Novel Formation of a Stable Sulphur Ylide *via* Alkylation of a Dialkyl Sulphide by a Sulphonium Ion

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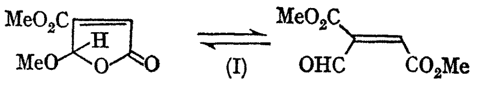
Summary Formation of a stable sulphur ylide (III) during attempted oxidation of dimethyl γ-bromomesaconate by dimethyl sulphoxide is described.

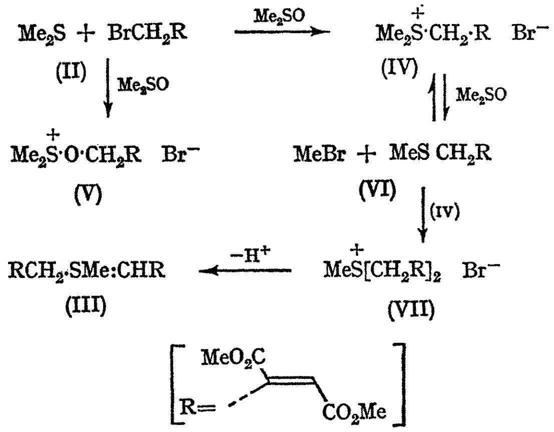
DURING one of our efforts to synthesise the methoxybutenolide (I), which was needed for the synthesis of a series of cross-conjugated diesters[†] by the Wittig condensation,



(I)

oxidation of dimethyl γ-bromomesaconate (II) with dimethyl sulphoxide in the presence of sodium hydrogen carbonate was attempted.[1] Instead of the expected butenolide (I), the highly stabilised, crystalline sulphur ylide (III), the suggested structure of which is fully supported by n.m.r., mass spectral, and analytical data, was isolated in 3% yield.

After consideration of the most probable modes of reaction, the following mechanism seems feasible as a reaction path for the formation of the sulphur ylide (III):



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[†] Details about these investigations will be published elsewhere.

The sulphonium salt (IV), which is a reaction product of dimethyl γ-bromomesaconate (II) and dimethyl sulphide, is regarded as the key intermediate in the formation of the ylide (III). Dimethyl sulphide probably is generated in low yield by oxidation of the bromo-ester (II) by Me_2SO, since the intermediate alkoxy-sulphonium salt (V)[2] was actually isolated in 4% yield and characterised as its crystalline tetraphenylborate.

The sulphonium salt (IV) then dissociates to methyl bromide and the sulphide (VI), which is alkylated by the sulphonium salt (IV) rather than dimethyl γ-bromomesaconate (II), to produce the ylide (III) *via* the intermediate sulphonium salt (VII). The ylide formation step is believed to be much faster than the alkylation step since, despite several attempts, the suggested intermediate sulphonium salt (VII) has not up to now been isolated. All the other suggested intermediates have been characterised as such and their structures proved by independent synthesis. For instance, treatment of a pure sample of the sulphonium salt (IV) with sodium hydrogen carbonate in Me_2SO gave the ylide (III) in 80% yield, but when 1 mole equivalent of the sulphide (VI) was added to a similar reaction mixture, the weight of ylide (III) produced was increased by 50%. Furthermore, when the sulphide (VI) was heated for 2 hr. at 70° with 1 mole equivalent of dimethyl γ-bromomesaconate (II) in Me_2SO in the presence of sodium hydrogen carbonate, the ylide (III) was formed in 6% yield, but on addition of 1 mole equivalent of dimethyl sulphide to the same reaction mixture, the ylide (III) was produced in 36% yield after 1 hr. at room temperature. The latter experiment provides striking evidence in favour of the sulphonium salt (IV) as the major alkylating agent.

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[1] N. Kornblum, W. J. Jones, and G. J. Anderson, *J. Amer. Chem. Soc.*, 1959, **81**, 4113.

[2] It has recently been demonstrated by several investigators that oxidations with Me_2SO proceed *via* intermediate alkoxysulphonium salts; *e.g.* K. Torssell, *Acta Chem. Scand.*, 1967, **21**, 1; W. W. Epstein and F. W. Sweat, *Chem. Rev.*, 1967, **67**, 247.

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