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A Novel Approach to Catalytic Desulfurization of Coal

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Abstract. The nonionic superbase $P(MeNCH_2CH_2)_3N$ (**A**) efficiently desulfurizes trisulfides to disulfides and monosulfides, disulfides to monosulfides, and propylene sulfide to propene. $S{=}P(MeNCH_2CH_2)_3N$ (**B**) was formed as the sulfur acceptor. $P(NMe_2)_3$ was a much poorer desulfurizing agent than **A** under the same reaction conditions. Thiocyanates and triphenylphosphine sulfide were also desulfurized with **A**, but N-(phenylthio)phthalimide formed $[A{-}SP]^+$ phthalimide in quantitative yield.

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.

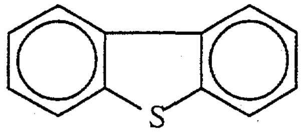
B. Optimize the conditions for the HDS reaction

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

(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.

DISCLAIMER

C. Determine the product(s) and the pathway of the novel redox reaction that appears to *quantitatively* remove sulfur from dibenzothiophene (DBT) when R = Bu when $FeCl_3$ is used as a catalyst.



DBT

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

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

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

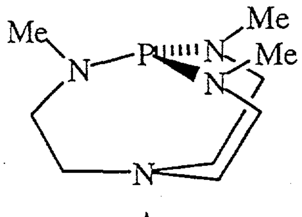
F. Explore the efficacy of PR_3/Fe^{3+} in removing sulfur from petroleum feedstocks, heavy ends (whether solid or liquid), coal tar and discarded tire rubber.

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

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

Results

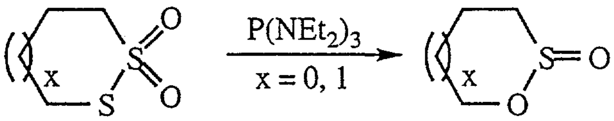
In this document we report that the highly basic phosphine A, which was developed



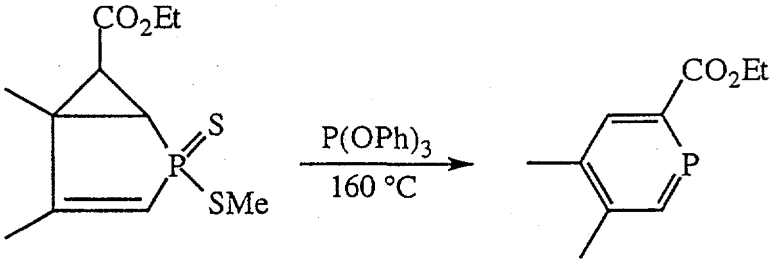
A

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.

The Use of A as a Desulfurizing Agent. 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,[1-5] trisdimethylaminophosphine,[4,6-8] trisdiethylaminophosphine,[4,7-10] triethylphosphite,[1] trimopholinophosphine[4,7] and tributylphosphine[11,12] 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,[13] thiols[14] and organometallic dithiocarboxylates;[15] trisdiethylaminophosphine effects reaction 1; triphenylphosphite effects reaction 2;[16] and very recently thiol groups have been reductively eliminated photochemically from L-cysteine derivatives in the presence of triethylphosphite and triethylboron.[17]

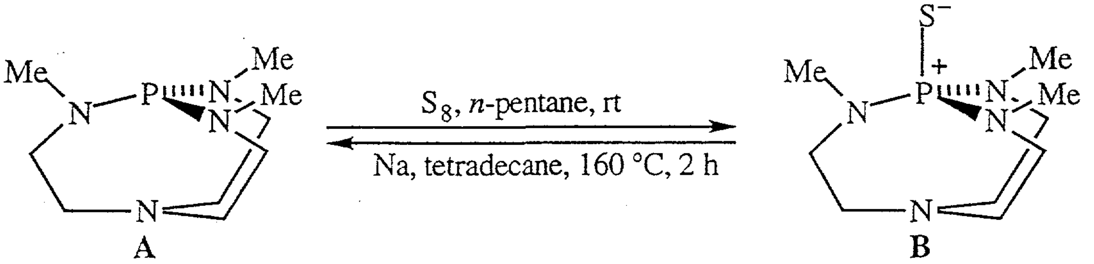


(1)



(2)

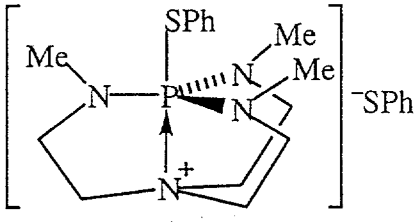
In the course of our ongoing investigations on new synthetic applications of the exceedingly strong nonionic base and catalyst **A** first reported from our laboratories[18-20] and now sold commercially by Strem Chemicals, we found that **B** could be formed from **A** in the presence of sulfur.[21] Recently, we found that **B** could be desulfurized with excess sodium in refluxing toluene or in tetradecane at 160 °C. These results suggested a potential application of **A** in desulfurizing organosulfur compounds in a cyclic process since **A** can be recycled as shown in eqn. 3. Here we report desulfurizations with **A** under mild conditions.



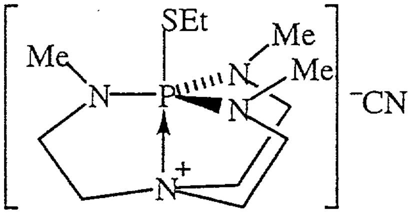
(3)

Using 1.0 equiv of **A**, trisulfides were desulfurized primarily to disulfides with monosulfides as minor products at room temperature and the formation of **B** as the only other product (entries 1-3, Table 1). With more than 2.0 equiv of **A**, benzyl trisulfide was desulfurized to benzyl monosulfide via benzyl disulfide (entry 4, Table 1). 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 1). Increasing the steric hindrance of the disulfide obviously decreased the desulfurization rate (entries 7 and 12, Table 1). Although $(Me_2N)_3P$ was effective for desulfurizing trisulfides to disulfides and some activated monosulfides to sulfur-free compounds,[4,6] it showed much poorer desulfurizing efficiency than **A** under the same reaction conditions (entries 5, 8, 9 and 11, Table 1). 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 **A** within 3 h (entries 4 and 5, Table 1). For disulfides,

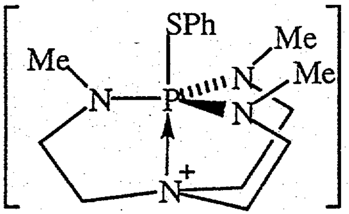
$(Me_2N)_3P$ led to poor desulfurization efficiencies (entries 8, 9 and 11, Table 1). Phenyl disulfide could not be efficiently desulfurized at room temperature by **A** and raising the temperature led to the formation of **C** (entry 15, Table 1). The ^{31}P NMR spectrum of the reaction mixture of phenyl disulfide with **A** 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 **B**). 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 **A** lost sulfur to give propene in high yield at room temperature (entry 16, Table 1).



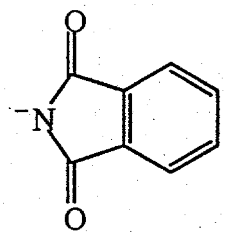
C



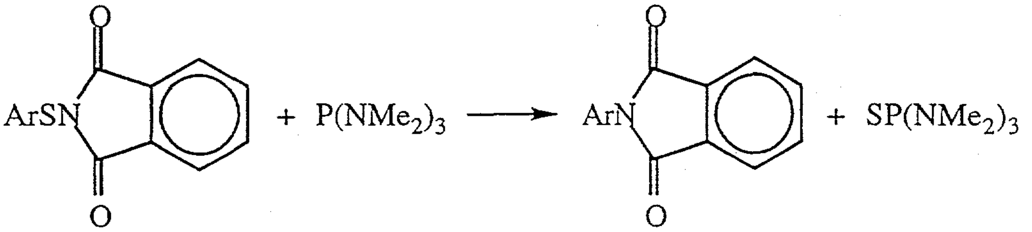
D



E



Thiocyanates were desulfurized to their corresponding cyanides (entries 1, 2, Table 2). In the reaction of ethyl thiocyanate with **A** at room temperature, **D** (δ^{31}P = 50.7 ppm) and **B** were formed in roughly equivalent amounts according to ^{31}P NMR integration, but raising the temperature decomposed **D** to ethyl cyanide and **B** presumably via nucleophilic attack of cyanide anion at the Et-S bond. **A** and N-(phenylthio)phthalimide reacted cleanly at room temperature forming **E** quantitatively.[22] Analogues of **E** wherein the cation is $ArSP(NMe_2)_3^+$ (Ar = Ph or *p*-MeC_6H_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:[23]



(4)

Even triphenylphosphine sulfide was desulfurized in moderate yield by **A** (60%, entry 4, Table 2) indicating that **A** is the stronger desulfurizing reagent. However, benzothiophene, dibenzothiophene and Illinois No. 6 coal were not desulfurized by **A** under conditions employed herein nor at elevated temperatures.

Conclusions

Compound **A** 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 **A** to act as a stronger nucleophile for sulfur. However, the nucleophilicity of **A** is not sufficiently strong to remove sulfur from benzothiophene or dibenzothiophene. We had thought that the compact cage-like nature of **A** might allow this molecule to penetrate the pores of a coal such as Illinois No. 6. If **A** could remove sulfur from coal by a catalytic mechanism (for which we have some evidence using PBu_3) then **A** might function more effectively in this regard than PBu_3. However, this is unfortunately not what we observed and in the next report we will describe the results of our return to the main objectives of this project.

It should be noted that the PI received an unsolicited invitation from the organizers of the Symposium on Microscopic Studies of Coal and Carbon to give a paper[24] at the 216th ACS National meeting held in Boston in August of 1998.

Experimental Section. Under argon, 1.0 mmol of substrate was added to a solution of A in the solvent and the reaction was carried out under the conditions stated in Tables 1 and 2. The reaction mixtures were subjected to GC, GC/MS or ^{31}P NMR analyses.

References

1. Dittmer, D. C.; Kotin, S. M. *J. Org. Chem.* 1967, *32*, 2009.
2. Sato, T.; Hino, T. *Tetrahedron* 1976, *32*, 507.
3. Middleton, D. L.; Samsel, E. G.; Wiegand, G. H. *Phosphorus and Sulfur* 1979, *7*, 339.
4. Harpp, D. N.; Smith, R. A. J. Am. Chem. Soc. 1982, *104*, 6045.
5. Rastetter, W. H.; Spero, D. M.; Adams, J. *J. Org. Chem.* **1982**, *47*, 2785.
6. Harpp, D. N.; Orwig, B. A. *Tetrahedron Lett.* **1970**, *31*, 2691.
7. Harpp, D. N.; Ash, D. K.; Smith, R. A. *J. Org. Chem.* **1980**, *45*, 5155.
8. Harpp, D. N.; Vines, S. M. *J. Org. Chem.* **1974**, *39*, 647.
9. Harpp, D. N.; Gleason, J. G. *J. Org. Chem.* **1968**, *33*, 4181.
10. ibid. *Tetrahedron Lett.* **1969**, *19*, 1447.
11. Field, L. D.; Wilkinson, M. P. *Tetrahedron Lett.* **1997**, *38*, 2779.
12. Brandt, P. F.; Rauchfuss, T. B. *J. Am. Chem. Soc.* **1992**, *114*, 1926.
13. Cadogan, J. I. G. in "Organophosphorus Reagents in Organic Synthesis", Academic Press: New York, 1979.
14. Salim, A.; Tillet, J. G. *Phosphorus, Sulfur, Silicon Relat. Elem* **1991**, *60*, 215.
15. Touchard, D.; Fillaut, J. L.; Dixneuf, P. H.; Toupet, L. *J. Organomet. Chem.* **1986**, *317*, 291.

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

17. Gonzalex, A.; Valencia, G. *Tetrahedron: Asymmetry* **1998**, *9*, 2761.

18. Schmidt, H.; Lensink, C.; Xi, S. K.; Verkade, J. G. *Z. Anorg. Allg. Chem.* **1989**, *75*, 578.

19. Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233.

20. D'Sa, B. A.; Kisanga, P.; Verkade, J. G. *J. Org. Chem.* **1998**, *63*, 3961.

21. Tang, J. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1993**, *115*, 1660.

22. Compound **E**, a yellow crystalline solid, was obtained by evaporating the solvent from the reaction mixture. ^{1}H NMR ($CDCl_3$): δ 7.83, 7.67, 7.62, 7.43, 7.34 and 7.23 (1:1:2:3:1:1 H, m each, 9C*H* aromatic protons), 2.98 and 2.94 (6H, t each, $3CH_2$), 2.76 (6H, t, $3CH_2$), 2.73 (9H, d, $3CH_3$). ^{13}C NMR (CD_3CN): δ 174.9 (C=O), 135.8, 135.7, 131.4, 131.2, 131.1, 130.8, 130.7, 130.7, 129.6, 127.3, 51.78, 50.54(d), 37.65(d). ^{31}P NMR: δ 44.3 ppm. Anal. Calcd. for $C_{14}H_9NO_2SP$ (255.3): C, 65.87; H, 3.55; N, 5.49. Found: C, 65.42; H, 3.40; N, 5.30.

23. Harpp, D. N.; Orwig, B. A. *Tetrahedron Lett.* **1970**, *31*, 2691.

24. 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 (invited symposium lecture).

Table 1. Desulfurization of alkyl sulfides with sodium.

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

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

Table 2. Desulfurization of alkylthio compounds with sodium.

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

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