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LETTERS

Mild and Efficient Desulfurization of Alkyl Sulfides with Sodium

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Abstract: The reactions of dialkyl mono- and disulfides and functionalized alkylthio compounds with sodium in refluxing hydrocarbon solvent (tetradecane, mesitylene or toluene) resulted in sulfur-free products in very high yields. © 1998 Elsevier Science Ltd. All rights reserved.

Chemical removal of sulfur from liquid fossil fuels and coals has received much attention because conventional hydrodesulfurization (HDS) can not effectively desulfurize polycyclic aromatic sulfur compounds, such as benzo[*b*]thiophene (BT), dibenzo[*b,d*]thiophene (DBT) and their derivatives. Among the chemical approaches directed to desulfurization of organosulfur compounds, reductive desulfurization has been considered to possess potential. Unfortunately, procedures involving $LiAlH_4$ in refluxing ethanol[1] and Li in refluxing dioxane[2] were found difficult to repeat.[3] Procedures using sodium at 350 °C and pressures of 200-1200 psi in the presence of hydrogen gave 51-99% sulfur removal from DBT with 45.6-93.2% yields of biphenyl.[4] Nickel boride was reported to desulfurize DBT to biphenyl in 83% of yield.[5] Trivalent organophosphorus compounds are known to desulfurize acylic dialkyl trisulfides to disulfides, and disulfides to monosulfides in moderate yields.[6-9] Recently we reported that Li and Na efficiently desulfurize BT and DBT and their derivatives at relatively modest temperatures (110-254 °C) somewhat exceeding the melting points of the metals, in inert hydrocarbon solvents at atmospheric pressure.[3] In this communication we show that this method is quite general and efficient for a variety of dialkyl and alkyl-aryl organosulfur compounds. The approach reported here also constitutes a significant improvement over the desulfurization of these compounds with sodium in liquid ammonia.[10]

Although alkyl sulfides **1-3** did not desulfurize at 110 °C or 164 °C, at 254 °C, the corresponding alkanes were formed in high yields along with only small amounts of the corresponding alkylmercaptans (Table 1). The reactions of cyclohexene sulfide (**4**) and propylene sulfide (**5**) in refluxing toluene gave essentially quantitative yields of cyclohexene and propylene, respectively. Benzyl methyl sulfide (**6**) and disulfide (**7**) were efficiently desulfurized to toluene, ethylbenzene, and/or bibenzyl. Raising the reaction temperature improved the desulfurization of benzyl phenyl sulfide (**8**) because at lower temperature Bz-S bond cleavage by sodium was the predominant process (Table 1). The complete desulfurization of 2-phenyl-1,3-dithiane (**9**) can be envisioned to occur *via* the pathway indicated in Scheme 1. Changing the temperature results in an altered product distribution (Table 1).

Functionalized alkyl sulfides **10-13** were desulfurized without destruction of their remaining functionalities, and without the formation of desulfurized coupling products. For example, pyrrolidine (from

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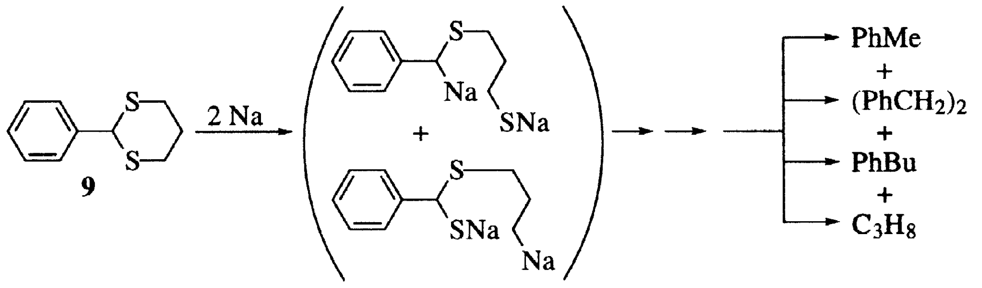
Table 1. Desulfurization of alkyl sulfides with sodium.

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.



Scheme 1

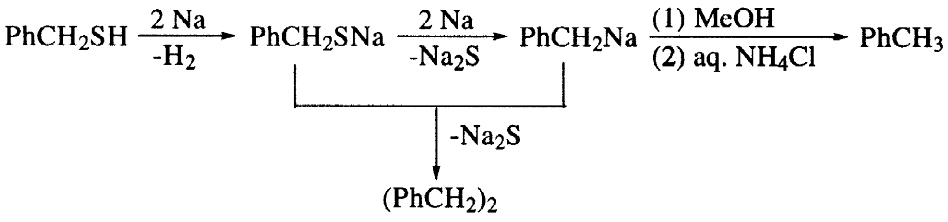
12) and THF (from **13**) were not detected by GC analysis (Table 2). Compound **14** in the presence of sodium in toluene or mesitylene at room temeprature produced an orange precipitate. That the precipitate is the corresponding enolate is indicated by the recovery of the starting material when the reaction mixture was treated with MeOH followed by aqueous NH_4Cl. This enolate intermediate was efficiently desulfurized to propiophenone in mesitylene at a relatively low temperature (164 °C). Interestingly, benzylmercaptan (**15**) was desulfurized to toluene and bibenzyl in 85.2% conversion within 13.5 hours,

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.

presumably according to Scheme 2. Substrate **16** underwent a similar reaction to generate triphenylmethane and hexaphenylethane. The reaction of benzyl thiocyanate (**17**) gave the PhC-S bond cleavage product PhMe and the desulfurized intramolecular coupling product bibenzyl, but benzyl cyanide was not detected. The reaction of alkenyl sulfone **18** occurred predominantly *via* CH-S bond cleavage resulting in styrene as the major product and thiophenol as the minor product (Table 2).



Scheme 2

We have demonstrated herein that sodium efficiently desulfurizes a variety of dialkyl sulfides , alkyl-aryl sulfides and alkylthiol compounds under relatively mild conditions.

General procedure: Under argon, sodium (10.0 mmol), organosulfur substrate (1.0 mmol) and solvent (3 mL of tetradecane or 5 mL of toluene or mesitylene) was 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, unreacted sodium was destroyed with methanol (5 mL) at 0 °C under argon. Saturated aqueous NH_4Cl (40 mL) was then added to the mixture followed by extraction with Et_2O (3 x 80 mL). The organic phase was dried over $MgSO_4$, filtered and then used directly for product analysis by GC. For the reaction involving **10**, the extraction solvent was THF while for **13** it was *n*-hexane.

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