

THE PREPARATION OF
1,2-DITHIOLS FROM EPISULFIDES

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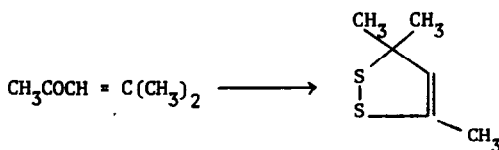
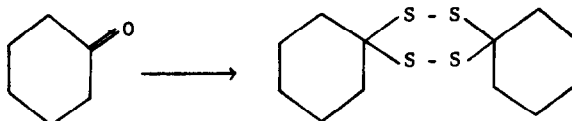
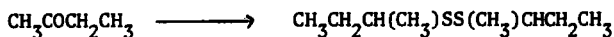
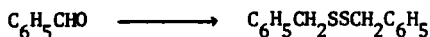
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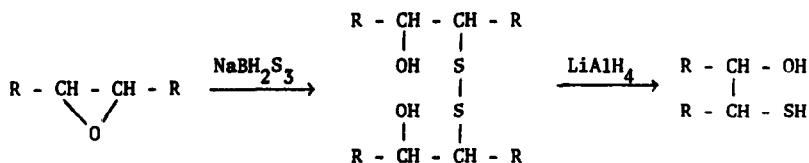
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The reaction of sulfur with borohydrides, such as sodium borohydride, in the presence of an appropriate solvent such as tetrahydrofuran (THF) leads to the formation of a sulfurated hydride NaBH_2S_3 . The preparative reactions and reducing properties of these hydrides have been summarized recently (1). Beside reduction, sulfurated sodium borohydride has shown sulfurating properties, the orientation of the reaction towards reduction or sulfuration being determined by the reaction temperature, the proportion of substrate to sulfurated hydride and the structure of the substrate.

With aldehydes and ketones various sulfides have been obtained, the following examples illustrating the behavior of NaBH_2S_3 under sulfurating conditions.

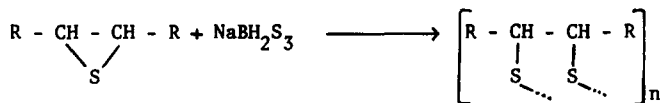


With epoxides, the sulfurated hydride behaves as a reducing and sulfurating agent to give, with high yields, the corresponding disulfide dialcohol (2).

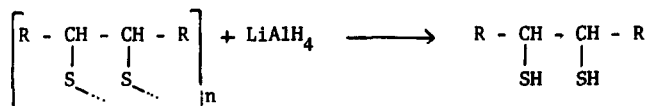


The reduction of the disulfide dialcohol by LiAlH_4 leads to quantitative yields of the corresponding α mercaptols, thus offering a much improved synthetic approach to this type of compounds.

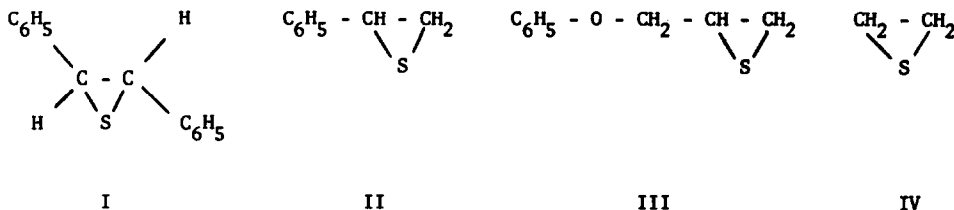
We have examined the extension of this reaction to the episulfides and have found a behavior similar to the epoxides, the only difference resulting from the much lower stability of the episulfides, even under mild experimental conditions. Such an instability, leading in some cases to extensive polymerization, was to be expected, according to the literature (3). The reaction of NaBH_2S_3 with episulfides can be represented by the following equation,



further treatment with LiAlH_4 giving the 1,2-dithiol.



The yield of 1,2-dithiol can vary rather widely, depending mainly upon the structure and stability of the starting episulfide. For example, with I, the reaction leads to trans stilbene only. With II, a yield of 65% of the 1,2-dithiol has been obtained and with III, the sulfuration reaction also took place as expected. With IV, only polymeric material was observed.



Consequently, NaBH_2S_3 behaves as a sulfurating agent, with episulfides, in a way similar to its reaction with epoxides, the limiting factor being the stability of the starting episulfide. However, the intermediate disulfide dithiol exists in a polymeric state and cannot be isolated and purified. Elementary analysis has confirmed the addition of a sulfur atom on the episulfide, at this stage.

Experimental.

In a typical experiment, a mixture of NaBH_4 (250 mg) and sulfur (630 mg) is treated, in a dry flask (50 ml), by 15 ml of anhydrous THF. After 15 min. of stirring at room temperature under nitrogen atmosphere, 6.5×10^{-3} mole of NaBH_2S_3 is thus generated. To this suspension of the reagent, 1.0 g (6×10^{-3} mole) of III in 2 ml of THF is added slowly at 0°C . The episulfides have been prepared by the method of Bordwell (4). After the addition, the temperature of the reaction mixture is increased to 25° over twelve hours. After this contact, the crude product is treated with 10 ml of water. By extractions with chloroform and drying over MgSO_4 , a crude polysulfide (1.66 g) is obtained. This polysulfide is purified by chromatography on a silica gel column ($\text{CCl}_4/\text{CHCl}_3$ mixture) the purified polysulfide being recovered in the chloroform elution. This viscous material contains 31.52% of sulfur (calculated for $\text{C}_9\text{H}_{10}\text{OS}_2$: S, 32.32) and is treated, in solution in 10 ml of THF, at 0° , by 1.0 g (2.6×10^{-2} mole) of LiAlH_4 . After a contact of six hours at 25° , followed by the usual hydrolysis and extractions, 0.70 g of a crude material is obtained and fractionated again as above, over a silica gel column. This purification gives 75% of the crude material as the 1,2-dithiol derived of III. NMR: 2 protons between 1.2 and 2.1 δ (SH); 3 protons between 2.7 and 3.5 δ (CH, CH_2); 2 protons between 3.9 and 4.3 δ ($-\text{OCH}_2$); 5 protons between 6.7 and 7.5 δ (C_6H_5). This 1,2-dithiol gives the expected thioacetal (catalyst: $\text{BF}_3 \cdot \text{Et}_2\text{O}$, yield 82%) with p-nitrobenzaldehyde, yellow crystals, m.p. $82-85^\circ$. Calculated for

$C_{16}H_{15}O_3NS_2$: C, 57.66; H, 4.54; N, 4.20; S, 19.20. Found: C, 57.72; H, 4.88; N, 4.34; S, 18.88.

Mass spectrometry: molecular ion: 333.

Acknowledgment.

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