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LITHIUM ALUMINIUM HYDRIDE REDUCTION OF SOME ORGANO-SULPHUR COMPOUNDS.

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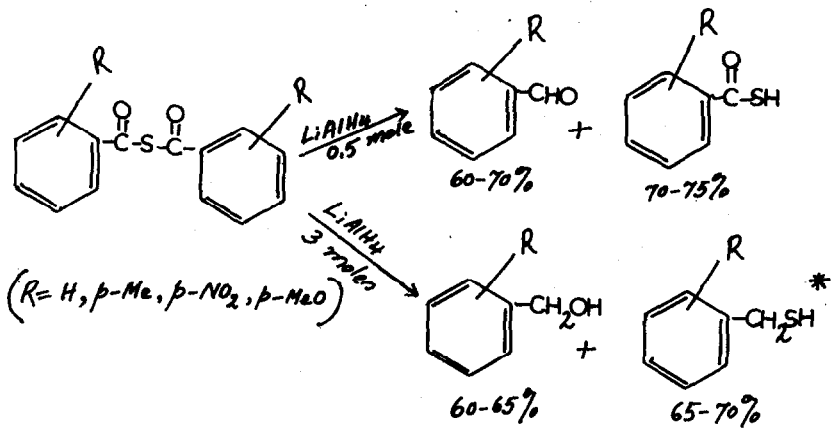
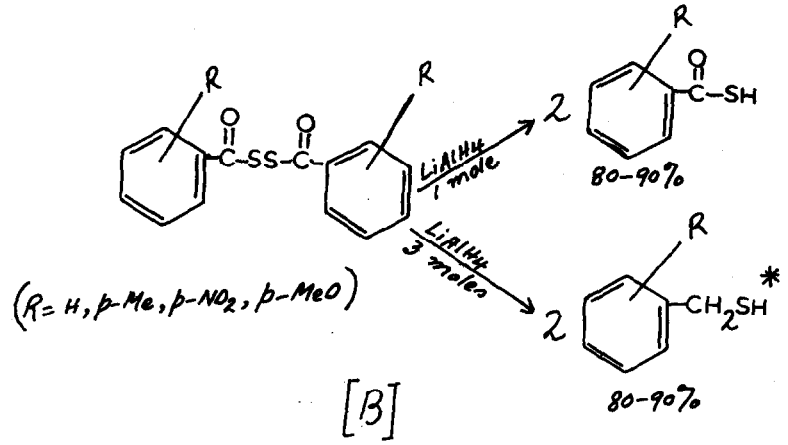
Although lithium aluminium hydride is known to be effective in reducing certain types of organo-sulphur compounds, its action on compounds having the linkage -CC-S- or -CS-S- does not appear to have been extensively studied. Newman and his co-workers obtained difluorodecanol by the reduction of ethyl difluorothiodecanoate with $LiAlH_4$, and they reported that the products had mercaptan-like odour (1). Bobbio studied the hydrogenolysis of thiolesters using the same reagent and he obtained both mercaptans and alcohols, the latter corresponding to the acyl groups (2). We report here the reduction of compounds of the type Ar-CO-S-CO-Ar (A), Ar-CO-SS-CO-Ar (B), Ar-CS-SS-CS-Ar (C) and Ar-CO-SH (D) using lithium aluminium hydride in ether and reaction period of one hour. The results are summarised in the next pages.



[A]



[B]

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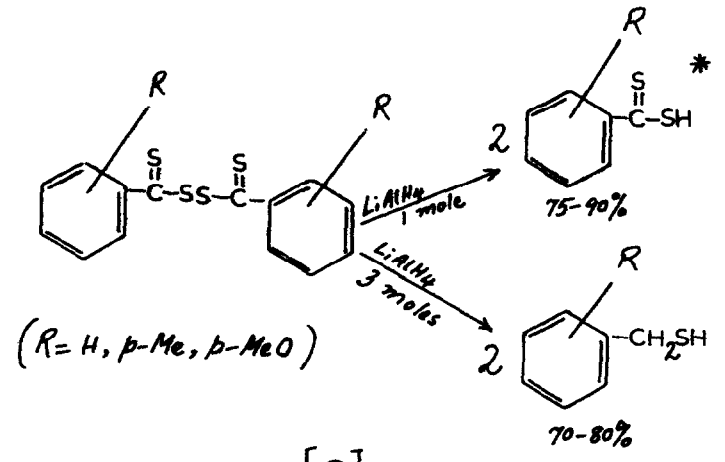
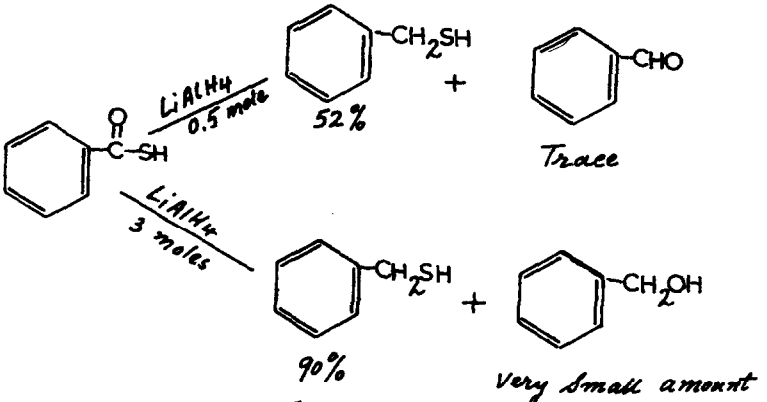
* p-Aminobenzyl mercaptan was obtained from the corresponding nitro derivative.



[C]



[D]

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* p-Methoxydithiobenzoic acid was not reduced further.

With 0.5 mole of $LiAlH_4$, compounds of the type (A) give first the aldehyde and the thioacid through hydrogenolysis at the -CO-S- bond; however with one mole of the reagent, (B) and (C) yield the corresponding acid through cleavage of the sulphur-sulphur linkage. With 3 moles of the reagent, compounds of the type (A) yield both alcohols and mercaptans, the mercaptans apparently being obtained from the reduction of the thioacids. (B) and (C) under that condition yield mainly the mercaptans, the alcohols being formed in very small amounts from (B) only. This behaviour of the thioacids was confirmed by treating thiobenzoic acid itself (D) with $LiAlH_4$ when benzyl mercaptan was obtained in 90% yield, and benzyl alcohol was formed in very small amount. However, with 0.5 mole of the hydride, benzaldehyde is formed in trace amount. In any case, the main reaction route in the case of thioacids does not appear to be the cleavage of -CO-S- linkage, which is in contrast to the observed behaviour of compounds of the type Ar-CO-SR (2).

REFERENCES

(1) Melvin S. Newman, Mary W. Renoll and Irving Auerbach, J. Am. Chem. Soc., 70 , 1023 (1948).

(2) F. A. Bobbio, J. Org. Chem., 26, 3023 (1961). These results were verified by us using benzyl thiobenzoate when both alcohol and mercaptan were obtained in high yields.