biphenolate anion. A variety of acids do not facilitate this sulfur-removal reaction for thiophenes by themselves, however. Thus for some as yet unknown reason, labile hydrogens carry out this function in the coal matrix, and seem to do so only when minerals are present, as is shown by the lack of desulfurization of the demineralized coal samples in entry 7 of Table 7 wherein only 31.3% of (organic) sulfur removal was obtained and a 95.6% mass recovery was realized.

Effect of liquid ammonia

Birch reduction has been used to reduce a variety of functional groups in organic synthesis. The reactions of Illinois No. 6 coal with Na or Li in liquid ammonia gave comparable desulfurization efficiencies (56-57% of sulfur removal) with a *ca*. 32% weight loss of the coal sample (Table 8). It is well known that treatment of coal with an alkali metal in liquid NH_3 renders the coal more vulnerable to extraction by organic solvents. In our study (Table 8, entries 3 and 5), the water-soluble species in the reaction residues would include Na_2S or Li_2S which had to be extracted from the residue to render a meaningful sulfur analysis.

The mass balance problem

Although the reaction of coal with Bu_3P at 250 ºC under atmospheric pressure appears to be a generally efficient route to desulfurizing coals, the problem of mass balance is still a persistent one, however, because part of the coal is extracted into the Bu_3P and part of the Bu_3P remains in the coal matrix at Bu_3P, $Bu_3P{=}S$, $Bu_3P{=}O$ and Bu_3PH^+ phenolates, according to ^{31}P CP MAS NMR spectroscopy. This severely obfuscates the meaning of the S elemental analysis in terms of actual sulfur removal.

We first summarize the mass balance problem that has not to date been satisfactorily solved. Reaction 1 as written is greatly oversimplified because we showed earlier in this project that

Bu_3P is incorporated into the residue as its oxide, sulfide and as its protonated cation. Moreover, coal components are undoubtedly solubilized judging from the very dark coloration of the extract and proton NMR spectroscopy. Separation of the extract components has also not been achieved thus far. We considered the use of equation 6 wherein M = mass, SM = starting material, Res = residue, and Rem = removal.

$$\%S_{Rem} = \left(\frac{M_{SM} \text{ x } \%S_{SM} - M_{Res} \text{ x } \%S_{Res}}{M_{SM} \text{ x } \%S_{SM}} \right) \text{ x } 100\% \qquad (6)$$

Because M_{Res} in this equation does not simply represent the loss of coal components by reaction and/or solubilization, and because M_{Res} can sometimes exceed M_{SM} (see entry 7, Table 1), this equation is not valid. We thus opted for equation 7, which disregards the mass changes that have occurred.

$$\%S \text{ removal} = \left(\frac{\%S_{SM} - \%S_{RES}}{\%S_{SM}} \right) \text{ x } 100\% \qquad (7)$$

As a strategy to solve the mass balance problem, we designed an apparatus that we believed would allow us to perform more accurate mass balances, as well as expose the coal sample to fresh Bu_3P throughout the extraction process. The design we developed is similar to that of a Soxhlet apparatus, but its appearance and function are quite different. The problem with the Soxhlet apparatus is that there is considerable hang-up of an extractant by adsorption on all the surfaces above the liquid, including the extraction chamber and the inside of the reflux condenser. The Soxhlet cup also retains considerable Bu_3P by absorption into the fibrous cup material. It is thus not feasible to weigh the adsorbed and absorbed Bu_3P in the apparatus because the mass of this material is small relative to that of the apparatus and that of the cup containing the extracted coal.

The apparatus we designed, built and used greatly minimizes glass surface. It consists of a 50 mL flask fitted with a small water-cooled cold finger at the end of which is suspended an "envelope" constructed from filter paper. The envelope contained the weighed coal sample to be extracted. Several grams of Bu_3P were accurately weighed into the flask via a syringe and the Bu_3P was refluxed at 250ºC. The cold finger condensed the Bu_3P and allowed the hot condensate to wash through the filter paper. At the end of the run, the flask was allowed to cool to room temperature. The hang-up of Bu_3P on the relatively small amount of glass surface was calculated to be small compared with the original mass of liquid whose total volume we calculated from its density. (Accumulation of a drop of Bu_3P at the end of the cold finger was prevented by a stainless steel hook connecting the end of the cold finger to the filter paper holding the sample.) After a volumetric aliquot of extract was withdrawn and weighed in a syringe, we calculated the new density of the extract and also calculated reasonably precisely how much mass the coal had lost by extraction.

It was necessary to realize, however, that a corrected mass also had to be calculated for the amount of Bu_3P that was trapped in the coal residues, and an extract density correction had to be made for the Bu_3P trapped (absorbed) in the filter paper. The former was done by phosphorus elemental analysis of the extracted coal sample, and the latter correction was carried out as follows. The filter paper containing the extracted sample was transferred to a clean apparatus of the same design, and the paper was then washed with refluxing ether. The filter paper envelope was then dried and weighed to estimate the coal mass loss which was then compared with that calculated from the mass gain of the extract. Sulfur elemental analyses on both the extract and the extracted residue were then compared and used as checks on the accuracy of the sulfur elemental analysis. All of the manipulations had to be carried out under nitrogen or argon to prevent oxidation of the Bu_3P.

A potential complication of the calculated sulfur removal would be the sulfur that is trapped in the residue as $Bu_3P{=}S$ (which was detected by CP MAS ^{31}P NMR spectroscopy). We believed this would be a negligible problem because of constant exposure of the sample to pure hot condensed Bu_3P that would wash out the $Bu_3P{=}S$ much more completely. Thus in our sealed tube experiments mentioned earlier, a mixture of extract (containing dissolved $Bu_3P{=}S$) and coal residue would unfortunately be present throughout the heating cycle, which allowed an equilibrium to be established between the $Bu_3P{=}S$ dissolved in the extract and that which would be trapped in the coal.

After carrying out a series of experiments with this apparatus, we found to our chagrin that the degree of sulfur extraction was variable and poor. We determined that the problem was that the temperature of the tributylphosphine passing through the coal inside the filter paper was actually considerably below 250 ºC, owing to the fact that the reflux finger cooled the refluxing tributylphosphine too greatly, even when no coolant was allowed to flow through the finger. Thus the envelope and its contents was unable to reach 250 ºC, the temperature at which the extraction efficiency is highest according to the results described earlier.

It should be pointed out that it was also very difficult to control the level of the reflux line in the apparatus while still maintaining a liquid flow through the envelope at a sufficiently high temperature for extraction. There appeared to be too much conduction of heat away from the filter paper/coal sample and too little flow of tributylphosphine through the coal. Thus most of the liquid extractant appeared to flow over the outside of the envelope.

We believed we could solve this problem by using tea bag cloth, which is more porous and would hopefully still retain the powdered coal if the mesh was not too fine. A series of such experiments was carried out until the funding of the grant ran out at the end of June, 2000. Despite varying the ways in which we folded and attached the tea bag cloth to the bottom of the cold finger, the hot tributyl phosphine consistently eroded the bag material to the point where the bag would disintegrate. Moreover, we were still unable to achieve a 250 ºC extraction temperature inside the coal sample.

We are very disappointed that we were still unable to solve the mass balance problem because by doing so, we would be far more confident of the fascinating, but puzzling, chemistry that we believe goes on in the coal matrix, especially the evidence we have that suggests that we are extracting at least some of the sulfur from thiophene compounds. That is, pure thiophenes in refluxing Bu_3P do not lose significant amounts of sulfur regardless of the presence of a variety of metal ions and/or $HPBu_3^+$ and/or a catalytic amounts of coal that we have tried. Yet, several coals upon boiling in tributyl phosphine appear to give up large percentages of the organic (including thiophenic) and pyritic sulfur present in high-sulfur coals.

There *is* some good news concerning this vexing problem, however. After the funds in the grant account were expended, we were recently able to obtain a small amount of University funding to have our Glass Shop build a somewhat more sophisticated apparatus that we have designed. We believe the new apparatus should solve the mechanical problems we have had with previous designs, thereby giving us more precise and therefore more reliable answers.

The latest apparatus has a very small funnel fitted just below the cold finger. The funnel will have a small plug of glass wool packed into its stem. The glass wool-packed funnel will be weighed and then loaded with a small sample (about one gram) of coal after which the funnel will be re-weighed to give us an accurate weight of the coal sample. The funnel fits snuggly into a small spiral of resistance wire fitted through the wall of the flask. The resistance wire will heat the funnel and its contents to 250 ºC under an atmosphere of an inert gas. This temperature will then be maintained by controlling the reflux rate to a level sufficiently low to prevent the funnel from overflowing with extract. Such an overflow would probably carry with it small coal particles suspended in the liquid and would destroy the accuracy of the mass balance.

After the extraction run is completed, a volumetric aliquot of extract will be removed for elemental and density analysis, and the contents of the funnel will be thoroughly rinsed by refluxing ether in the apparatus. After vacuum drying the funnel at room temperature, the funnel and its contents will be weighed to inform us of how the weight of the coal may have increased (owing to chemically bound or physically trapped tributyl phosphine) or may have decreased (owing to coal dissolution and sulfur extraction) or some combination of the two sets of processes.

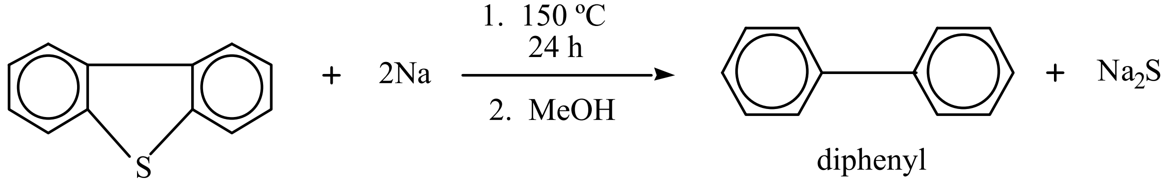
It may be noted that the purpose of the plug of glass wool in the funnel is not only to retain all of the coal in the funnel throughout the extraction process, but also to allow for a weighing receptacle that can be completely freed (via the refluxing ether rinse) of all tributylphosphine that is not chemically bound to the coal or physically trapped in small coal pores to which even ether has no access. In order to achieve total coal retention in the funnel during extraction, we may have to experiment with the tightness with which we pack the glass wool into the funnel stem. If coal particle passage through the glass wool plug still poses a problem, we could place a small layer of sand on top of the glass wool plug before adding the coal sample. Sand of different meshes could be used to control the flow of the extract through the funnel.

Elemental analyses of the coals and the particle-free extracts will then give us the data we need for securing definitive answers to the very intriguing questions that still remain after being frustrated in our previous attempts. We believe our efforts “beyond the call of duty” is a worthwhile one.

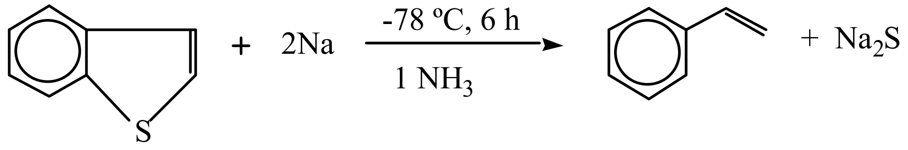
Quantitative Sulfur Removal from Organosulfur Compounds with Active Metals

Using gc analysis we have discovered that elemental sodium (which is about five times cheaper per mole than PBu_3) cleanly removes sulfur from dibenzothiophene, DBT (and other organic sulfur compounds) under very mild conditions (reaction 8).

We have also shown that BT loses part of its sulfur in liquid ammonia at –78 ºC (reaction 9).



DBT (8)

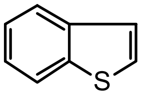


BT (9)

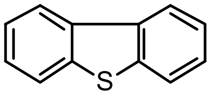
Amoco sent us some petroleum samples that contain less than 1% organic sulfur. If we were able to successfully remove the sulfur, Amoco indicated a strong interest in supporting our research efforts and if the economics were favorable, the process could become commercial. We spent considerable time and effort optimizing conditions for applying our process to Amoco's samples. Because of their volatility, we developed experimental conditions for desulfurization using metallic sodium in a sealed ampoule which was contained in a pressurized steel pressure vessel. We sent our treated samples to Amoco but never heard form them again despite repeated phone calls and emails.

To appreciate the results we obtained in these experiments, some background is appropriate. HDS processes are carried out at room temperatures above 400 °C and at high pressures,[10,11] and are practiced on an immense industrial scale. Considerable effort aimed at developing new types of transition metal catalysts for these processes has been expended,[12] and until very recently,[13] these investigations did not appear to be very promising for effective desulfurization of benzo[b]thiophene (BT, **1**), dibenzo[b,d]thiophene (DBT, **2**), or their derivatives (Chart 1) many of which occur in substantial amounts, particularly in heavier crudes and distillation residua.

Chart 1



1



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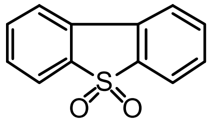

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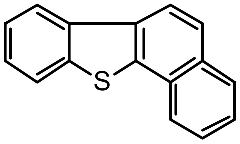

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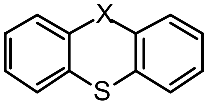
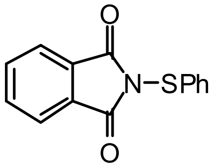


5: X = NH; **6**: X = O
7: X = S; **8**: X = C=O



9

Because these polycyclic aromatic sulfur compounds are so recalcitrant to conventional HDS processes, a variety of other approaches directed at this goal have been explored including direct catalytic hydrogenation, molten hydroxide treatment, oxidative and reductive processes, acid-promoted hydrolysis and single electron transfer reactions.[14] Among these methodologies, reductive desulfurization has been considered to possess potential. An early report on the desulfurization of DBT (**2**) and its derivatives over freshly prepared Raney nickel in ethanol seemed to be an ideal method,[15] but it has been found difficult to reproduce.[16] In our hands this approach provided only a 1.5% yield of the desulfurized product, namely, biphenyl.

Although the reductive desulfurization of DBT (**2**) with lithium in refluxing dioxane was reported to produce biphenyl in 41% yield,[16] our attempts to repeat this experiment resulted in a 2% yield of this product and only a 5% conversion of the starting material. Sulfur removal from aromatic hydrocarbons has been reported by treatment with molten Na at 150-250 °C and *ca.* 30 bar H_2 in an autoclave, after which only 1 ppm sulfur remained.[17] In the presence of H_2, > 99% sulfur removal from DBT with Na was achieved giving biphenyl as the major product.[18]

It is known that diphenyl sulfide can be cleaved by potassium in 1,2-dimethoxyethane and hydrocarbon solvents such as benzene and toluene with the formation of phenyl and thiophenolic anions and phenyl radicals.[19] In this case, PhSH was the primary product, although benzene (except in the case where benzene was used as the solvent), biphenyl and DBT (**2**) were identified as by-products. Using Li/biphenyl solutions in THF, aromatic carbon-sulfur bonds (e.g., of DBT) were predominantly cleaved at 0 °C within 2 hours but without desulfurization.[20] Mixtures of NaH or LiH with a nickel compound efficiently desulfurized a variety of organosulfur compounds including DBT.[21]

Recently, several other reducing systems involving nickel compounds were reported for desulfurization, namely, nickelocene/$LiAlH_4$,[22] nickel boride generated *in situ* from the reaction of $NiCl_2{\bullet}6H_2O/NaBH_4/MeOH$,[24,24] nickel and cobalt boride,[25] a Raney nickel/sodium hypophosphite system,[26] and $[(i\text{-}Pr_2PCH_2CH_2)_2NiH]_2$[27] which promoted the desulfurization of DBT at room temperature. Aquathermolysis of arenethiols and aryl sulfides in the presence of sodium also afforded sulfur-free compounds.[28] Microbial desulfurization of DBT sulfone resulted in complete sulfur removal[29] while plasma desulfurization of DBT produced products such as toluene and benzene in moderate yields.[30]

Treatments of petroleum fractions with Na can be roughly divided into two categories, namely, the distillates that are generally relatively free of thiophenes, and the high-boiling fractions and residua that tend to concentrate them. In the former category, up to 99% sulfur removal by sodium at 250-325 °C in a pressure vessel has been reported for gasolines.[31] Naphthalene fractions have also been desulfurized by Na: 93% desulfurization at 140-220 °C,[32] ~100% at 150-250 °C under 10-30 bar H_2 pressure,[33] and 91% at 310-340 °C at 500-1000 PSI of H_2.[34] A phenanthrene fraction was quantitatively desulfurized with Na at 125 to 200 °C[35] and a hydrocarbon oil fraction was >90% desulfurized by a mixture of excess Na and NaOR.[36] Residua treated with Na lost 75-95% of their sulfur at 350-400 °C at H_2 pressures of ca. 200 PSI[37] and virtually all of their sulfur at 350 °C under 10000 PSI.[38] Rates of sulfur removal by Na from organic sulfides and thiophenes at 200 °C in organic solvents in sealed tubes have been recorded.[39] Solutions of $(n\text{-}Pr)_2S$, *n*-BuSH and petroleum were essentially completely desulfurized by passage through a layer of liquid Na in a column at 165 °C.[40] However, thiophene under these conditions lost only part of its sulfur.[40] The desulfurization of a concentrated gasoline by reaction with Na metal on Al_2O_3 was investigated at 1 atm and 200-300 °C.[41] Here the removal of thiophenic compounds is dependent on the Na content of the reagent and the reaction temperature. Treatment of heavy oil with Na at 340-450 °C under H_2 pressure (≥ 50 PSi) essentially desulfurizes the oil with formation of Na_2S.[42] An improved process for the desulfurization of petroleum feeds utilizing Na at ~250 °C in the presence of excess of H_2 to Na was recently reported by Brons, et al.[43]

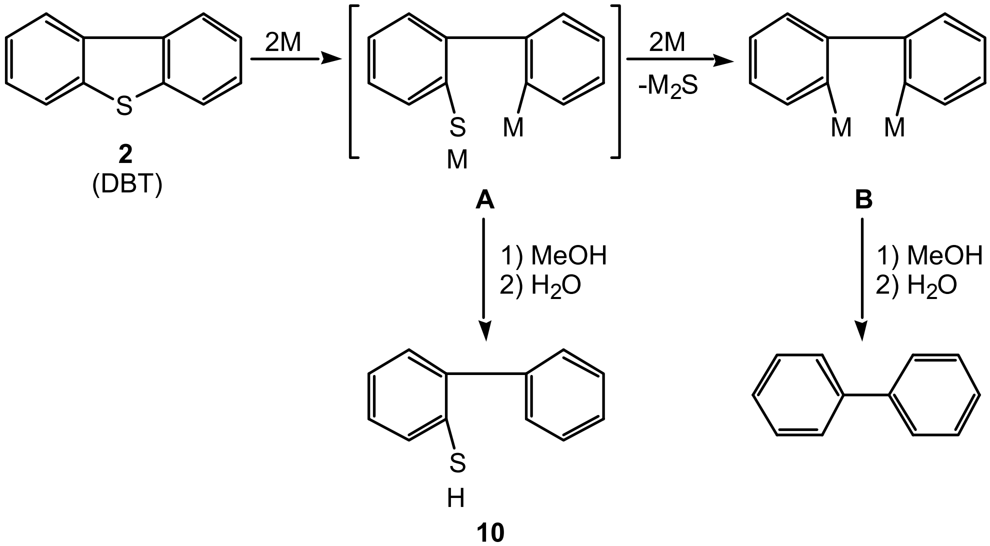
Whereas Li in $EtNH_2$ effectively reduces sulfide links in asphaltenes,[44] kerogens[44] and episulfides,[45] only 35-85% sulfur removal was accomplished with Li for high-boiling petroleum fractions and this metal was ineffective at room temperature in separate experiments on several thiophenes and on PhSPh.[46]

Trivalent organophosphorus compounds (e.g., triphenylphosphine,[47] tributylphosphine,[48] trialkylphosphites,[47c,49] and tris(dialkylamino)phosphines[47f,50]) have been reported to desulfurize acyclic organosulfur compounds. Thus dialkyl trisulfides are converted to the corresponding disulfides or monosulfides, β-keto sulfides are transformed to ketones, and sulfenimides are converted to amines in moderate yields. However, these reagents do not desulfurize polycyclic aromatic sulfur compounds. A MeOH/*t*-BuLi mixture has been shown to be effective in desulfurizing trienyl and allenyl phenyl sulfoxides.[51]

We have found[52] that reactions of polycyclic aromatic sulfur compounds (including BT and DBT) as well as a variety of acyclic organosulfur compounds with lithium or sodium in a hydrocarbon solvent at the comparatively low temperature of 254 and 150 °C, respectively, lead to remarkably effective desulfurization *without requiring added hydrogen gas*.

The reaction of DBT (**2**) with lithium (mp 180 °C) in refluxing dioxane (bp 100 °C) or with sodium (mp 97.8 °C) in refluxing THF (bp 67 °C) gave poor conversions of starting materials and yields (GC) of the desulfurized product biphenyl (Table 9). However, by raising the reaction temperature well above the melting point of the metals (Table 9), biphenyl was formed in essentially quantitative yield. A plausible reaction pathway is shown in Scheme 1 in which intermediate **A** has been shown to form when DBT is treated with Li at 0 °C in THF.[53] The detection of a trace of *o*-mercaptobiphenyl (**10**) in the quenched reaction mixture indicates that **A** is an intermediate that easily loses M_2S in the presence of excess alkali metal to form **B** which in turn produces biphenyl upon solvolysis. Gilman et al.[16] also confirmed the formation of intermediate **A** by quenching the reaction of lithium and DBT in refluxing dioxane with CO_2. After carbonation and hydrolysis, about equal amounts of **10** and biphenyl were obtained indicating a two-step cleavage. The participation of radicals in this mechanistic scheme is also possible in view of evidence for such a process put forth for a reaction in which 50% desulfurization of PhSPh was accomplished in benzene by K.[19] In the reaction of DBT with K in THF, **10** and biphenyl were obtained as the products.[53] A radical anion mechanism was

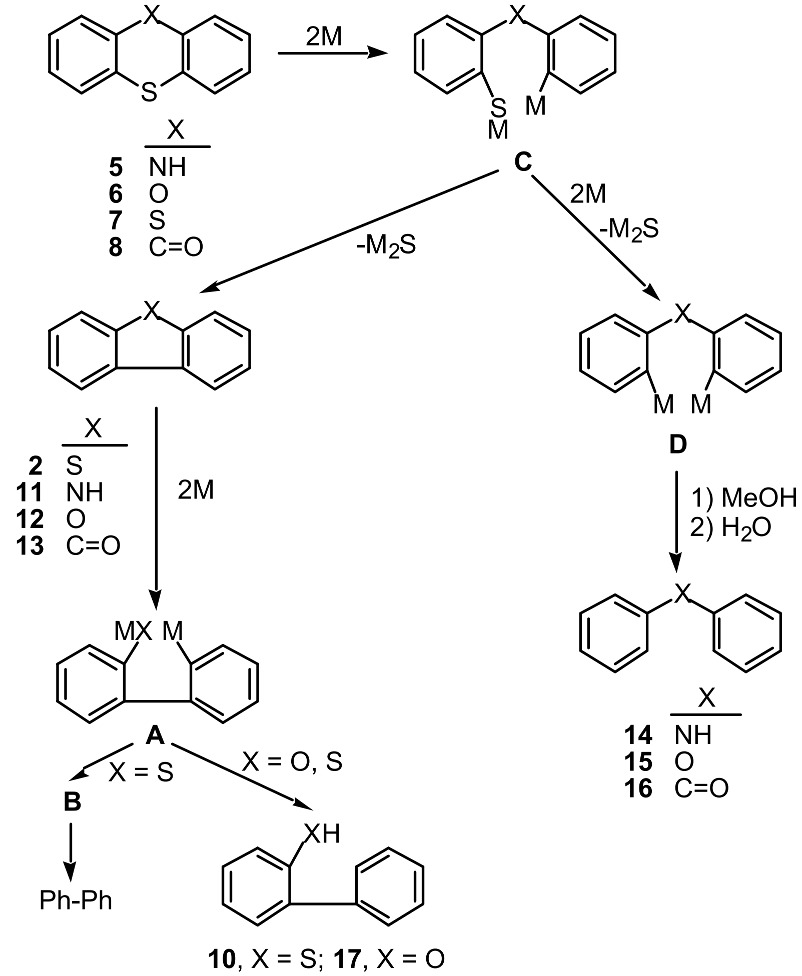
Scheme 2



proposed for the desulfurization of DBT with Na in decahydronaphthalene.[18] At temperatures above the melting point of the metal, the metal was observed to be dispersed into miniscule molten beads which would be expected to enhance the reaction rate. Although oleic acid is well known to improve the dispersion of the alkali metals in hydrocarbon solvents, our attempts to improve product yields by the addition of this dispersant were not successful (Table 9).

Molten Li and Na in inert hydrocarbons also showed very high desulfurization capabilities with other polycyclic aromatic sulfur compounds (Table 9). Reactions of BT (**1**), dibenzothiophene sulfone (**3**), and 1,2-benzodiphenylene sulfide (**4**) cleanly gave styrene, biphenyl and 2-phenylnaphthalene, respectively. In the presence of Li or Na the organosulfur heterocycles **5**-**8** containing an additional bridging heteroatom or group gave the variety of reactions (via the postulated pathways) shown in Scheme 3. The initial cleavage of the C-S bond generates intermediate **C** which then follows two predominating pathways to form **2** and **11-13** (via M_2S elimination and ring-closure) and the organometallic intermediate **D** which is subsequently solvolyzed to give the ring-opened products **14-16**. Compounds **2** and **12** can undergo ring-opening by the metal to form intermediate **A** which (as shown in Scheme 2) can provide biphenyl, **10** and **17**. The reactions of phenothiazine (**5**) and thioxanthen-9-one (**8**) produced the ring-opened products diphenylamine (**14**) and benzophenone (**16**), respectively, as the minor products, and the ring-closure products carbazole (**11**) and 9-fluorenone (**13**), respectively, as the major products (Table 9). Phenoxathiin (**6**) was selectively desulfurized to

Scheme 3



10, X = S; **17**, X = O

the ring-opened diphenyl ether (**15**) by lithium, but its reaction with sodium resulted in the production of phenol, **15** and **17** at the lower temperature of 150 °C. Here phenol could arise from cleavage of C-O bond of the intermediate **C** to give sodium phenolate and sodium thiophenolate (which then undergoes desulfurization with additional metal). Diphenyl ether (**15**) is expected from solvolysis of intermediate **D** (X = O), and *o*-hydroxybiphenyl (**17**) can arise from a C-O bond cleavage of dibenzofuran (**12**) by the metal. The lack of detectable amounts of dibenzofuran in these experiments is consistent with an earlier report of its cleavage by an alkali metal.[16] An intermediate in the reaction of thianthrene (**7**) with Li in refluxing tetradecane and Na in Bu_3P at 150 °C (Table 9) is DBT (**2**) which can then be further desulfurized to biphenyl.

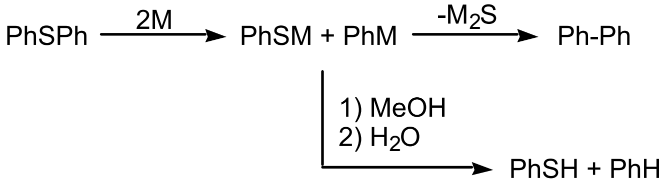
Except for diphenyl sulfide, reactions of organosulfur compounds containing one or more phenylthio groups with sodium generally underwent quantitative conversions, giving thiophenol as the major product at 110 °C or 150 °C (Table 10). Although diphenyl sulfide showed the lowest reactivity in this reaction, quantitative conversion to biphenyl was observed at 254 °C. At this temperature conversions of the remaining substrates to hydrocarbon products were very good, except for 1,3-bis(phenylthio)propane which gave thiophenol as the major product. Interestingly in this respect, $PhSCH_2SPh$ is more readily converted to $PhCH_2Ph$, Ph-Ph and (presumably) CH_4 under similar conditions while $(PhS)_3CH$ requires 15 h at 254 °C for quantitative reduction to Ph-Ph and (presumably) CH_4. Support for the pathway shown in

Scheme 4 and a similar pathway shown in Scheme 5 comes from a study under similar conditions in which benzyl thiol and triphenylmethyl thiol were desulfurized with Na to form PhMe and $(PhCH_2)_2$, Ph_3CH and $(Ph_3C)_2$, respectively.[53] It is also known that phenyl benzyl sulfide can be desulfurized to form benzene, toluene and bibenzyl, as well as thiophenol as C-S cleavage products.[51]

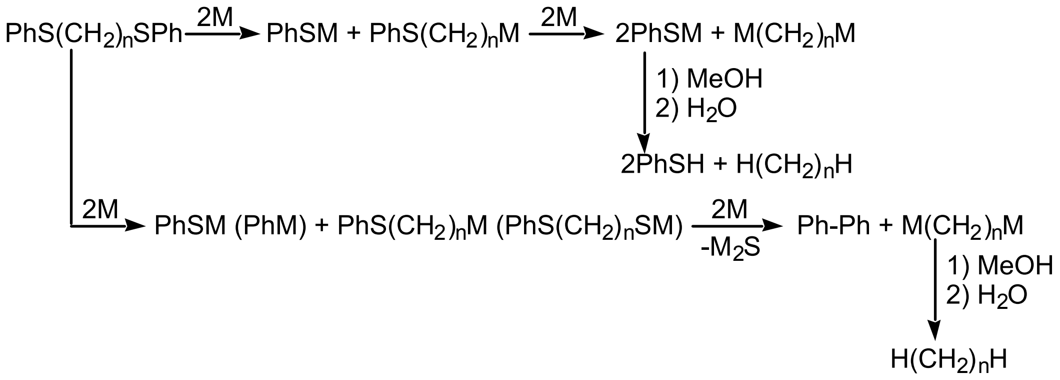
It is reasonable to suppose that the phenyl anion of PhM formed by cleavage of the aromatic carbon-sulfur bond of Ph_2S nucleophilically attacks PhSM to eliminate M_2S and form biphenyl (Scheme 4). If such a nucleophilic reaction is quenched before completion, thiophenol and benzene would be obtained as observed. A similar explanation applies to the mechanism shown in Scheme 5. It is interesting that raising the reaction temperature leads to the reaction of PhSM and PhM to form Ph-Ph.

Apparently Ar-S bonds in acyclic organosulfur compounds are comparatively stable to cleavage by Na and Li at relatively low temperatures, thus accounting for sodium thiophenolate as the main intermediate at 110 °C or 150 °C, which subsequently converts to thiophenol via methanolysis as shown in Scheme 5 for PhSPh and $PhS(CH_2)_nSPh$, respectively.

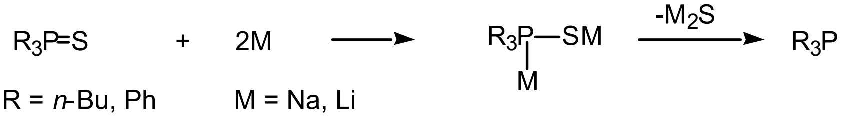
Scheme 4



Scheme 5



Scheme 6



Although only small amounts of biphenyl were detected with substrates treated with sodium at 110 °C or 150 °C, both sodium and lithium revealed a much higher activity for cleaving Ar-S bonds at 254 °C. Apparently the phenyl metalate that forms subsequently attacks the corresponding metal thiophenolate present in the reaction mixture to form biphenyl and metal sulfide. Dibenzyl sulfide, disulfide and trisulfide were easily desulfurized to form toluene as the major product and bibenzyl as the minor product (Table 10). In the reaction of dibenzyl disulfide with lithium, a 20.9% GC yield of dibenzyl monosulfide was formed with only 80% conversion of the starting material. The substantially complete reaction of benzyl sulfone with sodium at 254 °C to generate toluene required a relatively long time (23 h).

Although triphenylphosphine was reported to desulfurize diphenyl disulfide to diphenyl sulfide,[10b] no other reports have appeared describing the desulfurization of phenylthio-containing organosulfur compounds by means of trivalent organophosphorus compounds. Such reagents are known, however, to desulfurize dialkyl trisulfides to disulfides or monosulfides, and dialkyl disulfides to monosulfides.[47,48,50] Interestingly, Li and Na at 254 °C quantitatively desulfurize tributylphosphine sulfide and triphenylphosphine sulfide. A plausible pathway is shown in Scheme 6. This procedure is substantially more convenient than that involving trifluoroacetic anhydride,[54] LiAlH$_4$,[55] or hexachlorosilane[56] for such phosphorus-sulfur compounds.

It is unclear whether tributylphosphine played a role in the desulfurization of BT (**1**), DBT (**2**) and thianthrene (**7**) (Table 9) when it was used as the solvent. Thus although product yields were not improved, it was effective in dispersing the metal. However, PBu$_3$ did not significantly affect the rates of these reactions, nor did PBu$_3$ itself desulfurize BT or DBT.

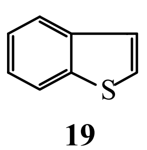
The reactions of N-(phenylthio)phthalimide (**9**) produced no detectable quantities of N-phenylphthalimide (Table 9). While cleavage of the N-S bond by sodium gave an 84% GC yield of thiophenol and a 90% yield of phthalimide as the major products, the reaction with lithium gave a more complicated reaction mixture containing additional unidentified products.

In conclusion, we have shown for the first time that thiophenes (**1**, **2**, **3** and **4**) are quantitatively desulfurized cleanly to styrene, biphenyl and 2-phenylnaphthalene, respectively, with Na or Li in tetradecane at 150 or 254 °C, respectively, without necessitating the presence of hydrogen or a hydrogen-donor solvent. Interestingly, Li at 254 °C was somewhat more efficacious than sodium for cyclic **5**, **6** and **8** which is probably due to the lower temperature employed with Na. Neither metal did very well against **9**. At 254 °C, both metals quantitatively desulfurized PhSPh, PhSSPh, Bu$_3$P=S and Ph$_3$P=S, while one of the metals did so in the case of PhSCH$_2$SPh, PhS(CH$_2$)$_3$SPh and PhCH$_2$SCH$_2$Ph. Although starting material conversions were 100% for (PhS)$_3$CH, PhCH$_2$SSCH$_2$Ph, PhCH$_2$SSSCH$_2$Ph and (PhCH$_2$)$_2$SO$_2$ for at least one of the metals at 254 °C, only 95-98% of sulfur-free products could be identified. Whether the unidentified remainder products are sulfur free is not known at this time. The procedure described here provides an attractive potential route for desulfurizing coal and petroleum liquids, as well as for sulfur-containing intermediates in organic synthesis.

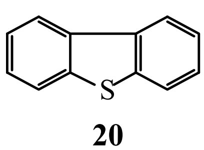
Reductive Desulfurization of Organosulfur Compounds with Sodium in Liquid Ammonia

Birch reduction is known to reduce a variety of functional groups,[57] and here we report the results of our investigation of the application of this reaction to a range of organosulfur compounds (Tables 11 and 12).

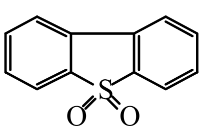
Treatment of BT (**1**) with Na/liq. NH$_3$ gave 2-ethylthiophenol in 99% yield and a small amount of ehtylbenzene (Table 11). Although similar treatment of DBT (**20**) and DBT sulfone (**21**) produced moderate amounts of the desulfurized product biphenyl, DBT gave a black residue with a sulfur content of 1.81%, and the overall sulfur removal based on the sulfur content of the starting material was an impressive 92.3%. In the



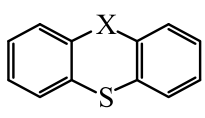
19
(BT)



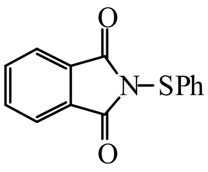
20
(DBT)



21



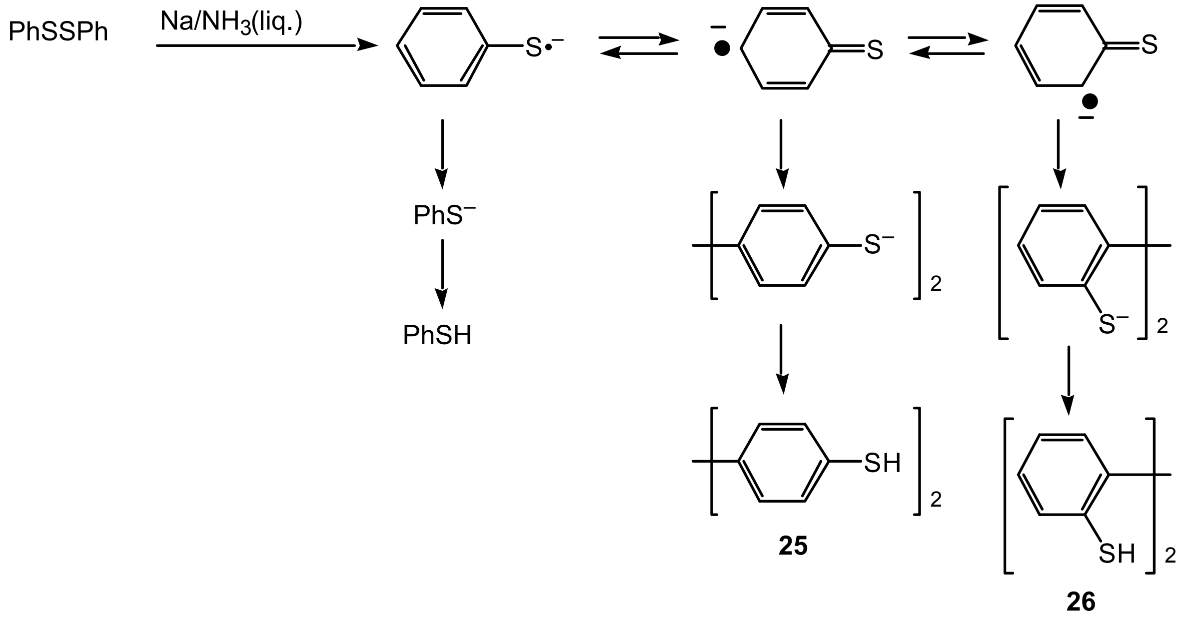
22, X = S; **23**, X = NH; **24**, X = O



27

case of **21**, 2-phenylthiophenol was the major product. Thiophenols, the only products from the reduction of thianthrene (**22**), may well be formed via a pathway resembling that shown in Scheme 7. 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 11), 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 11).

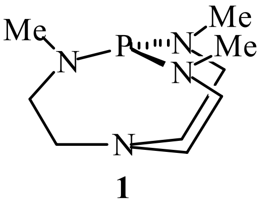
Scheme 7



Using sodium in liquid ammonia, it is curious that benzothiophene (**19**) 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 reduction was intractable, its sulfur content suggested the overall, 92% of the sulfur had been removed under the mild conditions employed here.

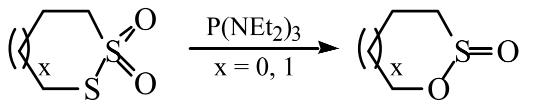
P(MeNCH₂CH₂)₃N: An Efficient Desulfurizing Reagent

Here we report that the highly basic phosphine **1**, which was developed in our laboratories and is now commercially available, is an unusually powerful desulfurizing reagent for a variety of organosulfur compounds, but not for benzothiophene, dibenzothiophene or coal.

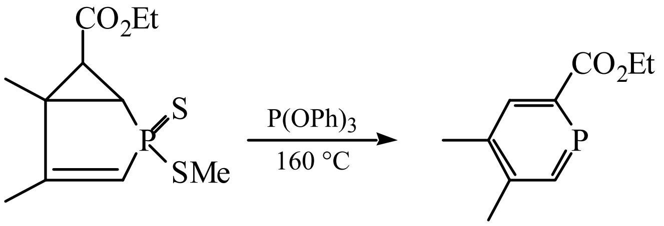


1

The desulfurization of organosulfur compounds with trivalent organophosphorus reagents has been studied for more than four decades. For example, one or more of the reagents triphenyl phosphine,[58-62] trisdimethylaminophosphine,[61,63-65] trisdiethylaminophosphine,[61,64-67] triethylphosphite,[58] trimorpholinophosphine[61,64] and tributylphosphine[68,69] have been employed to convert trisulfides to the corresponding disulfides or monosulfides, β-keto sulfides to ketones, and sulfenimides to amines in moderate yields. Trialkyl phosphines can be used to remove sulfur from thioethers,[70] thiols[71] and organometallic dithiocarboxylates;[72] trisdiethylaminophosphine effects reaction 10; triphenylphosphite effects reaction 11;[73] and recently thiol groups have been reductively eliminated photochemically from L-cysteine derivatives in the presence of triethylphosphite and triethylboron.[74]

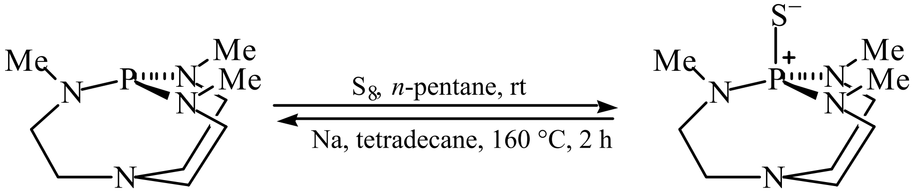


(10)



(11)

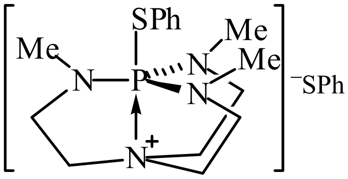
In the course of our ongoing investigations on desulfurizations of organosulfur compounds and on new synthetic applications of the exceedingly strong nonionic base and catalyst **1** first reported from our laboratories[75-77] and now sold commercially by Aldrich Chemicals, we found that **2** could be formed from **1** in the presence of sulfur.[78] Recently, we found that **2** could be desulfurized with excess sodium in refluxing toluene or in tetradecane at 160 °C. These results suggested a potential application of **1** in desulfurizing organosulfur compounds in a cyclic process since **1** can be recycled as shown in eqn. 12. Here we report desulfurizations with **1** under mild conditions.



1 **2**

(12)

Using 1.0 equiv of **1**, trisulfides were desulfurized primarily to disulfides with monosulfides as minor products at room temperature and the formation of **2** as the only other product (entries 1-3, Table 13). With more than 2.0 equiv of **1**, benzyl trisulfide was desulfurized to benzyl monosulfide via benzyl disulfide (entry 4, Table 13). Disulfides such as propyl, butyl, methyl benzyl and benzyl disulfides were efficiently desulfurized to monosulfides at room temperature or at 40 °C (entries 6, 10, 13 and 14, Table 13). Increasing the steric hindrance of the disulfide obviously decreased the desulfurization rate (entries 7 and 12, Table 13). Although $(Me_2N)_3P$ was effective for desulfurizing trisulfides to disulfides and some activated monosulfides to sulfur-free compounds,[61,63] it showed much poorer desulfurizing efficiency than **1** under the same reaction conditions (entries 5, 8, 9 and 11, Table 13). Using excess $(Me_2N)_3P$, benzyl trisulfide was desulfurized to benzyl disulfide (39.6%) and benzyl monosulfide (42.9%) in THF at room temperature within 25.5 h, but under the same conditions it was quantitatively desulfurized to dibenzyl monosulfide by **1** within 3 h (entries 4 and 5, Table 13). For disulfides, $(Me_2N)_3P$ led to poor desulfurization efficiencies (entries 8, 9 and 11, Table 13). Phenyl disulfide could not be efficiently desulfurized at room temperature by **1** and raising the temperature led to the formation of **3** (entry 15, Table 13). The ^{31}P NMR spectrum of the reaction mixture of phenyl disulfide with **1** in tetradecane at 160 °C revealed a major peak at 45.1 ppm in addition to a small peak at 76.3 ppm (assigned to **2**). Acidifying the same reaction mixture with 1N HCl led to the formation of phenylthiol which was detected by GC/MS analysis. Interestingly, propylene sulfide in the presence of **1** lost sulfur to give propene in high yield at room temperature (entry 16, Table 13).



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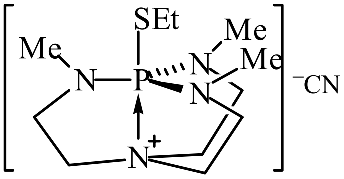

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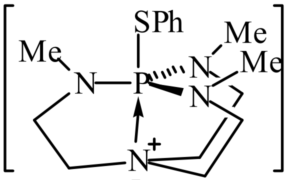
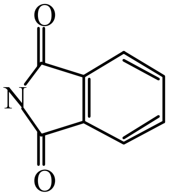
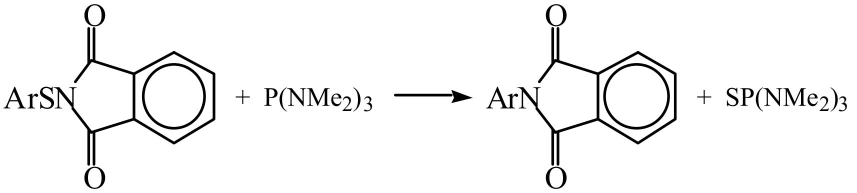


5



Thiocyanates were desulfurized to their corresponding cyanides (entries 1, 2, Table 14). In the reaction of ethyl thiocyanate with **1** at room temperature, **4** (δ^{31}P = 50.7 ppm) and **2** were formed in roughly equivalent amounts according to ^{31}P NMR integration, but raising the temperature decomposed **4** to ethyl cyanide and **2** presumably via nucleophilic attack of cyanide anion at the Et-S bond. Compound **1** and N-(phenylthio)phthalimide reacted cleanly at room temperature forming **5** quantitatively. Analogues of **5** wherein the cation is ArSP(NMe$_2$)$_3^+$ (Ar = Ph or *p*-MeC$_6$H$_4$) have been suggested (on the basis of transient ^{31}P chemical shifts at ~60 ppm) as intermediates in the desulfurization of the corresponding thioaryl phthalimides:[79]



(13)

Even triphenylphosphine sulfide was desulfurized in moderate yield by **1** (60%, entry 4, Table 13) indicating that **1** is the stronger desulfurizing reagent. However, benzothiophene, dibenzothiophene and Illinois No. 6 coal were not desulfurized by **1** under conditions employed herein nor at elevated temperatures.

In conclusion, we have shown that compound **1** is a more powerful desulfurizing agent than its acyclic counterpart P(NMe$_2$)$_3$ and it is also more potent than PPh$_3$ in this respect. This observation is attributable to partial donation of electron density from the axial nitrogen to the phosphorus in a transannular interaction that can enrich the electron density on phosphorus, which in turn allows **1** to act as a stronger nucleophile for sulfur. However, the nucleophilicity of **1** is not sufficiently strong to remove sulfur from benzothiophene or dibenzothiophene. We had thought that the compact cage-like nature of **1** might allow this molecule to penetrate the pores of a coal such as Illinois No. 6. If **1** could remove sulfur from coal by a catalytic mechanism (for which we have some evidence using PBu_3) then **1** might function more effectively in this regard than PBu_3. However, this is unfortunately not the case.

Experimental Details

Speciation and Quantitation of $SPBu_3$ and PBu_2 in Reaction 1

Gas chromatographic analyses were carried out on Hewlett-Packard 6980 GC system with a 25 *m* 200 μ diameter HP fused silica c capillary coated with HP-1 cross-linked methyl silicone (0.33 μ*m*). Elemental analyses of sulfur in coal residues and extracts were conducted by Desert Analytics Laboratory, Tucson, Arizona, USA. Bu_3P was purified by reacting it with CS_2 to form the $Bu_3P{\bullet}CS_2$ adduct and then distilling the CS_2 from this crystalline adduct under reduced pressure to decompose it to pure Bu_3P. Coal samples were purchased from Argonne National Laboratory, Argonne, Illinois, USA. Demineralized Illinois No. 6 was prepared by reacting the coal with $LiAlH_4$ in refluxing THF followed by washing with diluted HCl, H_2O, and MeOH.

Coal/PBu_3 reaction

In a typical reaction, about one g of Illinois No. 6 (or coal-derived pyrite, of FeS) was mixed with *ca.* 5 mL of PBu_3. After heating at 250 ºC for 48 h under an atmosphere of N_2, the mixture was allowed to cool to room temperature. The reaction vessel was then cooled to liquid N_2 temperature and evacuated to 0.3 mm. The closed system was then subjected to vacuum distillation at 130 – 140 ºC until no more liquid distilled. The distillate was then analyzed by gas chromatography using a Hewlett Packard 6890 GC System after dissolving *ca.* 40 mg of distillate in about 10 mL of $ChCl_3$ using a volumetric flask. The GC oven temperature was 200 ºC and the carrier gas was helium.

DBT/PBu_3 reactions

In a typical run about 0.1 g of DBT was dissolved in *ca.* 5 mL of CH_3CN. To this was added 0.1 equivalent of phenol (or para-chloro phenol or HO_2CCF_3) 2 equivalents of cyclohexadiene and 2 equivalents of PBu_3. The reaction mixture was then heated under nitrogen for 24–48 h at 70 ºC. The solvent was removed in vacuo and the residue was dissolved in C_6D_6 or CD_3CN for ^{31}P NMR spectroscopic analysis. The percent sulfur removed was estimated by measuring the ratio of ^{31}P NMR peaks of $SPBu_3$ and PBu_3.

Reactions of coal with Bu_3P/(MeOH)

Coal was treated with methanol in the manner indicated in Table 2 and the reactions were carried out under argon. The work-up of the reactions was the same as above.
Reactions of coal-related material with Bu_3P: Under argon, 1.000 g of coal-related material (as indicated in Table 7) and 7 mL of Bu_3P were added to the reactor (1.0 mmol of biphenol was added as indicated) and the reaction was carried out at 250 ºC for 48 h. The work-up procedure was the same as that above.

Other coals and coal materials

Under argon, coal (1.000 g or 0.500 g) Bu_3P (7 mL) or hydrocarbon solvent (3-5 mL), and other substances as indicated in Tables 3-7 (i.e., Celite, Na or Li, etc.) were added to a 50 mL two-necked Schlenk bottle fitted with a condenser connected at the top to an argon line. The mixture was vigorously stirred at the temperatures and times shown in the tables. After cooling the reaction mixture to room temperature, 5 mL of ethyl ether was added followed by filtration. Where Na or Li was used, the first work-up step included quenching unreacted metal with 5 mL of methanol at 0 ºC under argon. The solid was copiously washed with diethyl ether until no $Bu_3P{=}S$ was detected by GC analysis and then it was further washed with water or other solvent as indicated in Tables 9 and 10. The residue was then dried in vacuo for elemental analysis.

Reaction of coal with M/liq NH_3

Under argon, 30 mL of liquid ammonia was added to a 150 mL two-necked Schlenk bottle charged with 1.000 g of coal, Na or Li (30 mmol) was added in portions (see Table 8). The reaction mixture was vigorously stirred at –78 ºC under a slow argon flow for 3 h and then ammonia was evaporated by slowly warming the reaction mixture to room temperature. The unreacted metal was then quenched with 5 mL of methanol at 0 ºC under argon. The mixture was filtered and washed with diethyl ether and further washed as indicated in the tables. The solid was then dried in vacuo for elemental analysis.

Quantitative Sulfur Removal from Organosulfur Compounds with Active Metals

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 4Å 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 Tables 9 and 10 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.

Reactions of organosulfur compounds with Li and Na

Under argon, the metal (10.0 mmol), organosulfur compound (1.0 mmol) and solvent (3 mL) of tetradecane, Bu_3P, or 15 mL of toluene) were 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 9 and 10. After cooling the reaction mixture to room temperature, the unreacted metal was destroyed with methanol (10 mL) at 0 °C under argon. Then saturated aqueous NH_4Cl (40 mL) was added to the mixture followed by extraction with Et_2O (3 × 60 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated by rotary evaporation for GC analysis or for isolation by column chromatography. For substrate **1** in Table 9 and for dibenzyl organosulfur compounds (Table 10), the organic phases were used directly for product analysis.

To demonstrate that the methanolic NaOMe solutions generated during the room-temperature work up procedure are not responsible for desulfurizing the aromatic sulfur compounds, DBT was treated with Na in MeOH and also with Na plus Bu_3P in MeOH for 1.5 h. This was followed by the work up procedure given above and GC analysis. Only starting material could be detected in both cases and no Bu_3PS was detected in the second experiment.

Reductive Desulfurization of Organosulfur Compounds in Liquid Ammonia

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 4Å molecular sieves. All the products were identifed 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.

General reaction procedure

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 ºC for 3 h under argon. Then ammonia was evaporated by slowly warming the reaction mixture to room temperature. Methanol (10 mL) was added to 0 ºC followed by 40 mL of saturated NH_4Cl. Ether extracts (3 x 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 9 were collected and washed alternately with Et_2O and H_2O and then dried in vacuo. In the cases of BT (Table 9) and dibenzyl sulfide, disulfide, trisulfide and sulfone (Table 10), the organic phases were used directly for the analysis of the products.

$P(MeNCH_2CH_2)_3N$: An Efficient Desulfurizing Reagent

Under argon, 1.0 mmol of substrate was added to a solution of **1** in the solvent and the reaction was carried out under the conditions stated in Tables 13 and 14. The reaction mixtures were subjected to GC, GC/MS or ^{31}P NMR analyses.

Patent/Publication Activities

Verkade, J. G.; Mohan, T.; Angelici, R. J. "Catalytic Hydrodesulfurization of Coal", US Patent 5,437,696, August 1, 1995.

Verkade, J. G.; Mohan, T. "Mild Desulfurization of Sulfur-Bearing Material", US Patent 5,509,945, April 23, 1996.

Erdmann, K.; Mohan, T. and Verkade, J. G. "^{31}P Solid State NMR Study of Coals Treated with Phosphorus Reagents", *Energy and Fuels* **1995**, *9*, 354.

Erdmann, K.; Mohan, T.; Verkade, J. G. "HPLC and ^{31}P NMR Analysis of Phenols in Coal Liquefaction Oils", *Energy and Fuels* **1996**, *10*, 378.

Erdmann, K.; Mohan, T.; Verkade, J. G. "HPLC and ^{31}P NMR Analysis of Phenols in Coal Liquefaction Oils", *Energy and Fuels* **1996**, *10*, 378-385.

Yu, Z.; Mohan, T.; Erdmann, K.; Verkade, J. G. "31-P NMR Analysis of and Sulfur Removal from Coal Materials" Am. Chem. Soc. Div. Fuel Chem. Preprints 1998, *43*, 905-908.

Yu, Z.; Verkade, J. G. "Reductive Desulfurization of Organosulfur Compounds with Sodium in Liquid Ammonia:, *Phosphorus, Sulfur, Silicon* **1998**, *5*, 1.

Yu, Z.; Verkade, J. G. "Desulfurization of Organosulfur Compounds with Lithium and Sodium", *Energy and Fuels* **1999**, *13*, 23-28.

The PI received an unsolicited invitation from the organizers of the Symposium on Microscopic Studies of Coal and Carbon to give a paper at the 216th ACS National meeting held in Boston in August of 1998.

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Table 1 Desulfurization of Illinois No. 6 Coal with Bu_3P.[a]

entry	size (mesh)	temp/time (°C/h)	% mass recovery	% S (residue)	% P (residue)	% S removal
1	20	250/48	88.5	1.85	2.56	61.7
2	80	250/48	84.9	1.30	2.22	73.1[b]
3	100	250/48	76.9	1.15	3.83	76.2
4[c]	20	250/48	85.1	2.36	2.33	51.1
5[d]	80	250/48	90.2	1.15	0.81	64.3
6[e]	100	25-30/48	78.6	3.39	0.58	29.8
7[f]	100	>RT/0.41	106.8	3.28	4.62	32.1

[a] Reaction conditions: the coal samples (1.000 g, 4.83% S), Bu_3P (7 mL), 0.1 MPa. [b] After the reaction was complete, the reaction mixture was centrifuged and a small weighed amount of the supernant was removed and oxidized in air to constant weight to allow all the Bu_3P oxidize to $Bu_3P{=}O$. This oxidized sample was then submitted for sulfur elemental analysis. In this case, the calculated percent S removal based on the 0.74% sulfur content found in the oxidized supernant is 75.4%. [c] The coal sample was stirred in 30 mL of liq. NH_3 at –78 °C for 6 h and followed by evaporating the NH_3 before it was reacted with Bu_3P. [d] Celite (0.500 g) was added as a filter aid. [e] Sonicated at 1.0 AMPS in a water bath. [f] Sonicated by a probe (300 w, 5 x 5 min).

Table 2. Effect of Methanol Pretreatment of Illinois No. 6 Coal on its Desulfurization with Bu_3P.[a]

entry	pretreatment method[b]	Bu_3P (mL)	temp/time (°C/h)	% mass recovery	% S (residue)	% P (residue)	% S removal
1	A	-	65/24	~100	4.94	0	0
2	B	1	65/24	81.7	4.52	0.40	6.4
3	B	2	65/48	86.0	3.60	1.72	25.5
4	C	7	250/48	111.7	1.89	3.74	60.9
5	D	7	250/48	87.6	3.79	2.21	21.5
6	E	7	250/48	100.8	2.05	3.34	57.6
7[c]	C	7	250/48	100.0	1.79	3.70	62.9

[a]The coal samples (1.000 g, 20 mesh) contained 4.83 % S. [b]A: The coal was treated with methanol (8 mL) at reflux. B: The coal was swollen in methanol (8 mL) at room temperature for 24 h and then Bu_3P was added and the reaction mixture was refluxed. C: The coal was swollen in methanol (8 mL) at room temperature for 24 h, the methanol was evaporated on a rotary evaporator and then the Bu_3P was added. D: A mixture of Bu_3P and the coal preswollen in 8 mL of methanol at room temperature for 24 h was stirred at room temperature for 5 min followed by evaporating the methanol under vacuum. E: The mixture of coal, Bu_3P and methanol (8 mL) was stirred at room temperature for 24 h and then the methanol was evaporated. [c]Here a 0.500 g coal sample was used.

Table 3. Alkali Metal Regeneration of Bu_3P from $Bu_3P=S$ during Coal Desulfurization.[a]

entry	substrate	M (mmol)	temp/time (°C/h)	washing solvent	% mass recovery	% S (residue)	% P (residue)	% S removal
1	coal	Na (10)	250/48	$Et_2O/MeOH/H_2O$	65.3	1.22	1.38	74.7
2	coal	Li (10)	250/48	Et_2O/H_2O	69.6	1.93	1.03	60.0
3	$Bu_3P=S$[b]	Na (5)	200/24		-	-	-	100[c]
4	distillate[d]	Na (5)	200/24		-	-	-	100[e]

[a] Reaction conditions: Illinois No.6 coal (1.000 g, 100 mesh, 4.83 % S); solvent , Bu_3P (7 mL). [b] $Bu_3P=S$, 1.0 mmol. [c] GC analysis. [d] The distillate (5.33 g) was obtained by distilling under reduced pressure a reaction mixture of Illinois No. 6 coal (1.000 g, 100 mesh, 4.83 % S) heated with 7 mL of Bu_3P at 250 °C for 48 h. [e] No $Bu_3P=S$ was detected in the reaction mixture by GC analysis after the reaction was complete.

Table 4. Desulfurization of Illinois No. 6 Coal with Na or Li.[a]

entry	M	reaction solvent	temp (°C)	washing solvent[b]	% mass recovery	% S (residue)	% S removal
1	-	tetradecane	254	Et_2O	83.4	4.20	13.0
2	Na	tetradecane	254	Et_2O/H_2O	92.1	3.30	31.7
3	Li	tetradecane	254	Et_2O/H_2O	75.0	4.72	2.3
4	Na	mesitylene	164	Et_2O/H_2O	73.2	3.35	30.6
5	Na	toluene	110	Et_2O/H_2O	78.1	3.57	26.1

[a] Reaction conditions: coal sample (1.000 g, 100 mesh, 4.83 % S); metal (10 mmol); solvent, 3-5 mL; 0.1 MPa; 24 h. [b] After the reaction was quenched with methanol, the reaction residue was washed with the solvents indicated.

Table 5. Desulfurization of Illinois No. 6 Coal with Bu_3P under Various Conditions.[a]

entry	temp/time (°C/h)	% mass recovery	% S (residue)	% P (residue)	%S removal	% S removal[c]	δ ^{31}P[d] (residue)
1	200/48	86.9	2.49	1.63	48.4	62.8	33.3, 54.2[e]
2	250/24	86.0	1.64	1.86	66.0	81.3	31.5
3	300/24	82.0	0.66	3.46	86.3	96.5	31.7
4	250/48	83.5	0.37	3.87	92.3	~100	31.8
5	250/72	81.8	1.60	2.36	66.9	83.1	31.6, 53.0[d]
6[b]	250/48	93.0	0.36	4.02	88.8	93.6	32.5

[a] The coal, sample (0.500 g, 100 mesh contained 4.83 % S. [b] Celite (0.250 g) was added. [c] Results obtained from the sulfur elemental analyses of the oxidized extracts. (See entry 2 in Table 1.) [d] CPMAS NMR. [e] This peak is small and broad.

Table 6. Desulfurization of Other Types of Coals with Bu_3P.[a]

entry	seam (% S)	size (mesh)	% S (residue)	% P (residue)	% mass recovery	% S removal	^{31}P MAS NMR of residue (ppm)
1a	Illinois No. 6 (4.83)	20	2.45	2.18	72.0	49.3	32
1b	Illinois No. 6 (4.83)	100	0.37	3.87	83.6	92.3	32
2a	Upper Freeport (2.32)	20	0.39	1.76	74.8	83.2	32, 48.1[b]
2b	Upper Freeport (2.32)	100	0.43	1.50	80.8	81.5	32, 50.4[b]
3a	Pittsburgh No. 8 (2.19)	20	0.22	1.83	90.2	90.0	32, 56.7[b]
3b	Pittsburgh No. 8 (2.19)	100	0.32	1.70	78.8	85.4	31, 56[b]
4a	Beulap-Zap (0.80)	20	0.36	4.47	62.6	55.0	
4b	Beulap-Zap (0.80)	100	0.22	3.13	64.0	72.5	
5	Pocahontas No. 3 (0.66)	100	0.15	1.10	81.6	77.3	
6a	Wyodak-Anderson (0.63)	20	0.20	3.24	66.0	68.2	
6b	Wyodak-Anderson (0.63)	100	0.20	4.05	68.0	68.2	

Table 6 continued

entry	seam (% S)	size (mesh)	% S (residue)	% P (residue)	% mass recovery	% S removal	^{31}P MAS NMR of residue (ppm)
7a	Blind Canyon (0.62)	20	<0.05	1.92	81.6	>91.9	32, 51[b]
7b	Blind Canyon (0.62)	100	<0.05	1.42	81.2	>91.9	32, 56[b]
8a	Lewiston-Stockton (0.71)	20	0.14	1.03	89.2	80.3	
8b	Lewiston-Stockton (0.71)	100	0.19	1.24	76.4	73.2	
9	Hanna No. 80 (1.10)	100-200	0.69	2.58	68.2	37.3	
10	West Kentucky No. 9 (2.74)	100-200	1.67	2.07	78.4	39.0	

[a] Reaction conditions: coal sample, 0.500 g; Bu_3P, 7 mL; 250 °C; 48 h; 0.1 MPa. [b] The ^{31}P MAS NMR peak is small and broad and the singlet around 31 ppm is the major peak.

Table 7. Desulfurization of Coal-related Materials with Bu_3P.[a]

entry	substrate (%S)	% S (residue)	%C	%H	%N	% P (residue)	% mass recovery	% S removal
			residue					
1	coal-derived pyrite (41.00)	26.13	9.89	1.20	0.15	0.76	66.4	36.3
2	coal-derived pyrite (41.00)[b]	21.94	13.96	1.76	0.10	0.94	71.9	46.5
3	FeS_2 (52.73)	33.65	0.61	0.09		0.16	62.9	36.2
4	FeS_2 (52.73)[b]	31.34	5.75	0.84		1.92	44.9	40.6
5	FeS (36.47)	32.46	3.70	0.33		1.51	89.1	11.0
6	FeS (36.47)[b]	32.01	3.86	0.57		0.94	89.8	12.2
7	demineralized Illinois No. 6[c]	1.03				2.01	95.6	31.3

[a] Substrate, 1.000 g; Bu_3P, 7 mL; 250 °C; 48 h; 0.1 MPa. [b] Biphenol (0.186g, 1.0 mmol) was added. [c] 0.500 g.

Table 8. Desulfurization of Illinois No. 6 Coal with M/liq NH_3.[a]

entry	M	washing solvent	weight of residue (g)	% S (residue)	% N (residue)	% S removal
1	-	Et_2O	0.856	3.73	1.32	22.8
2	Na	Et_2O	1.096	2.72	1.50	43.7
3	Na	Et_2O/H_2O	0.682	2.05	1.40	57.6
4	Li	Et_2O	1.011	2.64	1.01	45.3
5	Li	Et_2O/H_2O	0.685	2.08	2.27	56.9

[a] The coal samples (1.000 g, 20 mesh) contained 4.83 % S and 1.16 % N.

Table 9. Desulfurization of Cyclic Organosulfur Compounds with Na or Li.[a]

substrate	M[b]	solvent	temp (°C)	conversion (%)	product yield (%)[c]
1	Na	toluene	110	96.4	styrene (95.4)
	Na	Bu_3P	150	90.4	styrene (86.7)
	Na	tetradecane	150	100	styrene (99.0)
	Li	tetradecane	254	100	styrene (99.0)
2	Li	dioxane	100	5.0	biphenyl (2.0)
	Na	THF	67	10.0	biphenyl (7.8)
	Na	toluene	110	75.2	biphenyl (75.0)
	Na	toluene[d]	110	38.8	biphenyl (38.4)
	Na	Bu_3P	150	99.3	biphenyl (99.0)
	Na	tetradecane	150	100	biphenyl (99.2)[e]
	Li	tetradecane	254	100	biphenyl (99.0)[e]
3	Na	tetradecane	150	100	biphenyl (99.9)[e]
	Li	tetradecane	254	100	biphenyl (98.0)
4	Li	tetradecane	254	100	2-phenylnaphthalene (99.9)
5	Na	tetradecane	150	77.5	**11** (54.0), **14** (23.3)
	Li	tetradecane	254	100	**11** (85.1), **14** (13.5)
6	Na	tetradecane	150	25.7	phenol (16.7), **15** (7.0), **17** (1.8)
	Li	tetradecane	254	100	**15** (99.5)
7	Na	tetradecane	150	100	biphenyl (99.8)
	Na	Bu_3P	150	99.1	**2** (0.6), biphenyl (98.0)
	Li[f]	tetradecane	254	100	**2** (0.1), biphenyl (99.7)
8	Na	tetradecane	150	100	**13** (70.8), **16** (9.2)
	Li	tetradecane	254	100	**13** (94.0), **16** (5.0)
9	Na	tetradecane	150	100	phthalimide (90.0) PhSH (84.0)
	Li	tetradecane	254	100	phthalimide (2.6) PhSH (42.7)

[a] The reaction time (24 h) was not optimized. [b] The molar ratio of metal to organosulfur compounds is 10:1 unless indicated otherwise. [c] GC analysis. [d] 10 mg of oleic acid was added. [e] Isolated yield (eluate, hexane, $R_f = 0.62$). [f] The molar ratio of Li to **7** is 20:1.

Table 10. Desulfurization of Acyclic Organosulfur Compounds with Na or Li.

substrate	M[a]	solvent	temp (°C)	time (h)	conversion (%)	product[b] yield (%)
PhSPh	Na	toluene	110	24	13.2	PhSH (12.0) Ph-Ph (0.8)
	Na	tetradecane	150	24	48.4	PhSH (43.6) Ph-Ph (4.0)
	Na	tetradecane	254	24	100	Ph-Ph (99.0)
	Li	tetradecane	254	21	100	Ph-Ph (99.0)[c]
PhSSPh	Na	toluene	110	24	100	PhSH (94.5) Ph-Ph (0.3)
	Na	tetradecane	254	17	100	Ph-Ph (99.0)
	Li	tetradecane	254	17	100	PhSH (2.0) Ph-Ph (97.0)
$\mathrm{PhSCH_2SPh}$	Na	tetradecane	150	8	100	PhSH (85.8) $\mathrm{PhCH_2Ph}$ (0.4)
	Na	tetradecane	254	5	100	PhSH (2.0) Ph-Ph (96.0) $\mathrm{PhCH_2Ph}$ (1.2)
	Li	tetradecane	254	5	100	Ph-Ph (96.1) $\mathrm{PhCH_2Ph}$ (0.2)
$\mathrm{(PhS)_3CH}$	Na	tetradecane	150	8	100	PhSH (76.7) Ph-Ph (18.3)
	Na	tetradecane	254	5	100	Ph-Ph (97.8)
	Li	tetradecane	254	5	100	Ph-Ph (94.0)
$\mathrm{PhS(CH_2)_3SPh}$	Na	tetradecane	150	7	100	PhSH (88.5)
	Na	tetradecane	254	7	100	PhSH (66.8), Ph-Ph (32.0)
	Li	tetradecane	254	7	100	PhSH (60.2), Ph-Ph (21.1)
$\mathrm{PhCH_2SCH_2Ph}$	Na	tetradecane	150	3	100	$\mathrm{(PhCH_2)_2}$ (16.2) PhMe (82.0)
	Li	tetradecane	254	3	100	$\mathrm{(PhCH_2)_2}$ (11.4) PhMe (85.1)
$\mathrm{PhCH_2SSCH_2Ph}$	Na	tetradecane	150	3.5	100	$\mathrm{(PhCH_2)_2}$ (36.4) PhMe (61.5)
	Li	tetradecane	254	3.5	80.0	$\mathrm{(PhCH_2)_2}$ (9.5) PhMe (45.5) $\mathrm{(PhCH_2)_2S}$ (20.9)
$\mathrm{PhCH_2SSSCH_2Ph}$	Na	tetradecane	150	4	100	$\mathrm{(PhCH_2)_2}$ (43.3)[d] PhMe (46.0)
	Li	tetradecane	254	4	100	$\mathrm{(PhCH_2)_2}$ (14.5) PhMe (81.5)
$\mathrm{(PhCH_2)_2SO_2}$	Li	tetradecane	254	5	100	$\mathrm{(PhCH_2)_2}$ (7.2) PhMe (88.0)
	Na	tetradecane	254	5	100	PhMe (95.0)
$\mathrm{Bu_3P{=}S}$	Na	toluene	110	24	81.9	$\mathrm{Bu_3P}$ (81.9)[e]

	Na	tetradecane	254	24	100	Bu_3P (100)[e]
	Li	tetradecane	254	24	100	Bu_3P (100)[e]
$Ph_3P=S$	Na	tetradecane	150	24	5.0	Ph_3P (5.0)
	Na	tetradecane	254	24	100	Ph_3P (100)
	Li	tetradecane	254	24	100	Ph_3P (100)

[a]The molar ratio of metal to organosulfur compound is 10:1. [b]GC analysis. [c]Isolated yield (eluate, hexane). [d]Isolated yield (eluate, hexane, $R_f = 0.57$). [e]Partially oxidized to $Bu_3P=O$ by air exposure.

Table 11. 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 12. 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.

Table 13 Desulfurization of trisulfides, disulfides and monosulfides using **1**[a]

entry	sulfide	equiv of **A**[b]	solvent	temp./time (°C/h)	product(s)[c] (yield (%))
1	PrS$_3$Pr	1.0	THF	rt/4	PrS$_2$Pr (95.0), PrSPr (2.2)
2	BuS$_3$Bu	1.0	THF	rt/4	BuS$_2$Bu (95.0), BuSBu (2.0)
3	BnS$_3$Bn	1.0	THF	rt/3	BnS$_2$Bn (74.0), BnSBn (12.4)
4	BnS$_3$Bn	~1.1[d]	C_6H_6	rt/3	BnS$_2$Bn (94.0)[7]
5	BnS$_3$Bn	2.2	THF	rt/1.5	BnS$_2$Bn (94.0), BnSBn (2.8)
				rt/3	BnSBn (>99.0)
6	BnS$_3$Bn	2.2[e]	THF	rt/3	BnS$_2$Bn (7.7), BnSBn (36.7)
				rt/25	BnS$_2$Bn (39.6), BnSBn (42.9)
7	PrS$_2$Pr	1.1	C_6H_6	40/26	PrSPr (100)
8	^{i}PrS$_2$^{i}Pr	1.1	toluene	110/17	^{i}PrS^{i}Pr (30.0)
				110/64	^{i}PrS^{i}Pr (100)
9	^{i}PrS$_2$^{i}Pr	1.2[d]	C_6H_6	80/48	^{i}PrS^{i}Pr (<50)[10]
10	PrS$_2$Pr	1.1[e]	C_6H_6	40/26	PrSPr (11.0)
11	PrS$_2$Pr	2.2[e]	C_6H_6	40/26	PrSPr (38.8)
12	BuS$_2$Bu	1.1	C_6H_6	40/26	BuSBu (100)
13	BuS$_2$Bu	1.1[e]	C_6H_6	40/26	BuSBu (10.4)
14	^{t}BuS$_2$^{t}Bu	1.1	toluene	110/17	^{t}BuS^{t}Bu (10.7)
				110/65	^{t}BuS^{t}Bu (45.0)
15	^{t}BuS$_2$^{t}Bu	>100[d]	-	80/48	^{t}BuS^{t}Bu (1.0)[10]
16	BnS$_2$Me	1.0	THF	rt/19	BnSMe (97.0)
17	BnS$_2$Bn	1.0	THF	rt/1	BnSBn (98.0)
18	BnS$_2$Bn	1.2[d]	C_6H_6	80/4	BnSBn (92.0)[10]
19	PhS$_2$Ph	1.0	THF	rt/48	PhSPh (<5.0)
		1.2	tetradecane	160/18	PhSPh (7.0), **C** (90.0)[f]
20	propylene sulfide	1.0	C_6H_6	rt/19[g]	propylene (>95.0)

[a] Reaction conditions: 0.1 MPa, sulfide (1.0 mmol), solvent (5 mL). [b] **1** was used in all cases except where P(NMe$_2$)$_3$ was employed as indicated. [c] The products were analyzed by GC. [d] P(NEt$_2$)$_3$ used as the base instead of **1**. [e] P(NMe$_2$)$_3$ used as the base instead of **1**. [f] Determined by ^{31}P NMR spectroscopy. [g] The reaction time was not optimized.

Table 14 Desulfurization of other sulfur-containing substrates using **1**[a]

entry	substrate	equiv of **1**	solvent	temp./time (°C/h)	product(s)[b] (yield (%))
1	EtSCN	1.0	THF	40/10	EtCN (95.0)
2	$PhCH_2SCN$	1.0	CH_3CN	35/14	$PhCH_2CN$ (95.0)
3	N-(phenylthio)phthalimide	1.0	pentane	rt/14	**E** (99.0)[c]
4	$Ph_3P=S$	1.1	toluene	110/20	Ph_3P (60.0)[d]
5	$Bu_3P=S$	1.1	toluene	110/20	Bu_3P (<5.0)
6	$(Me_2N)_3P=S$	1.1	toluene	110/20	$(Me_2N)_3P$ (<5.0)[d]

[a] Reaction conditions: 0.1 MPa, substrate (1.0 mmol), solvent (5 mL). [b] The products were analyzed by GC. [c] Product **E** was characterized by ^1H, ^{13}C and ^{31}P NMR and elemental analysis. [d] The yield was obtained by ^{31}P NMR integrations.