A Novel Approach to Catalytic Desulfurization of Coal

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Prof. John G. Verkade, PI

Gilman Hall

Iowa State University

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Abstract. A gas chromatographic method has been developed for the quantitation of sulfur removed from coal as tributyl phosphine sulfide ($SPBu_3$). This method also works very well for speciating and quantitating the products of sulfur removal from organosulfur removal from organosulfur compounds such as dibenzothiophene. 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 the

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

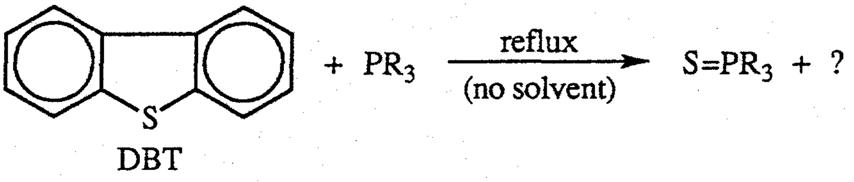
R groups (including R = H), and also on extraction, impregnation and sonication conditions.

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



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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.

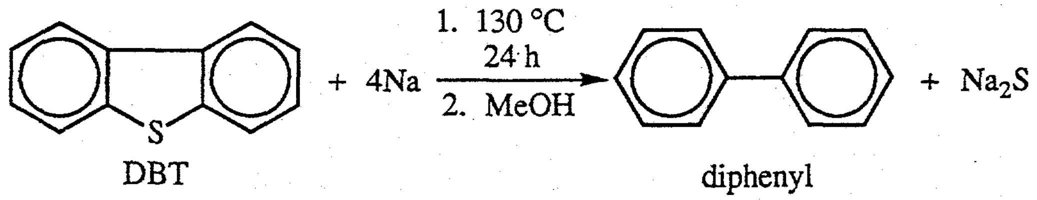
G. Explore the possibility of using water-soluble PR_3 compounds and Fe^{3+} to remove sulfur from petroleum feedstocks and heavy ends in order to remove the SPR_3 (and Fe^{3+} catalyst) by water extraction (for subsequent HDS of the SPR_3).

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.

Summary of Progress. We have developed a reliable analytical method for the analysis of the sulfur removed from coal using tributyl phosphine, PBu_3 (see reaction 1 in Objective A and, more specifically reaction 4 below). The method involves gas chromatographic (gc) analysis of the

$$\underset{4.96\%\ \mathrm{S}}{\text{Ill No 6}} + \mathrm{PBu_3} \xrightarrow[48\ \mathrm{h}]{\text{reflux}} \text{residue} + \underset{(\mathrm{SPBu_3})}{\text{extract}} \qquad (4)$$

$SPBu_3$ in the extract. Using this approach combined with elemental analysis for sulfur of both the residue and the extract, up to ca 90% of the sulfur can be removed from the coal. 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 5). We have also made the rather exciting



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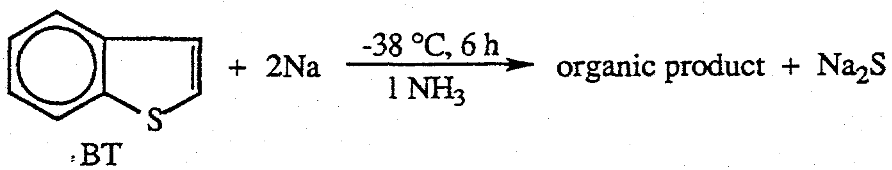
discovery that benzothiophene (BT) loses 100% of its sulfur to elemental sodium in only **6 hours** when the reaction is carried out in liquid ammonia at **-38 °C** (reaction 6)!



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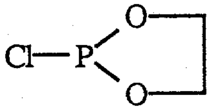
Amoco recently sent us a petroleum distillate sample that contains less than 1% organic sulfur. If we can successfully remove the sulfur, Amoco would like to support our research efforts. If the economics are favorable, the process could become commercial.

A recent 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 usefulness for these purposes in analyzing phenols in CONSOL coal liquefaction samples.

Results. We have found that ^{31}P NMR analyses of sulfur as $SPBu_3$ in coal extracts are unreliable. Thus ratios of peak integrations for $PBu_3/SPBu_3$ were at variance with elemental analyses. Part of this problem could be attributed to the presence of paramagnetic mineral materials extracted from the coal that broaden the NMR peaks thus interfering with quantitation of the peak areas. Quantitatively separating PBu_3 from $SPBu_3$ by column chromatography also failed. Attempts to remove PBu_3 cleanly from the extract via reaction 7 were also not successful. Following several

$$SPBu_3 + PBu_3 + KHSO_4 \longrightarrow SPBu_3 + \underline{HPBu_3^{+}K^{+}SO_4^{2-}} \qquad (7)$$

other attempts to quantitate sulfur removal from coal and from organosulfur compounds, as well as additional experiments to speciate and quantitate extracted materials, we have finally developed a satisfactory method. Part of the reason for the success of the method is that it employs a guard column for the gc in order to remove metal species (extracted from the coal) that would damage the gc column. Our technique has proven to be the method of choice for a number of reasons that will become evident later in this report.

In Table 1 is summarized preliminary data for the reaction of Illinois No. 6 coal with PBu_3 as shown in reaction 4. This reaction is carried out under a blanket of nitrogen or argon in a centrifuge tube equipped with a reflux condenser. The weighed amount of Celite added in the third experiment in order to aid in the separation of the residue from the centrifugate is seen by comparison with the second experiment to make no substantial difference in the analyses. It was surprising to observe the large but relatively constant difference in the analyses of % S removal as judged by the residues and the extracts. The discrepancy may be due at least in part to partial loss of PBu_3 into the slow inert gas stream at the reflux temperature of the PBu_3 (250 °C) despite the presence of the condenser, and also absorption of PBu_3 and/or $SPBu_3$ into the coal. It is clear that careful mass balances will have to be carried out. Also, elemental sulfur analyses of the extracts will be carried out to determine if they corroborate our gc data. It is apparent, however, that if the elemental sulfur analysis carried out on the residue by an outside analytical firm can be believed, about 90% of the sulfur is removed from Illinois No. 6 at the relatively low temperature of 250 °C. Moreover, it appears that lower or higher temperatures and shorter and longer times do not improve this value. Thus we have reasonably optimized the conditions of reaction 4, which constitutes a substantial accomplishment of Objective A.

For reasons that completely elude us at this time, DBT does not give up its sulfur to any substantial extent (according to gc analysis) in refluxing PBu_3, regardless of the presence of substances we once thought were catalysts for the process (e.g., *para*-chloro phenol, $FeCl_3$, Illinois No. 6) and also many others (Table 2). We were apparently misled earlier by what we later realized is the unreliability of ^{31}P NMR analyses in these experiments. We therefore sought other reagents for the removal of sulfur from organosulfur compounds such as DBT. A survey of the literature plus experiments in our laboratories revealed that PPh_3, $P(OMe)_3$ and $P(NR_2)_3$ compounds are only partially successful. Over the past ten years, other investigators have employed lithium aluminum hydride, potassium naphthalenide and single electron transfer reagents which are low-valent metal complexes based on nickel and iron with variable success. These are also relatively expensive materials.

Since elemental lithium and sodium are relatively cheap and since no reports could be found for their use in removing sulfur from organosulfur compounds, we embarked on a series of trial experiments which are now described. The procedure is summarized in Scheme 1 wherein R(S)

Scheme 1

$$\mathrm{R(S)} + \mathrm{M} \xrightarrow{\text{heat}} \xrightarrow{\text{methanol}} \xrightarrow[\text{ammonium chloride}]{\text{saturated}}$$

(M = Li or Na)

$$\xrightarrow[\text{ether}]{\text{extraction with}} \xrightarrow[\text{magnesium sulfate}]{\text{dry with}} \xrightarrow{\text{evaporate}}$$

analyze residue by gc

denotes an organosulfur compound. After heating the organosulfur compound with the metal, the excess metal is destroyed with methanol according to reaction 8. Saturated aqueous ammonium

$$2\mathrm{M} + 2\mathrm{MeOH} \longrightarrow 2\mathrm{MOMe} + \mathrm{H_2} \tag{8}$$

chloride (NH_4Cl) drives the organic materials out of the water and these are then extracted into ether. The ether solution is dried and evaporated to leave the entire organic product mixture which is then analyzed. The analyses are summarized in Table 3. It is seen from this table that DBT and BT can be cleanly desulfurized by sodium in tetradecane to give diphenyl (C_6H_5-C_6H_5) and styrene ($C_6H_5CH{=}CH_2$) under quite mild conditions (i.e., 130 °C, 24 h). Because of the higher melting point of Li (179 °C) compared with Na (98 °C), higher temperatures are required for the Li reactions.

Also noteworthy in Table 3 is the observation that PBu_3 also works well in these reactions. Because we do observe small amounts of $SPBu_3$ in the gc traces of such reactions, we wondered whether such an intermediate would react with Na or Li in reaction 9. As seen in Table 4, this

$$\mathrm{SPBu_3} + 2\mathrm{M} \longrightarrow \mathrm{M_2S} + \mathrm{PBu_3} \tag{9}$$

transformation occurs very efficiently. Whether PBu_3 really does function as an intermediate here has not been proven by our data so far, however.

Reactions of DBT and BT with Na in liquid ammonia are even more surprising. The sequence of steps in the experiment is shown in Scheme 2. In the case of DBT, a black polymeric

Scheme 2

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

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

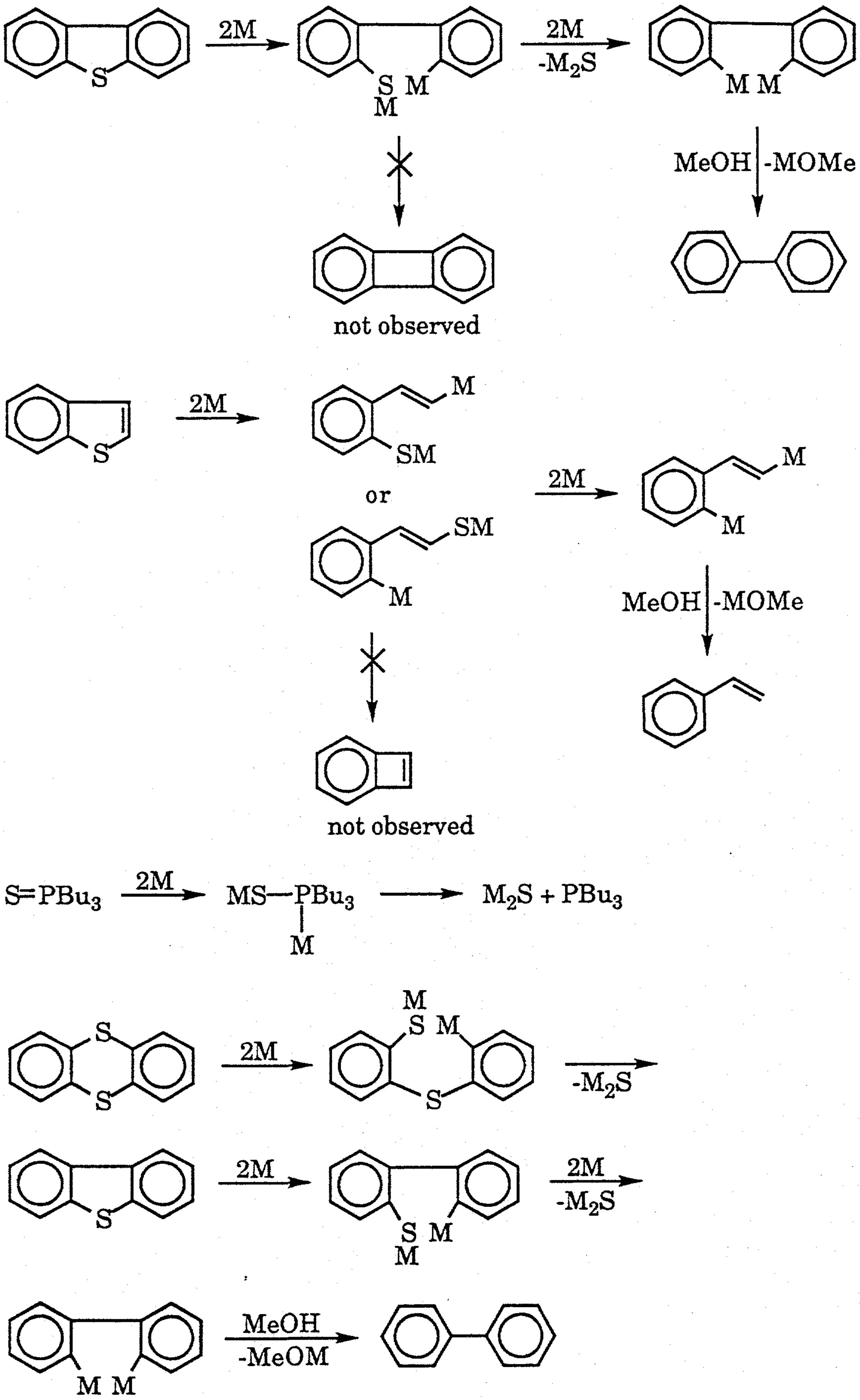
residue is obtained from which 77% of the sulfur has been removed and 99.2% of the DBT has been destroyed. When we initially add PBu_3 to the reaction mixture and heat at 130 °C for 3 h after step 2 in Scheme 2, then 100% of the DBT is destroyed and 99.2% of the sulfur is removed. With BT, the same procedure gives no black residue, but shows 100% S removal as measured by gc analysis even when no heat is applied after the second step in Scheme 2. Without PBu_3 present BT is completely destroyed giving 100% styrene.

Possible pathways for the removal of sulfur from the organosulfur compounds discussed here are shown in Scheme 3.

Conclusions. The reactions involving Na and Li we have investigated are not catalytic at this point. However, they do potentially offer an efficient and relatively inexpensive way of removing sulfur from petroleum fractions. Thus both the metals and the Na_2S product are insoluble in hydrocarbons and so separation is not a problem. Moreover, the reactions occur under very mild conditions. Thus treatment at a temperature of ~130 °C at atmospheric pressure is much less energy intensive than the 400-450 °C and high pressures required for molybdenum hydrodesulfurization catalysts.

These reactions also offer the possibility of desulfurizing coal since liquid NH_3 dissolves the sodium and the resultant solution would 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 -38 °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 would be expected to proceed more quickly and less than 6 h might well suffice. The coal could be washed with liquid NH_3 to

Scheme 3


2M
S M
M
2M
-M2S
M M
MeOH
-MOMe
not observed
2M
M
SM
or
SM
M
2M
M
M
MeOH
-MOMe
not observed
S=PBu3
2M
MS—PBu3
M
M2S + PBu3
S
S
2M
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S M
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-M2S
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2M
-M2S
M M
MeOH
-MeOM

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.

Reactions of coal(S) with PBu_3. In a dry box, the coal(S) sample and Bu_3P (cf. Table 1) were added to a 50 mL centrifuge tube which was then fitted with a condenser connected at the top to a N_2 or Ar line. The reaction mixture was stirred at the indicated temperature (Table 1) for 24-72 hours after which the reaction mixture was cooled to room temperature. The vessel fitted with a septum was weighed and centrifuged. In the dry box, a weighed amount of the extract (ca. 1.1 g) was placed into a 2 mL vial and the contents were stirred in air for oxidation (of the excess PBu_3 to $OPBu_3$) until constant weight. This sample was then submitted for elemental analysis of the sulfur removed from the coal. The remaining reaction mixture was diluted with 15 mL Et_2O, filtered and washed with Et_2O (5 x 15 mL) and then (4 x 15 mL) of CH_2Cl_2. After drying in vacuo, the residue was also submitted for elemental analysis of sulfur.

Reactions of DBT, BT and their derivatives with Na or Li. Under Ar, the metal (5.0-15.0 mmol) the organosulfur compound (1.0 mmol) and solvent (3 mL of tetradecane or Bu_3P, or 20 mL of toluene) were added to a two-necked Schlenk bottle fitted with a condenser. The reaction mixture was vigorously stirred at a temperature higher than the melting point of the metal (Table 3) for the indicated times. The reaction mixture was then cooled to room temperature and quenched with MeOH (10 mL) at 0 °C. After warming to room temperature, saturated aqueous NH_4Cl (40 mL) was added to the reaction mixture followed by extraction with Et_2O (3 x 60 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated by rotatory evaporation for gc analysis. All the products were identified by comparison with the authentic samples.

Reactions of DBT or BT with Na/liquid NH_3. 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 x 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 x 5 mL) MeOH (3 x 5 mL) and Et_2O (3 x 5 mL) and dried in vacuo. The dry residue was used for the elemental sulfur analysis.

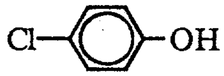
Table 1. Conditions for sulfur removal from Illinois No. 6 using PBu_3

coal wt (g)	PBu_3 vol (mL)	T (°C)	t (hrs)	% sulfur removal	
				residue analysis[a]	extract analysis[a]
1.0[b]	7	250	48	79.7	87.5
0.5	7	250	48	92.5	100
0.5[b]	7	250	48	89.1	100
0.5	7	200	48	49.8	61.1
0.5	7	300	24	86.7	93.9
0.5	7	250	24	66.9	79.6
0.5	7	250	72	67.7	80.9

[a] Based on elemental analysis. [b] Mixture contains a weighed amount of Celite.

Table 2. Unsuccessful potential catalysts for the removal of sulfur from DBT by PBu_3.[a]

$FeCl_3$



$NiCl_2 \cdot 6H_2O$

$SnCl_4 \cdot 5H_2O$

$TiCl_4$

$Cr(CO)_6$

$W(CO)_6$

$Fe_2(CO)_9$

$PtCl_2$

Si_2Cl_6

Ir

MoS_2

SmI_2

SiO_2

Al_2O_3

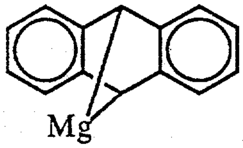
$RhCl_3$

AgI_2

$LiAlH_4$

$NaBH_4$

Cp_2TiCl_2



Ph_2PLi

CoI_2

4A molecular sieves

Baker's yeast

Ill No. 6 coal

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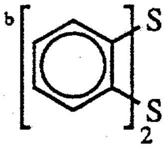
[a] At 250 °C for 24 h.

Table 3. Conditions for and analysis of organic products obtained via Scheme 1.

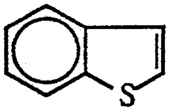
organo sulfur compound	metal	solvent	T (°C)	t (hrs)	% con-version	C_6H_5-C_6H_5 %
DBT	Li	dioxane	100	24	<5	2.0
DBT	Li	PBu_3	250	24	93.0	92.7
DBT	Li	PBu_3[a]	250	22	97.9	97.5
DBT	Li	PBu_3	250	44	98.2	98.1
DBT	Li	tetradecane	254	24	100	99.9
DBT	Na	PBu_3	130	24	100	99.9
DBT	Na	PBu_3	150	20	99.3	99.0
DBT	Na	toluene	110	24	75.2	75.0
DBT	Na	tetradecane	150	24	100	99.9
DBT	Na	tetradecane	130	24	100	99.9
DBT	Na	tetrahydrofuran	70	24	<10	7.8
$C_{12}H_8S_2$[b]	Li[a]	tetradecane	254	24	80.8	79.5
$C_{12}H_8S_2$	Li	tetradecane	254	24	100	99.9
$C_{12}H_8S_2$	Na	toluene	110	24	55.3	3.3
BT[c]	Li	tetradecane	254	24	80.8	79.5[d]
BT	Na	tetradecane	150	24	93.2	91.4[d]
BT	Na	toluene	110	24	53	3.3[d]
BT	Na	PBu_3	150	24	90.4	86.7[d]

[a] 10 mg oleic acid added.

[b]



[c]



[d] The product is styrene.

Table 4. Conditions and yields of PBu_3 for reaction 8.

M	solvent	T °C	t hrs	%PBu_3 yield
Li	tetradecane	254	24	100
Na	tetradecane	150	24	99.7
Na	toluene	130	24	81.8