Copper-catalysed Thermal Reactions of Acetylenic Sulphides with Diazoacetate. Acetylenic Sulphonium Ylides

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Summary Copper-catalysed thermal reactions of methyl diazoacetate with acetylenic sulphides gives (alkynylthio)-acetates, possibly *via* an acetylenic sulphonium ylide; the reactivity of the acetylenic sulphides is higher than that of diethyl sulphide.

Carbenes and carbenoids add to acetylene less readily than to olefins.[1] While only a few cases are known of such carbene reactions with acetylene–oxygen bonds, which lead to cyclopropene rearrangement products,[2] there are no reports on the reaction with acetylene–sulphur bonds. We report here that acetylenic sulphonium ylides are formed in the reaction of methoxycarbonyl carbene with acetylenic sulphides.

The reactions are conveniently carried out in the absence of solvent at elevated temperature. Heating an equimolar mixture of methyl diazoacetate and the acetylenic sulphide (Ia) in the presence of a catalytic amount of anhydrous $CuSO_4$ at 60° for 10 min gave a 35% yield (g.l.c.) of compound (IIa) instead of the expected cyclopropene derivative. Structure (IIa) is in accord with the observed spectral data: ν_{max} 2180 and 1745 cm^{-1}; δ 3·51 (s, 2H), 3·77 (s, 3H), and 7·2—7·5 (m, 5H); *m/e* 206. Similar reactions of methyl diazoacetate with the sulphides (Ib) and (Ic) in the presence of $CuSO_4$ gave the (alkynylthio)-acetates (IIb) and (IIc)(34 and 15% yields, respectively). No cyclopropene derivatives or rearrangement products were obtained.

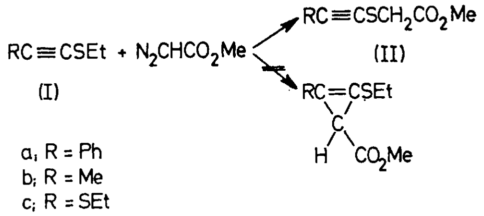
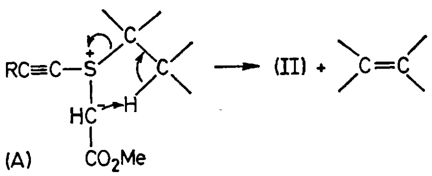


Table. Competitive reactions of methyl diazoacetate to sulphides ($CuSO_4$; 60°).

Reactant	Product	Relative Reactivities
$Me_2C{=}CHMe$	$Me_2\overbrace{C\cdot CHMe\cdot C}HCO_2Me$	1
EtSEt	$EtSCH_2CO_2Me$	7·1
$Me_2C{=}CHSEt$	$Me_2C{=}CHSCH_2CO_2Me$	4·6
$MeC{\equiv}CSEt$	$MeC{\equiv}CSCH_2CO_2Me$	9·2

By analogy with the reaction with alkyl sulphides,[3] the formation of compounds (II) may involve attack of methoxycarbonyl carbene on sulphur to form the acetylenic sulphonium ylide followed by cyclic elimination of olefin, although trapping of the acetylenic sulphonium ylide (A) was not successful.



The relative reactivity of the sulphur atom in the acetylenic sulphide compared with various other sulphides was investigated by competitive reactions with trimethylethylene. The results (Table) show that the acetylenic sulphide is the most reactive, probably owing to the contribution from the resonance structure $R\text{–}\overset{+}{C}{=}C{=}\overset{-}{S}\text{–}Et$, which is possible because sulphur can expand its valence shell.

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[1] W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971.

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[3] W. Ando, T. Yagihara, S. Kondo, K. Nakayama, H. Yamato, S. Nakaido, and T. Migita, *J. Org. Chem.*, 1971, **36**, 1732.