

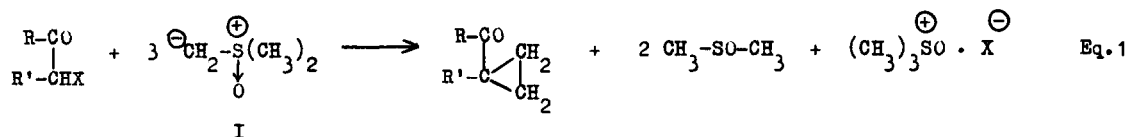
THE REACTION OF DIMETHYLOXOSULPHONIUM METHYLIDE WITH α -HALOCARBONYL COMPOUNDS :
A NEW SYNTHESIS OF CYCLOPROPANES

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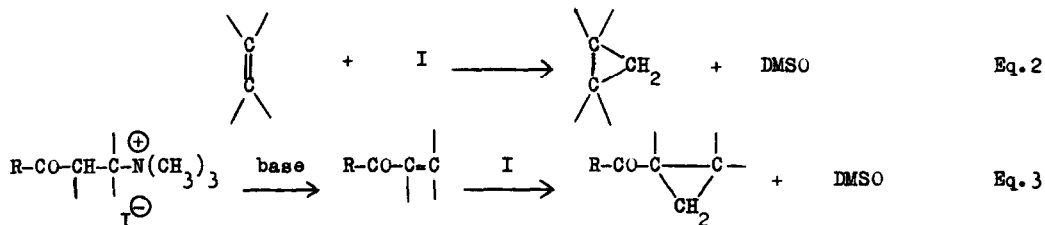
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Following our previous researches on the chemistry of sulfur ylides (1-5), considering the scarcity of information on the reactivity of dimethyloxosulphonium methylide (I) towards halocompounds (4-6), we are now investigating the behaviour of (I) towards some classes of halocompounds. We wish to report here the results of our preliminary study on the reaction of (I) with primary and secondary α -halocarbonyl compounds. We found that they react in the cold with three moles of (I), according to the following equation:

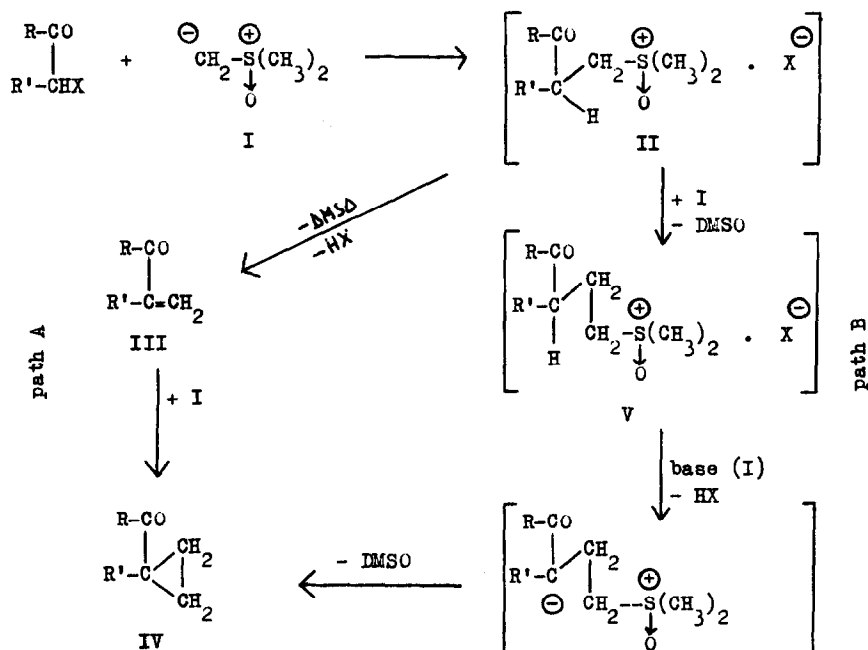


It is known that (I) can give rise to cyclopropanes by reacting with double bonds (7-10) (Eq.2) or with the quaternary salts of Mannich bases (Eq.3) (11):



In both cases the ylide (I) supplies only one methylene to the cyclopropane ring. In our case (Eq.1) the synthesis involves a double participation of the ylide with an overall introduction of two methylenes in the molecule, a behaviour that has been first noted by us in the reaction of (I) with 1,3-dipoles (1-5) and later by J.J.Tufariello and L.T.C.Lee in the reaction with boranes (12).

In our opinion the reaction outlined in Eq.1 can proceed through the following paths :



First the halogen of the α -halocarbonyl compound is displaced by (I) to give the intermediate salt (II). According to path A (II) can be converted into an olefin (III) by a β -elimination and then the olefin can react with (I) to yield the cyclopropane (IV). On the other hand the salt (II) could also undergo a nucleophilic displacement by (I) to afford the homologous salt (V) which in turn, in the basic medium of the reaction, can give the cyclopropane by an intramolecular nucleophilic displacement (path B).

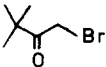





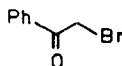
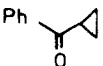
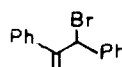
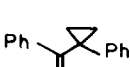
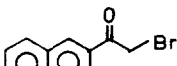
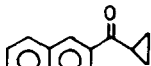
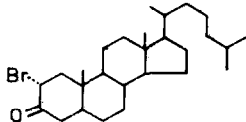
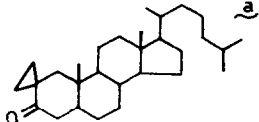
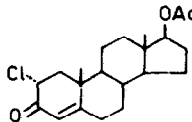
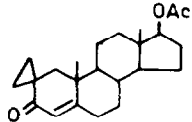
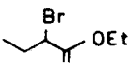
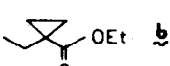
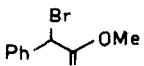
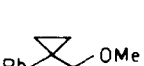
Of course both mechanisms could operate in competition.

The ketones and esters that have been reacted with (I) to yield cyclopropanes are reported in Table I. An inspection of the Table shows that this new method of cyclopropane synthesis seems to be general at least for α -haloketones. Moreover, in spite of the relatively low yields, the method can also be of preparative interest for the easy availability of the starting materials and the simplicity of the reaction.

The reactions were run by adding the haloketone or ester to a cold solution of (I) obtained according to Corey (13). After a few hours at room temperature the reaction mixture is poured in ice-water, extracted and the products isolated by chromatography. The yields⁽⁺⁾

(+) No attempt has been done to improve yields by modifying the conditions of the reaction.

TABLE I ●

	Ketone or Ester	Cyclopropane	Yield %
1.			33
2.			28
3.			30
4.			37
5.			35
6.			19
7.			15
8.			13
9.			32
10.			40

● All the cyclopropanes reported, except 7 and 9, were known. Their structures were usually determined by nmr and mass spectrometry and by comparison with the data from the literature, when available.

^a mp 80°C.

^b liquid, isolated by vpc.

in cyclopropane vary from 10% to 40%.

As minor by-products in some cases were isolated the methylene compounds $R-CO-C(CH_2)-R'$, the dehalogenated ketones or esters $R-CO-CH_2-R'$, the products of reductive coupling $R-CO-CH(R')-CO-R$ and the epoxides $R-C-CHX-R'$.



Further investigations in this field are in progress.

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