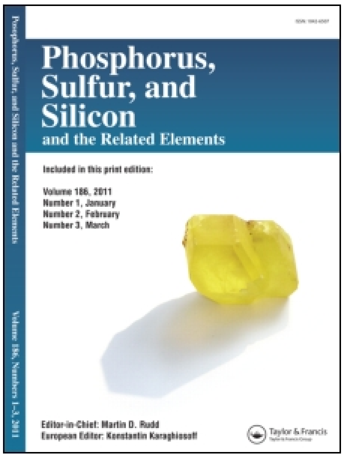

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REDUCTIVE DESULFURIZATION OF ORGANOSULFUR COMPOUNDS WITH SODIUM IN LIQUID AMMONIA

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REDUCTIVE DESULFURIZATION OF ORGANOSULFUR COMPOUNDS WITH SODIUM IN LIQUID AMMONIA

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Greater than 95% sulfur removal was observed when dialkyl mono or polysulfides were treated with Na in liquid ammonia. Polycyclic aromatic sulfur heterocycles were only moderately desulfurized under these conditions while phenylthio derivatives gave thiophenol as the major product and dithiophenols as the minor products.

Keywords: Desulfurization; sodium; liquid ammonia; organic sulfides

Because no catalyst has been discovered that efficiently desulfurizes thiophene derivatives directly, other routes have been sought. Several reductive desulfurization procedures were partially sucessful, but those utilizing $LiAlH_4$ in refluxing ethanol,[1] and Li in refluxing dioxane[2] were found difficult to repeat[3]. It was also reported that 51–99% sulfur removal from dibenzo[*b,d*]thiophene (DBT) could be achieved with sodium at 350 °C and a pressure of 200–1200 psi in the presence of hydrogen[4]. Nickel boride generated in situ was reported to reduce DBT to biphenyl in 83% yield[5]. Although trivalent organophosphorus compounds are known to desulfurize dialkyl trisulfides to disulfides and disulfides to monosulfides in moderate yields,[6–9] these reagents do not desulfurize polycyclic aromatic sulfur compounds.

Birch reduction is known to reduce a variety of functional groups, [10] and here we report the results of our investigation of the application of this reaction to a range of organosulfur compounds.

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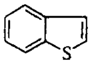
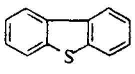
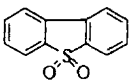
Treatment of BT (**1**) with Na/liq. NH_3 gave 2-ethylthiophenol in 99% yield and a small amount of ethylbenzene (Table I). Although similar treatment of DBT (**2**) and DBT sulfone (**3**) produced moderate amounts of the desulfurized product biphenyl, DBT gave a black residue with a sulfur content of 1.81% and the overall sulfur removal based on the sulfur content of the starting material was 92.3%. In the case of **3**, 2-phenylthiophenol was the major product. Thiophenols, the only products from the reduction of thianthrene (**4**), may well be formed via a pathway resembling that shown in Scheme 1. Here formation of the phenylthio radical anion leads to 4,4′-dithiophenol (**7**) and 2,2′-dithiophenol (**8**) after the reaction is quenched by methanol and aqueous NH_4Cl. For the polycyclic aromatics **5** and **6** (Table I), 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 I).



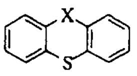
1
(BT)



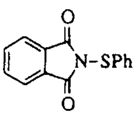
2
(DBT)



3



4, X = S; **5**, X = NH; **6**, X = O



9

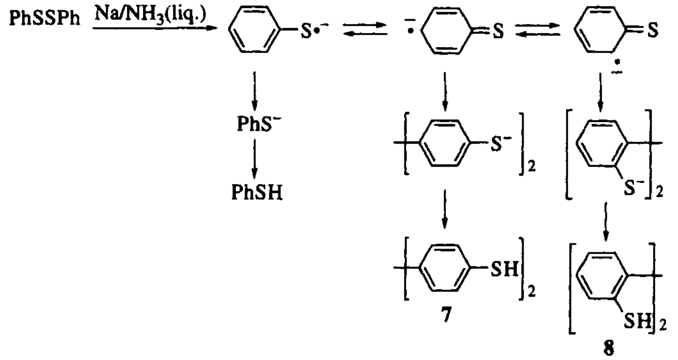
TABLE I Birch reductions of polycyclic aromatic organosulfur compounds

substrate	*conversion (%)*[a]	*product(%)*[a]
1	100	2- ethylthiophenol (99.0), $PhCH_2CH_3$ (0.9)
2[b]	99.2	Ph-Ph (20.9), residue (70 mg, 1.81%S)[c]
3	100	Ph-Ph (35.3), 2-phenylthiophenol (58.4)
4	100	PhSH (47.9), **7** (51.0), **8** (0.8)
5	96.8	PhSH (5.6), Ph_2NH (1.4), carbazole (0.1) residue (125 mg, 6.00% S)[d]
6	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] **2** (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%.

Birch reduction of all the compounds in Table II (except **9**) gave thiophenol as the major product and dithiols **7** and **8** as minor products, *indi-*

cating that aromatic C-S bonds are recalcitrant to Na/NH_3(1). Desulfurization of dibenzyl sulfide, disulfide, trisulfide and sulfone was very efficient, generating toluene and bibenzyl as the predominant minor product, respectively. Tributyl and triphenylphosphine sulfides were quantitatively desulfurized, giving tributylphosphine and the further reduction product diphenylphosphine, respectively.



SCHEME 1

TABLE II 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), **7** (11.4), **8** (4.1)
$PhS(CH_2)_3SPh$	PhSH (94.2), **7** (3.0), **8** (2.7)
$(PhS)_2CH_2$	PhSH (85.0), **7** (9.9), **8** (5.0)
$(PhS)_3CH$	PhSH (77.3), **7** (10.3), **8** (12.3)
9	PhSH (30.9), phthalimide (18.0), **7** (65.0), **8** (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.

In conclusion, Birch reduction is only moderately successful for desulfurizing polycyclic aromatic sulfur compounds, but it is quite efficient for dialkyl mono or polysulfides, dialkyl sulfones, and pentavalent phosphine sulfides. This procedure fails, however, for phenylthio substrates.

General experimental 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 °C for 3h under argon. Then ammonia was evaporated by slowly warming the reaction mixture to room temperature. Methanol (10 mL) was added at 0 °C followed by 40 mL of saturated NH_4Cl. Ether extracts (3 × 70 mL) of the mixture were dried over $MgSO_4$, filtered and concentrated by rotary evaporation for GC analysis. While this procedure was in progress, the residues indicated in Table I were collected and washed alternately with Et_2O and H_2O and then dried in vacuo. In the cases of BT (Table I) and dibenzyl sulfide, disulfide, trisulfide and sulfone (Table II), the organic phases were used directly for the analysis of the products.

Acknowledgements

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