

MECHANISM OF THE OXIDATION OF α -ACTIVE-METHYLENE SULFIDES BY DIMETHYL SULFOXIDE AND BENZOYL CHLORIDE

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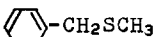
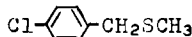
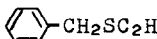
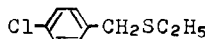
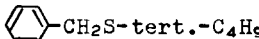

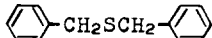
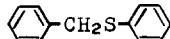
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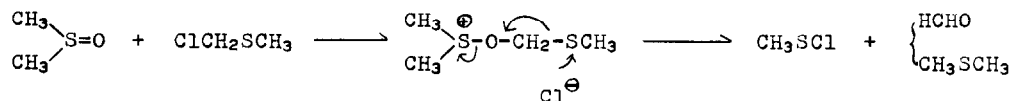
The oxidation of methyl groups of aromatic methyl ketones with formation of 1-aryl-2,4,6,8-tetraoxabicyclo[3.3.0]octanes using dimethyl sulfoxide(DMSO) and certain acid chlorides has been reported¹⁾.

The oxidation method is now extended to benzyl sulfides using DMSO and benzoyl chloride.

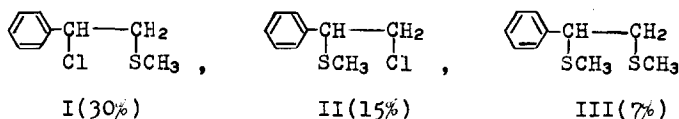
TABLE 1 The oxidation of benzyl sulfides to benzaldehydes

Benzyl sulfide	Yield(%) of benzaldehyde	Sulfide	Yield(%) of aldehyde
	85		77
	82		75
	61		89
	74		
	trace		

We have found that this oxidation proceeds via α -chloro sulfides which are obtained by chlorination of α -active-methylene sulfides by sulfenyl chloride. Carboxylic acid chlorides are known to react with sulfoxides to give α -chloro sulfides²⁾. Chloromethyl methyl sulfide derived from DMSO was further reacted with DMSO³⁾ to give methanesulfonyl chloride as illustrated below.

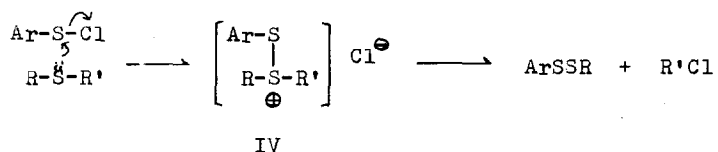


In the trapping experiment of methanesulfonyl chloride with styrene, following products were obtained⁴⁾.

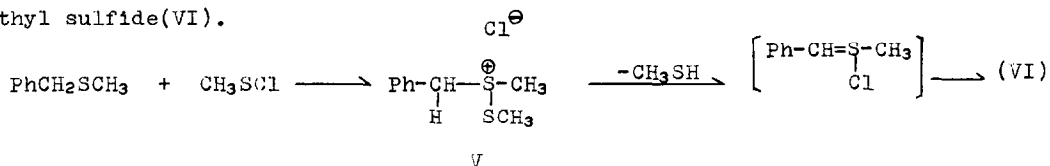


The above mechanism was substantiated by the fact that the reaction of chloromethyl methyl sulfide with ethyl phenyl sulfoxide in the presence of styrene gave a mixture (30%) of I and II, ethyl phenyl sulfide (89%) and paraformaldehyde (51%). Therefore, the oxidation of methyl ketones or benzyl sulfides is ascribed to the action of methanesulfonyl chloride and DMSO.

α -Chlorobenzyl methyl sulfide²⁾ was obtained by the reaction of methyl benzyl sulfide with methanesulfonyl chloride. An example of chlorination of sulfides by sulfonyl chlorides has not, to our knowledge, been previously reported. An example of the reaction of 2,4-dinitrobenzenesulfonyl chloride with monosulfides is that a bimolecular electrophilic attack of the sulfonyl chloride on the monosulfide gives a sulfonium ion type complex (IV) from which elimination of cationically most stable group occurs to give the products⁵⁾.



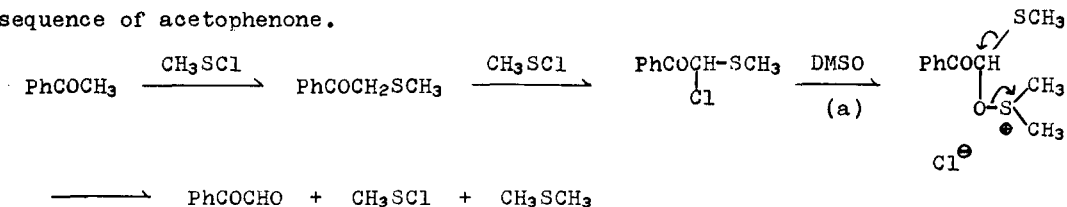
It seems most reasonable to assume that the chlorination of sulfide is effected by abstraction of a benzylic proton of the benzyl sulfide by thiomethoxy ion from the complex (V) to give an intermediate²⁾ which rearrange to α -chlorobenzyl methyl sulfide (VI).



In the formation of sulfonium ion type complex, electron-withdrawing phenyl group deactivated the sulfide sulfur towards electrophilic attack by the sulfonyl chloride (see Table 1).

The sulfide VI in DMSO was oxidized to give benzaldehyde as in the case of *o*-chloro-*o*-methylthio-acetophenone¹⁾.

Reaction of sulfenyl chlorides and methyl ketones occurs to give β -keto sulfides⁶⁾. Thus, following reaction scheme can be suggested as the oxidation sequence of acetophenone.



The step (a) corresponds to the reaction of chloromethyl methyl sulfide with DMSO.

Evidence that the oxidation of acetophenones or benzyl sulfides by sulfenyl chloride and DMSO is a general phenomenon is provided by effective catalytic action of other sulfenyl chlorides such as ethanesulfenyl-, *n*-butanesulfenyl- and trichloromethanesulfenyl chloride.

When subjected to the action of chloromethyl methyl sulfide and DMSO, phenacyl chloride was oxidized to phenylglyoxal, while benzyl chlorides gave dimethyl benzyl sulfonium chlorides quantitatively.

References

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