Reaction of Dimethyloxosulphonium Methylide with β-Diketones

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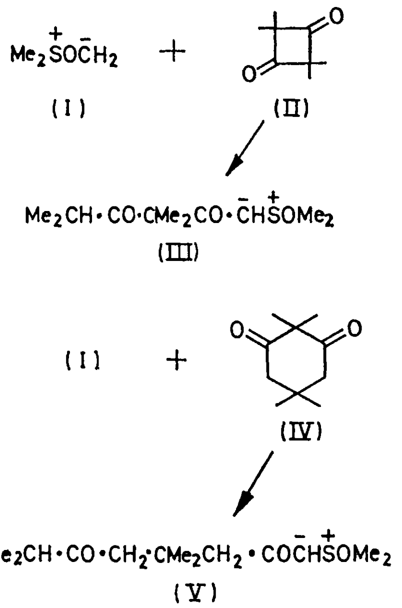
Summary Dimethyloxosulphonium methylide reacts with β-diketones to yield β-keto-oxosulphonium ylides.

THE reactions of sulphur ylides, first reported by Corey and Chaykovsky[1] to occur with aldehydes and ketones, have since been established to occur with other carbonyl systems.[2] These reactions have been extended to substrates such as isocyanates,[3] and the photodecomposition of β-ketosulphoxides has also been reported.[4]



The anion (I), generated from the reaction of trimethyloxosulphonium chloride with sodium hydride in tetrahydrofuran (THF), reacts with (II) to yield white crystals, m.p. 64·5—65°, identified as the β-keto-oxosulphonium ylide (III). This structural assignment is based on spectral characteristics [u.v.: λ_{max} (EtOH) 257 nm (ϵ 11,500);[2a] i.r.: λ_{max} (CCl_4): 5·86, 9·16, 9·88, and 11·1 μm; δ ($CDCl_3$) 1·08 (6H, d, *Me*$_2$CH), 1·35 (6H, s, *Me*$_2$C <), 2·9—3·3 (1H, m, Me$_2$C*H*), 3·45 (6H, s, *Me*$_2\overset{+}{S}$O), and 4·55 p.p.m. (1H, s, $\bar{C}HS^{+}O$); *m/e* 232 (M^+)] and satisfactory elemental analysis. The assignment is confirmed by the cleavage of (III) with zinc in acetic acid,[2a] to yield 3,3,5-trimethylhexane-2,4-dione, identified as its mono-2,4-dinitrophenylhydrazone,[5] m.p. 143—144°.

The formation of (III) may be formulated as a nucleophilic attack at one of the carbonyl carbons followed by electron migration and concomitant ring cleavage. Proton transfer to the resulting enolate system might be expected to take place readily, proceeding through a six-membered transition state, to yield (III).

When (IV) is submitted to the reaction, the ylide (V) is isolated, again identified by its spectral characteristics (u.v., i.r., n.m.r., and mass spectra), as well as cleavage to 4,4,8-trimethyloctane-2,6-dione on reaction with zinc in acetic acid.

The scope of this reaction is being investigated, especially whether its success depends on the cyclic and/or non-enolizable features of (II) and (IV). Initial results indicate that the substrate must be unable to enolize but need not be cyclic. Reaction with pentane-2,4-dione fails, but reaction with 2,2-dimethyl-1,3-diphenylpropane-1,3-dione yields isobutyrophenone, the expected sulphur-free cleavage product, isolated as its 2,4-dinitrophenylhydrazone[6] (m.p. 161—162°).

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