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IN SITU PREPARATION OF DISULFIDE BY THE REACTION OF TRIALKYL- AND TRIARYLBORONS WITH SULFUR

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The formation of disulfide by the reaction of organoboron compound with sulfur has not been encountered so far. We wish to report first successfull case of this reaction.

Dialkyldisulfide has been obtained by the reaction of trialkylboron with sulfur, followed by steam distillation in the presence of alkali. By a similar method diphenyldisulfide has also been obtained. This means that by the combination of this reaction with hydroboration, dialkyldisulfide can be obtained from olefine in situ.

An example of the experimental procedure was as follows:
Sulfur powder (3.7 g) was added to tricyclohexylboron (10.5 g) and kept at 130° for ten hours with stirring under nitrogen atmosphere. The reaction mixture was dissolved in ether (20 ml) and piperidine (9.3 g) was added. The mixture was kept at 30° for three hours with stirring, then steam distilled. The residue in flask was extracted with ether, dried over anhydrous sodium sulfate. By distillation in vacuum, dicyclohexyldisulfide (4.3 g) was obtained.

The distillate on steam distillation was extracted with ether after acidification with hydrochloric acid. After evaporation of the solvent, white crystals (4.9 g) was obtained, which was identified to be cyclohexylborinic acid.

$$(C_6H_{11})_3B \quad + \quad S \xrightarrow[\text{10 hrs}]{130°} C_6H_{11}SB(C_6H_{11})_2$$

$$\begin{tikzcd} {} \arrow[r, "\text{hydrolysis}"] & C_6H_{11}SH \arrow[d, "\text{Autoxidized}"] & + \quad (C_6H_{11})_2BOH \\ & 1/2\ C_6H_{11}\ SSC_6H_{11} & \end{tikzcd}$$

Another experiments are summarized in table 1.

B. M. Mikhailov[1] has studied the reaction of trialkylboron with sulfur and obtained thioester. H. Jenkner[2] has found to directly get the disulfide by the reaction of trialkylaluminium with sulfur without any succeeding treatment. A. Mailhe[3] has studied the reaction of Grignard reagent with sulfur to obtain mercaptane.

Table 1

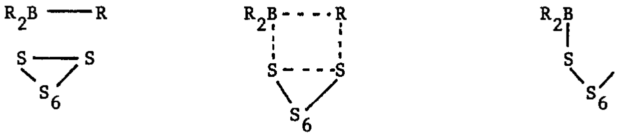
		Reaction conditions$^{\alpha}$		Yield (%)$^{\beta}$	
No.	R_3B	Temp.	Time	Disulfide	Mercaptane
1	$(C_6H_{11})_3B$	130°	10 hrs	33^{γ}, 48^{ω}	—
2	$(n\text{-}C_8H_{17})_3B$	130°	10	47	—
3	$(CH_2{=}CHCH_2)_3B$	130°	10	2.2	—
4	$(C_6H_5)_3B$	200°	13	64	5.5

α) Molar ratio of R_3B to sulfur was 1:2 (in No. 1, γ, 1:3).

β) The yield was based on sulfur used.

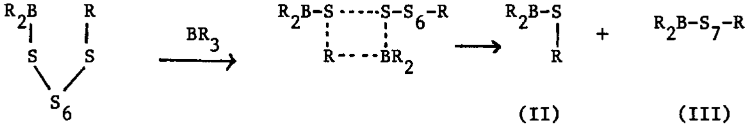
γ,ω) The reaction product was hydrolysed with piperidine (γ), with aq. sodium hydroxide (ω).

At 130° sulfur is molten state and consisted of S_x over 90 %, which composed of puckered ring structure of eight sulfur atoms. On the reaction course of trialkylboron with sulfur, considering less polarity of the bond between boron and carbon, the reaction does not seem to be similar to the nucleophilic attack of Grignard reagent to sulfur ring, but to lead polysulfide formation via a four-centered cyclic intermediate.



(I)

The polysulfide (I) might be react with unreacted trialkylboron to form thioester (II), which B. M. Mikhailov has obtained.



$$\text{(III)} \xrightarrow{BR_3} \text{(II)} + R_2B\text{-}S_6\text{-}R$$

Then thioester (II) might be hydrolysed in the presence of base such as piperidine or sodiumhydroxide to form thiol which is rapidly autoxidized to disulfide in the presence of alkali.

High temperature and long time are not always favorable to aliphatic disulfide formation, because the resinous materials become predominant in the product. The low yield of diallyldisulfide (No. 3) may be attributed to the presence of its allylic hydrogen atom, being easily abstrated and stabilized or followed polymerization with sulfur.

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