#4.

A Novel Approach to Catalytic Desulfurization of Coal

DOE Grant No.: DE-FG22-95PC95208 -4

Semi-Annual Report

Due: August 31, 1997

Prof. John G. Verkade, PI

Gilman Hall

Iowa State University

ACQUISITION & ASSISTANCE
1999 JUN 17 A 10:13
USDOE-FETC

Abstract. Remarkably mild conditions have been discovered for quantitative sulfur removal from dibenzothiophene and other organosulfur systems using relatively cheap elemental sodium.

Project objectives.

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

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

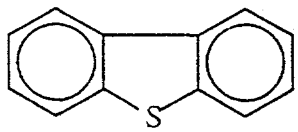
the R groups (including R = H), and also on extraction, impregnation and sonication conditions.

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

$$+ PR_3 \xrightarrow[\text{(no solvent)}]{\text{reflux}} S{=}PR_3 + ? \qquad (3)$$

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.

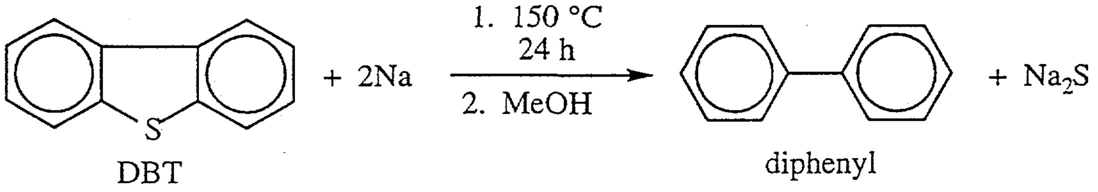
F. Explore the efficacy of PR_3/Fe^{3+} in removing sulfur from petroleum feedstocks, heavy ends (whether solid or liquid), coal tar and discarded tire rubber.

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.

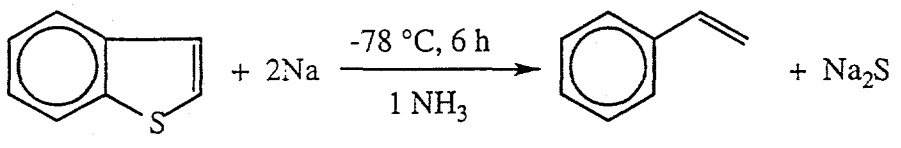
Results

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 4). We have also shown



(4)

that BT loses part of its sulfur in liquid ammonia at –78 °C (reaction 5).

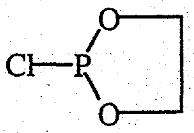


BT

(5)

Amoco sent us some petroleum distillate 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 from them again despite repeated phone calls and emails.

An Aldrich Chemical Co. catalog lists the compound below as a ^{31}P NMR derivatizing

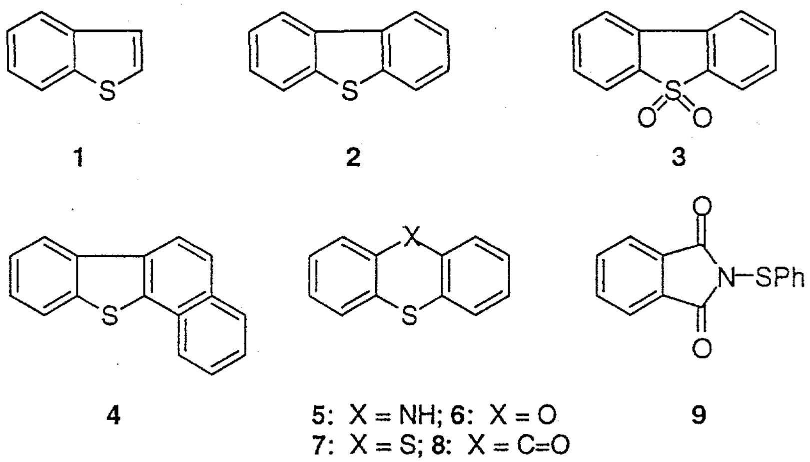


agent for speciating and quantitating mixtures of alcohols. The catalog cites our publication in which we describe its development and use in derivatizing and analyzing phenols in CONSOL coal liquefaction samples.[1]

<u>Removal of Sulfur from Organosulfur compounds with Li and Na.</u> 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,[2,3] 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,[4] and until very recently,[5] 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



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.[6] 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,[7] but it has been found difficult to reproduce.[8] 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,[8] 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.[9] In the presence of H_2, > 99% sulfur removal from DBT with Na was achieved giving biphenyl as the major product.[10] 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.[11] 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.[12] Mixtures of NaH or LiH with a nickel compound efficiently desulfurized a variety of organosulfur compounds including DBT.[13] Recently, several other reducing systems involving nickel compounds were reported for desulfurization, namely, nickelocene/$LiAlH_4$,[14] nickel boride generated *in situ* from the reaction of $NiCl_2{\bullet}6H_2O/NaBH_4/MeOH$,[15,16] nickel and cobalt boride,[17] a Raney nickel/sodium hypophosphite system,[18] and $[(i\text{-}Pr_2PCH_2CH_2)_2NiH]_2$[19] 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.[20] Microbial desulfurization of DBT sulfone resulted in complete sulfur removal[21] while plasma desulfurization of DBT produced products such as toluene and benzene in moderate yields.[22]

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.[23] Naphthalene fractions have also been desulfurized by Na: 93% desulfurization at 140-220 °C,[24] ~100% at 150-250 °C under 10-30 bar H_2 pressure,[25] and 91% at 310-340 °C at 500-1000 PSI of H_2.[26] A phenanthrene fraction was quantitatively desulfurized with Na at 125 to 200 °C[27] and a hydrocarbon oil fraction was >90% desulfurized by a mixture of excess Na and NaOR.[28]

Residua treated with Na lost 75-95% of their sulfur at 350-400 °C at H_2 pressures of ca. 200 PSI[29] and virtually all of their sulfur at 350 °C under 10000 PSI.[30] Rates of sulfur removal by Na from organic sulfides and thiophenes at 200 °C in organic solvents in sealed tubes have been recorded.[31] 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.[32] However, thiophene under these conditions lost only part of its sulfur.[32] The desulfurization of a concentrated gasoline by reaction with Na metal on Al_2O_3 was investigated at 1 atm and 200-300 °C.[33] 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.[34] 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.[35]

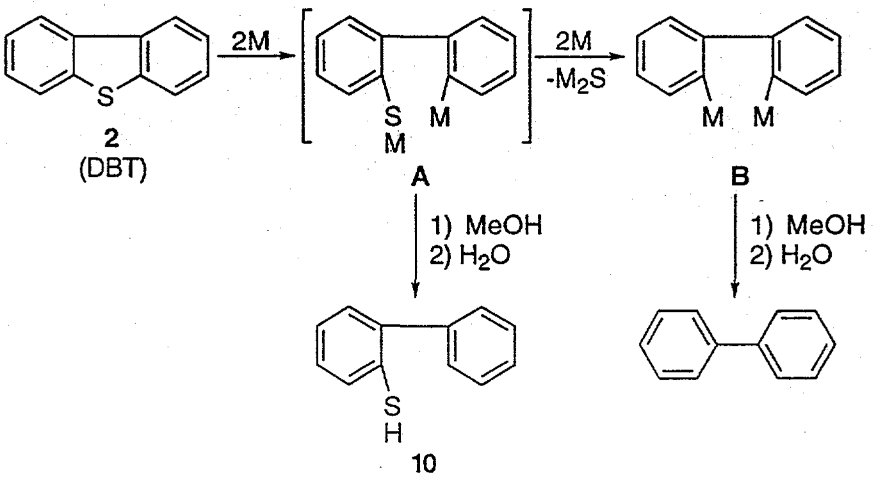
Whereas Li in $EtNH_2$ effectively reduces sulfide links in asphaltenes,[36] kerogens[36] and episulfides,[37] only 35-85% sulfur removal was accomplished with Li for high-boiling petroleum fractions and this metal was ineffective at room temperature in separate experiments on several thiophenes and on PhSPh.[38]

Trivalent organophosphorus compounds (e.g., triphenylphosphine,[39] tributylphosphine,[40] trialkylphosphites,[39c,41] and tris(dialkylamino)phosphines[39f,42]) 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.[43]

We have found[44] 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 1). However, by raising the reaction temperature well above the melting point of the metals (Table 1), 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.[45] 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.[8] 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

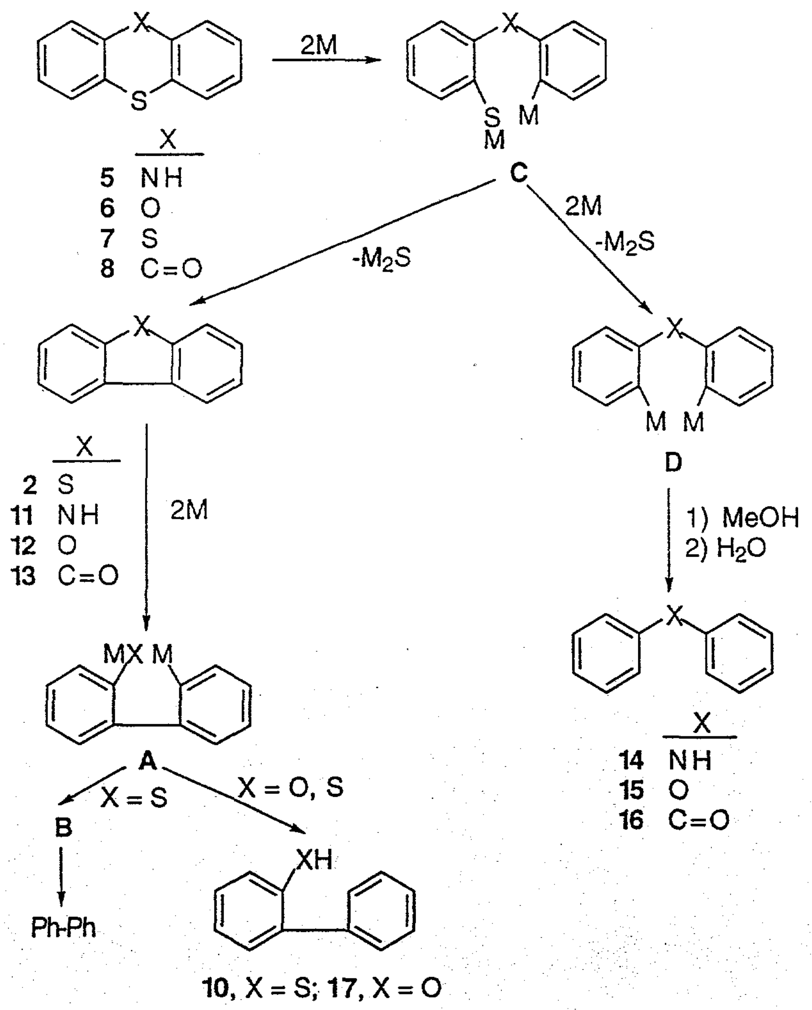
Scheme 1



possible in view of evidence for such a process put forth for a reaction in which 50% desulfurization of PhSPh was accompolished in benzene by K.[11] In the reaction of DBT with K in THF, **10** and biphenyl were obtained as the products.[45] A radical anion mechanism was proposed for the desulfurization of DBT with Na in decahydronaphthalene.[10] 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 1).

Molten Li and Na in inert hydrocarbons also showed very high desulfurization properties toward other polycyclic aromatic sulfur compounds (Table 1). 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 2. 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 in Scheme 1) 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

Scheme 2



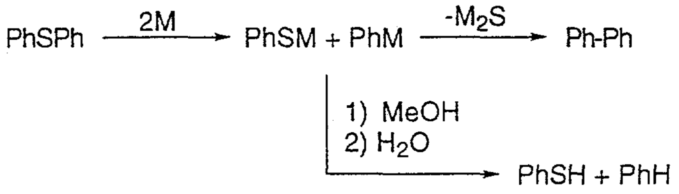
the major products (Table 1). Phenoxathiin (**6**) was selectively desulfurized to the ring-opened diphenyl ether (**15**) by lithium, but its reaction with sodium resulted in the production of phenol, **15** and **17** at the lower temperature of 150 °C. Here phenol could arise from cleavage of C-O 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.[8] An intermediate in the reaction of thianthrene (7) with Li in refluxing tetradecane and Na in Bu_3P at 150° (Table 1) 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 2). 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 3 and a similar pathway shown in Scheme 4 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.[45] 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.[43]

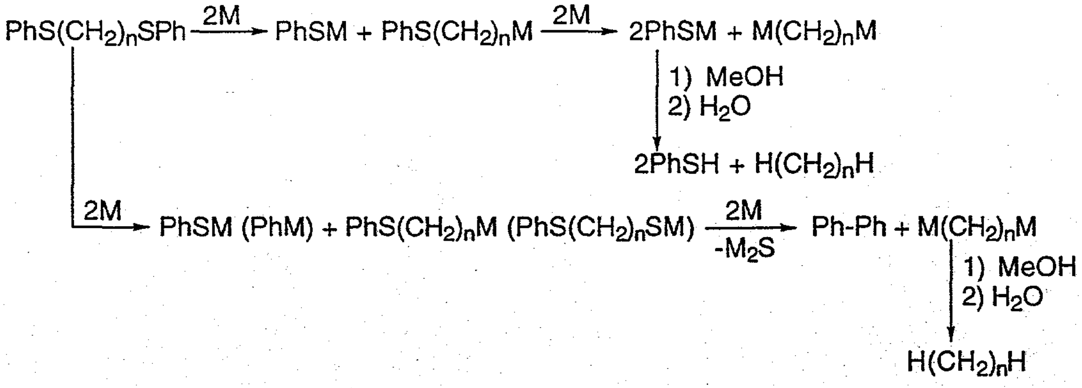
It is reasonable to suppose that the phenyl anion of PhM formed by cleavage of the aromatic carbon-sulfur bond of Ph_2S nucleophilically attacks PhSM to eliminate M_2S and form biphenyl (Scheme 3). If such a nucleophilic reaction is quenched before completion, thiophenol and benzene would be obtained as observed. A similar explanation applies to the mechanism shown in Scheme 4. 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 4 for PhSPh and $PhS(CH_2)_nSPh$, respectively.

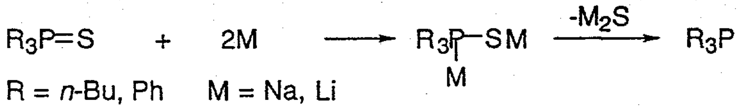
Scheme 3



Scheme 4



Scheme 5



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 formed 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 2). 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,[2b] 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.[39,40,42] Interestingly, Li and Na at 254 °C quantitatively desulfurize tributylphosphine sulfide and triphenylphosphine sulfide. A plausible pathway is shown in Scheme 5. This procedure is substantially more convenient than that involving trifluoroacetic anhydride,[46] $LiAlH_4$,[47] or hexachlorosilane[48] 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 1) 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 2). 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.

Removal of Sulfur from Organosulfur Compounds with Na in Liquid NH_3. Reactions of DBT and BT with Na in liquid ammonia are proving to be quite surprising in preliminary experiments. The sequence of steps in the experiment is shown in Scheme 6. In the case of DBT, a black

Scheme 6

$$\text{R(S)} + \text{Na} \xrightarrow[\text{-38 °C, 6 h}]{\text{liquid } NH_3} \xrightarrow[\text{liquid } NH_3]{\text{evaporate the}} \xrightarrow[\text{0 °C} \rightarrow \text{room temp.}]{\text{MeOH}}$$

$$\xrightarrow{\text{sat'd } NH_4Cl} \xrightarrow[\text{extraction}]{\text{ether}} \xrightarrow[MgSO_4]{\text{dry with}} \xrightarrow[\text{the solution}]{\text{concentrate}} \text{do gc}$$

polymeric residue is obtained from which 77% of the sulfur has been removed and 99.2% of the DBT has been destroyed.

Conclusions

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, $Bu_3P{=}S$ and $Ph_3P{=}S$, while one of the metals did so in the case of $PhSCH_2SPh$, $PhS(CH_2)_3SPh$ and $PhCH_2SCH_2Ph$. Although starting material conversions were 100% for $(PhS)_3CH$, $PhCH_2SSCH_2Ph$, $PhCH_2SSSCH_2Ph$ and $(PhCH_2)_2SO_2$ 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.

These reactions may offer the possibility of desulfurizing coal since liquid NH_3 dissolves the sodium and the resultant solution might easily penetrate the coal matrices since liquid ammonia has been shown by other investigators to readily do so. Although our liquid ammonia reactions take place at –37 °C, it would perhaps be more practical to carry out reactions with coal at room temperature in sealed vessels where the liquid ammonia would exert its vapor pressure of 9.75 atmospheres. At this relatively elevated temperature, the reaction may be expected to proceed more quickly, and less than 3 h might well suffice. The coal could be washed with liquid NH_3 to remove excess sodium, and both the excess sodium and the liquid ammonia could thus be recovered for recycling. The coal could be water washed to remove traces of NH_3 and Na_2S.

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 Tables 1 and 2 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.

<u>Reactions of Organosulfur Compounds with Li and Na.</u> 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 1 and 2. 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 1 and for dibenzyl organosulfur compounds (Table 2), 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.

Reactions of DBT or BT with Na/liquid NH_2. Under Ar, Na (30.0 mmol) was added in portions to the stirred mixture of DBT or BT (0.5-1.0 mmol) and liquid ammonia (60 mL) at –38 °C. In some cases Bu_3P (2.0 mmol) was present. The reaction was carried out for 6 hours. The excess NH_3 was slowly evaporated by allowing the reaction mixture to warm to room temperature. The unreacted Na was quenched with MeOH (10 mL) at 0 °C, the reaction mixture was allowed to warm to room temperature, and then saturated aqueous NH_4Cl (40 mL) was added. The mixture was extracted with Et_2O (3 × 60 mL) and the organic phase was separated and then dried with $MgSO_4$. After filtering and concentrating the solution it was subjected to gc analysis. The black residue collected during the extraction in the case of the DBT reaction was washed with water (4 × 5 mL) MeOH (3 × 5 mL) and dried in vacuo. The dry residue was used for the elemental sulfur analysis.

References

(1) Erdmann, K.; Mohan, T.; Verkade, J. G. *Energy and Fuels*, 1996, *10*, 378-385.

(2) (a) Weisser, O.; Landa, S. *Sulphide Catalysts, Their Properties and Applications*; Pergamon: Oxford, 1973. (b) Grange, P. *Catal. Rev.-Sci. Eng.* **1980**, *21*, 135. (c) Massoth, F. E. *Adv. Catal.* **1978**, *27*, 265. (d) Gates, B. C.; Katzer, J. R.; Schuit, G. C. A. *Chemistry of Catalytic Processes*, McGraw-Hill: New York, 1979.

(3) Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387 and references therein.

(4) (a) Agudo, A. L.; Benitez, A.; Fierro, J. L. G.; Palacios, J. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 835. (b) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Frediani, P.; Herrera, V.; Sánchez-Delgado, R. A. *J. Am. Chem. Soc.* **1993**, *115*, 2731, 7505. (c) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993**, *115*, 4943. (d) Garcia, J. J.; Maitlis, P. M. *J. Am. Chem. Soc.* **1993**, *115*, 12200. (e) Qian, W.; Ishihara, A.; Ogawa, S.; Kabe, T. *J. Phys. Chem.* **1994**, *98*, 907. (f) Garcia, J. J.; Mann, B. E.; Adams, H.; Bailey, N. A.; Maitlis, P. M. *J. Am. Chem. Soc.* **1995**, *117*, 2179. (g) Dailey, K. M. K.; Rauchfuss, T. B.; Rheingold, A. L.; Yap, G. P. A. *J. Am. Chem. Soc.* **1995**, *117*, 6396. (h) Bianchini, C.; Meli, A.; Patinec, V.; Sernau, V.; Vizza, F. *J. Am. Chem. Soc.* **1997**, *119*, 4945.

(5) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855 and references therein.

(6) (a) Utz, B. R.; Soboczenski, S. K.; Friedman, S. K. *Prep. pap.-Am. Chem. Soc., Div. Fuel Chem.* **1985**, *30*, 35. (b) Stock, L. M. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1994**, *39*, 74. (c) Collins, F. M.; Lucy, A. R.; Sharp, C. *J. Molec. Catal. A: Chem.* **1997**, *117*, 397.

(7) Blicke, F. F.; Sheets, D. G. *J. Am. Chem. Soc.* **1948**, *70*, 3768; **1949**, *71*, 4010.

(8) Gilman, H.; Esmany, D. L. *J. Am. Chem. Soc.* **1953**, *75*, 2947.

(9) Balazy, M.; Murphy, R. C. *Anal. Chem.* **1986**, *58*, 1098.

(10) Sternberg, H. W.; Delle Donne, C. L.; Markby, R. E.; Friedman, S. *Ind. Eng. Chem., Process Des. Dev.* **1974**, *13*, 433.

(11) Gerdil, R.; Lucken. E. A. C. *J. Chem. Soc.* **1963**, 5444.

(12) Eisch, J. J. *J. Org. Chem.* **1963**, *28*, 707.

(13) (a) Becker, S.; Fort, Y.; Vanderesse, R.; Caubere, P. *J. Org. Chem.* **1989**, *54*, 4848. (b) Fort, Y. *Tetrahedron Lett.* **1995**, *36*, 6051.

(14) Chan, M. C.; Cheng, K. M.; Ho, K. M.; Ng, C. T.; Yam, T. M.; Wang, B. S. L.; Luh, T. Y. *J. Org. Chem.* **1988**, *53*, 4466.

(15) Back, T. G.; Yang, K.; Krouse, H. R. *J. Org. Chem.* **1992**, *57*, 1986.

(16) Schut, J.; Engberts, J. B. F. N.; Wynberg, H. *Synth. Commun.* **1972**, *2*, 415.

(17) Back, T. G.; Baron, D. L.; Yang, K. *J. Org. Chem.* **1993**, *58*, 2407.

(18) Node, M.; Nishide, K.; Shigeta, Y.; Obata, K.; Shiraki, H.; Kunishige, H. *Tetrahedron* **1997**, *53*, 12883.

(19) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 10855.

(20) Katritzky, A. R.; Murugan, R.; Siskin, M. *Energy & Fuels* **1990**, *4*, 577.

(21) (a) Olson, E. S.; Stanley, D. C.; Gallagher, J. R. *Energy & Fuels* **1993**, *7*, 159. (b) Kim, B. H.; Kim, H. Y.; Kim, T. S.; Park, D. H. *Fuel Process. Technol.* **1995**, *43*, 87. (c) Kim, H. Y.; Kim, T. S.; Kim, B. H. *Biotechnol. Lett.* **1990**, *12*, 761.

(22) Suhr, H.; Henne, P.; Iacocca, D.; Ropero, M. J. *Liebig Ann. Chem.* **1980**, *3*, 441.

(23) Reggel, L.; Blaustein, B. D.; Delle Donne, C. L.; Friedman, S.; Steffgen, F. W.; Winslow, J. C. *Fuel* **1976**, *55*, 170.

(24) Kageyama, K.; Sato, T.; Takeda, K. Japanese Pat. 62220586; *Chem. Abstr. 109*, 110044.

(25) Handrick, K.; Koelling, G.; Mensch, F. Ger. Pat. DE 3429966 A1; *Chem. Abstr. 105*, 27040.

(26) Howard, K. A.; Winter, W. E.; Moritz, K. H.; Paynter, J. D. US Pat. US 4062762; *Chem. Abstr. 88*, 123629.

(27) Mensch, F. *Erdkohle, Erdgas, Petrochem.* **1976**, *29*, 167.

(28) Haskett, F. B. Swiss Pat. 740904; *Chem. Abstr. 89*, 27328.

(29) Kohn, E. M. US Pat. US 3755149; *Chem. Abstr. 80*, 50235.

(30) (a) Ohga, K.; Kurauchi, Y.; Nogami, J.; Morita, S. *Aromatikkusu* **1984**, *36*, 9; *Chem. Abstr. 101*, 37971. (b) Ohga, K.; Kurauchi, Y.; Tsuji, O.; Tanezaki, K.; Nogami, J.; Morita, S. *Nippon Kagaku Kaishi* **1983**, *7*, 1064; *Chem. Abstr. 99*, 90650. (c) Kurauchi, Y.; Wada, S.; Ohga, K.; Morita, S. *Aromatikkusu* **1980**, *31*, 6; *Chem. Abstr. 92*, 197688.

(31) Weinberger, S. M.; Navarro, L. J.; Bonilla, C. F. *Rev. Soc. Quim. Mex.* **1970**, *14*, 13; *Chem. Abstr. 73*, 27189.

(32) Gerlock, J. L.; Mahoney, L. R.; Harvey, T. M. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 23.

(33) Brons, G. B.; Meyers, R. D.; Bearden, R. US Patent 950502; *Chem. Abstr. 126*, 188347.

(34) (a) Brons, G.; Meyers, R. D.; Bearden, R.; MacLeod, J. B. US Pat. 9746638; *Chem. Abstr. 128*, 90873. (b) Bearden, R. Jr.; Baird, W. C.; Hammer, G. P. US Patent 750428, *Chem. Abstr. 86*, 142747.

(35) Hoffman, I. C.; Hutchison, J.; Robson, J. N.; Chicarelli, M. I.; Maxwell, J. R. *Org. Geochem.* **1992**, *19*, 371.

(36) Rajanikanth, B.; Ravindranath, B. *Indian J. Chem.* **1984**, *23B*, 879.

(37) Melikadze, L. D.; Gverdtsiteli, D. D. *Izv. Akad. Nauk Gruz. SSSR, Ser. Khim.* **1975**, *1*, 39; *Chem. Abstr. 84*, 7323a.

(38) (a) Sato, T.; Hino, T. *Tetrahedron* **1976**, *32*, 507. (b) Middleton, D. L.; Samsel, E. G.; Wiegand, G. H. *Phosphorus and Sulfur* **1979**, *7*, 339. (c) Dittmer, D. C.; Motin, S. M. *J. Org. Chem.* **1967**, *32*, 2009. (d) Rastetter, W. H.; Spero, D. M.; Adams, J. *J. Org. Chem.* **1982**, *47*, 2785. (e) Harpp, D. N.; Smith, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 6045.

(39) (a) Field, L. D.; Wilkinson, M. P. *Tetrahedron Lett.* **1997**, *38*, 2779. (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. (d) Touchard, D.; Fillaut, J. L.; Dixneuf, P. H.; Toupet, L. *J. Organomet. Chem.* **1986**, *317*, 291.

(40) Holand, S.; Ricard, L.; Mathey, F. *J. Org. Chem.* **1991**, *56*, 4031.

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

(42) Theobald, P. G.; Okamura, W. H. *J. Org. Chem.* **1990**, *55*, 741.

(43) Chatterjee, K.; Wolny, R.; Stock, L. M. *Energy & Fuels* **1990**, *4*, 402.

(44) Yu, Z.; Verkade, J. G. *Energy and Fuels* **1999**, *13*, 23-28.

(45) Yu, Z. K.; Verkade, J. G. *Tetrahedron Lett.* **1998**, *39*, 2671.

(46) Bruzik, K. S.; Stec, W. J. *J. Org. Chem.* **1990**, *55*, 6131.

(47) Luckenbach, R. *Tetrahedron Lett.* **1971**, *24*, 2177.

(48) Zon, G.; DeBruin, K. E.; Naumann, K.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7023.

Table 1. 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 2. 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)
$PhSCH_2SPh$	Na	tetradecane	150	8	100	PhSH (85.8) $PhCH_2Ph$ (0.4)
	Na	tetradecane	254	5	100	PhSH (2.0) Ph-Ph (96.0)

$PhCH_2SSSCH_2Ph$	Na	tetradecane	150	4	100	$(PhCH_2)_2$ (43.3)[d]
						PhMe (46.0)
	Li	tetradecane	254	4	100	$(PhCH_2)_2$ (14.5)
						PhMe (81.5)
$(PhCH_2)_2SO_2$	Li	tetradecane	254	5	100	$(PhCH_2)_2$ (7.2)
						PhMe (88.0)
	Na	tetradecane	254	5	100	PhMe (95.0)
$Bu_3P=S$	Na	toluene	110	24	81.9	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.

						$PhCH_2Ph$ (1.2)
	Li	tetradecane	254	5	100	Ph-Ph (96.1)
						$PhCH_2Ph$ (0.2)
$(PhS)_3CH$	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)
$PhS(CH_2)_3SPh$	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)
$PhCH_2SCH_2Ph$	Na	tetradecane	150	3	100	$(PhCH_2)_2$ (16.2)
						PhMe (82.0)
	Li	tetradecane	254	3	100	$(PhCH_2)_2$ (11.4)
						PhMe (85.1)
$PhCH_2SSCH_2Ph$	Na	tetradecane	150	3.5	100	$(PhCH_2)_2$ (36.4)
						PhMe (61.5)
	Li	tetradecane	254	3.5	80.0	$(PhCH_2)_2$ (9.5)
						PhMe (45.5)
						$(PhCH_2)_2S$ (20.9)