

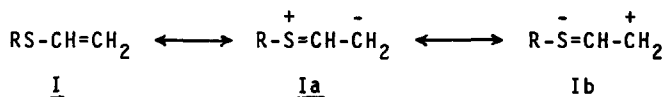
THERMAL DECOMPOSITION OF METHYL DIAZOACETATE
AND AZIDIFORMATE IN VINYL SULFIDES. IV.

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We have already reported that carbene and nitrene react with sulfur compounds to afford the corresponding sulfonium ylides^{1,2} and iminosulfuranes^{3,4}, and with allylic sulfides, these reactive species attack a sulfur atom 2.5-5 times more rapidly than the carbon-carbon double bond, and the main reaction proceeds via sulfonium ylides or iminosulfuranes⁵⁻⁸. On the other hand, in his pioneering work on thermolysis of ethyl diazoacetate in phenyl sulfide, Kaiser⁹ reported only the formation of the cyclopropylester. In more recent studies, Parham observed the formation of cyclopropanes in the reaction of dichlorocarbene with several vinyl sulfides^{10,11}. The remarkable difference in reactivities of a double bond between allylic and vinylic sulfides was probably attributed to the difference in nucleophilic character of the two double bonds, since vinyl sulfides are known to be electron rich olefins due to contributing structure of Ia.

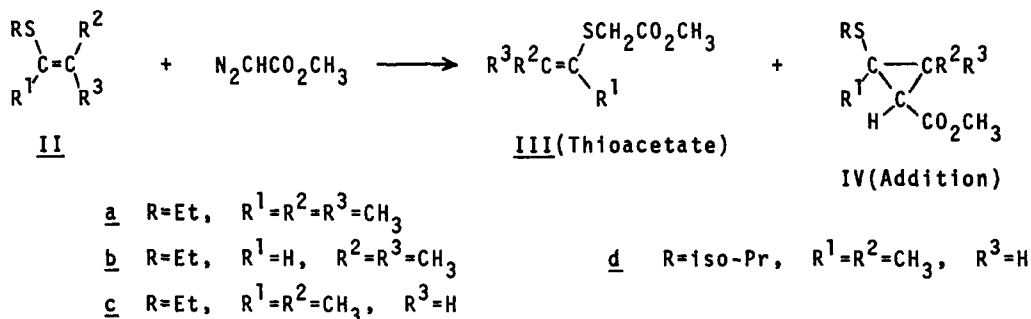


However, a contribution of the structure Ib is also possible owing to capability of a sulfur atom to expand the valence shell. This contribution may enhance the reactivity of the sulfur atom toward electrophilic carbene or nitrene.

This paper describes the first finding of the effective reactions of carbene and nitrene on sulfur atoms of vinyl sulfides.

Methyl diazoacetate (6.7 mmole) was dissolved in 30 mmole of trimethyl-

(ethylthio)ethylene (IIa) and thermolyzed at 150° for 6 hr. Vapor phase chromatographic analysis using several stationary phases detected two products IIIa and IVa formed in ca. 39 and 5% yields, respectively. The product IIIa proved to be methyl 1,2-dimethylpropenylthioacetate, and IVa was found to be the expected carbene addition product to the double bond. The structures of these products were determined by nmr and ir spectra, and elemental analysis.

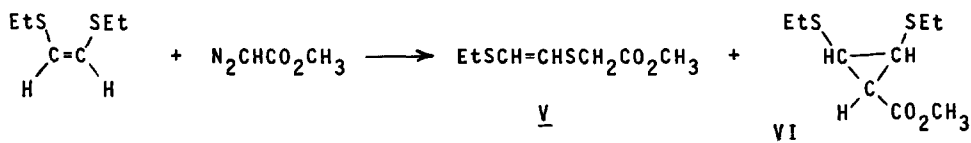


Similarly, a number of substituted vinyl sulfide gave rise to thioacetate as major products when treated with methyl diazoacetate as shown in Table I.

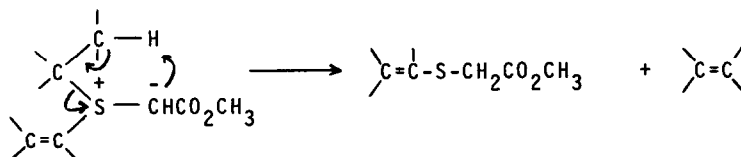
Table I
Thermolysis of Methyl Diazoacetate in Vinyl Sulfides.

<u>Sulfide</u>	<u>Thioacetate(III)</u>	<u>Cyclopropane(IV)</u>
IIa	39%	5%
IIb	21	3
IIc	29	5
IId	36	trace

The reaction of methyl diazoacetate with cis-diethylthioethylene afford a 38% yield of the thioacetate(V) and 6% of addition product(VI) of carbomethoxy-carbene to the olefin.

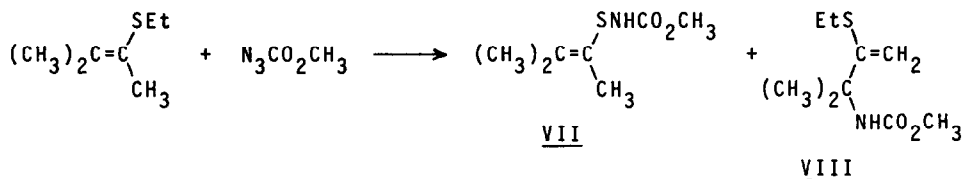


By analogy to the reaction with alkyl sulfides^{6,12}, the formation of these thioacetates may be formulated involving an attack of carbomethoxycarbene on the sulfur atom to form vinylsulfonium ylide followed by a cyclic elimination.



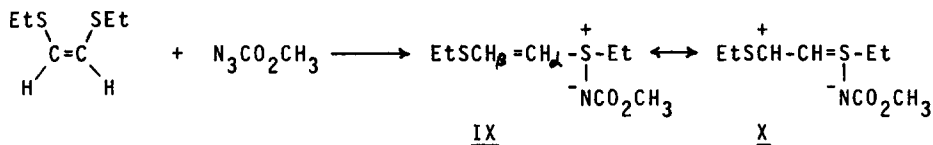
Data reveal that an attack of carbomethoxycarbene on sulfur appeared to be 4-5 times faster than addition on double bond. Furthermore, the competition reaction with trimethyl(ethylthio)ethylene and diethyl sulfide showed that the reactivity of carbomethoxycarbene on sulfur atom of vinyl sulfide was found to be higher than expected from electron withdrawing inductive effect of vinyl group. The enhancement in reactivity may be attributed to the contribution of structure Ib.

A similar sequence may be expected for the reaction of nitrene with vinyl sulfides. Thermolysis of methyl azidoformate in Ia at 100° gave two products VII and VIII in ca. 36 and 22% yields, respectively. Upon isolation, the product VII was proved to be methyl N-(1,1-dimethyl-2-ethylthio-2-propenyl)-carbamate.



Carbomethoxynitrene generated by the thermolysis and photolysis of methyl azidoformate attacks the double bond to form aziridine which is converted to VIII by the thermal rearrangement¹³. On the other hand, an attack of carbomethoxynitrene on a sulfur atom forming iminosulfurane, followed by 5-member cyclic elimination⁴ would lead to the formation of VII. In fact, the formation of iminosulfurane(IX) with vinyl sulfide was demonstrated in the reaction with *cis*-diethylthioethylene. The iminosulfurane(IX) showed a characteristic ir spectra at 1630 cm⁻¹, and the nmr spectra gave particularly

interesting evidence for the structure IX.



The β -vinyl proton (7.06 ppm, $J=9.0$ cps in cis form, and 7.34 ppm, $J=15.0$ cps in trans form) was more deshielded than the α -vinyl proton (6.16 ppm in cis form, and 5.99 ppm in trans form) as have been shown for vinyl sulfonium salts¹⁴. The electrons of the double bond must be delocalized to some extent through overlap of the carbon 2p orbital with the unoccupied 3d orbitals of sulfur as shown in contributing structure X.

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