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REACTIONS OF SEMIIONIC OXYGEN. III. DIVALENT METAL SALTS IN THE REACTION OF ALCOHOLS WITH DIMETHYL SULFOXIDE —— A NOVEL ALDEHYDE AND KETONE SYNTHESIS VIA METALATION (1)

Jack M. Tien, Hsien-Ju Tien and Jen-Shan Ting*

Department of Chemistry

Cheng Kung University, Tainan, Taiwan, China.

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Much work has been devoted in recent years to convert alcohols into the corresponding aldehydes and ketones with dimethyl sulfoxide (DMSO) in the presence of dicyclohexylcarbodiimide (2a), acetic anyhydride (2b), phosphorus pentoxide (2c) or sulfur trioxide (2d). However, to our knowledge, no divalent metal salts have been used to effect the reaction of alcohol and DMSO. Thus, we wish now to report this interesting result. During the reaction the corresponding carbonyl conpound is produced. This new method of preparing aldehyde and ketone appears to be of general practicability and convenience, especially when the metal salt is mercuric acetate.

A mixture of mercuric acetate (1 g.), DMSO (4 ml.) and an alcohol (6 ml.) was stirred magnetically and heated at about 130° in a glycerine bath for one to two hours. The clear solution gave off dimethyl sulfide and deposited orange mercuric oxide which soon disappeared along with some white precipitate which turned graish. The major product was separated by steam distillation and precipitated as its 2,4-dinitrophenylhydrazone. This hydrazone was identified by their mixing melting point with the authentic specimen and by comparison with their IR spetra. Benzyl alcohol, cyclohexanol and 2-butanol gave Benzaldehyde, cyclohexanone and 2-butanone in 86, 70 and 41% yields** respectively. This

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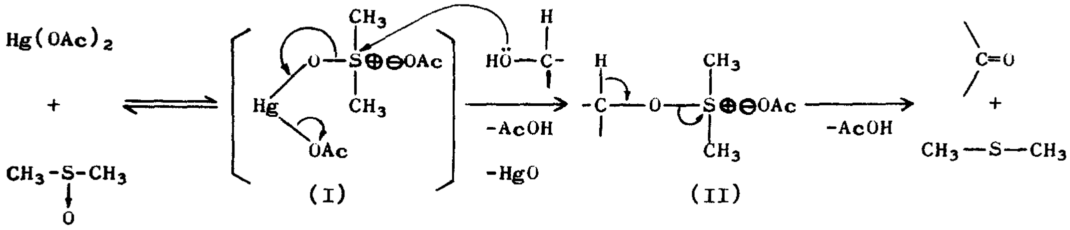
*Undergraduate Participant

** Based on the mercuric acetate

reaction can also be carried out at room temperature but at a much lower rate. When $Cd(OAc)_2 \cdot 2H_2O$, $Cu(OAc)_2 \cdot H_2O$, $Pb(OAc)_2 \cdot 3H_2O$ or $Zn(OAc)_2 \cdot 2H_2O$, was used instead of $Hg(OAc)_2$, the similar results were observed; but the yields of the corresponding carbonyl compounds were generally much lower.

The main reation seems to proceed through a key intermediate of acetoxymercurioxydimethylsulfonium acetate (I) which gives an alkoxydimethylsulfonium ion (II) originally postulated independently by Smith and Winstein (3a) and Hunsberger and Tien (3b). Thus, the mechanism via mercuration is suggested:



$$HgO + 2AcOH \rightleftharpoons Hg(OAc)_2 + H_2O$$

The scope and limitation of this reaction as well as the possible formation of dimethyl sulfide and metal salt complex (4), methyl thiomethyl ether derivative (2b), or other side-products are in the process of investigation.

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