Syntheses with Carbanions derived from Carbonyl-stabilized Ylides; Products from Reactions of Lithio-derivatives of Dimethylsulphonium Diacetylmethylide

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Summary The lithio-derivative prepared from dimethylsulphonium diacetylmethylide and n-butyl-lithium, reacted with a series of electrophiles to give alkylated and/or cyclic products.

CARBONYL-STABILIZED sulphonium ylides, such as sulphonium phenacylides, react with alkyl halide,[1] sulphonyl chloride,[2] and acid anhydride[3] at the ylide carbon atom. In contrast, bis-carbonyl-stabilized sulphonium ylides are said to be stable and have no similar nucleophilic reactivity. By using this stability the lithiation of a bis-carbonyl-stabilized sulphonium ylide and its potential synthetic utility without decomposition of the sulphonium group has been investigated.

Dimethylsulphonium diacetylmethylide (**1**) was lithiated at the acetyl methyl position with Bu^nLi or lithium di-isopropylamide (1 equiv.) in tetrahydrofuran (THF) or dimethoxyethane (DME) at −10 to −15 °C under nitrogen.†

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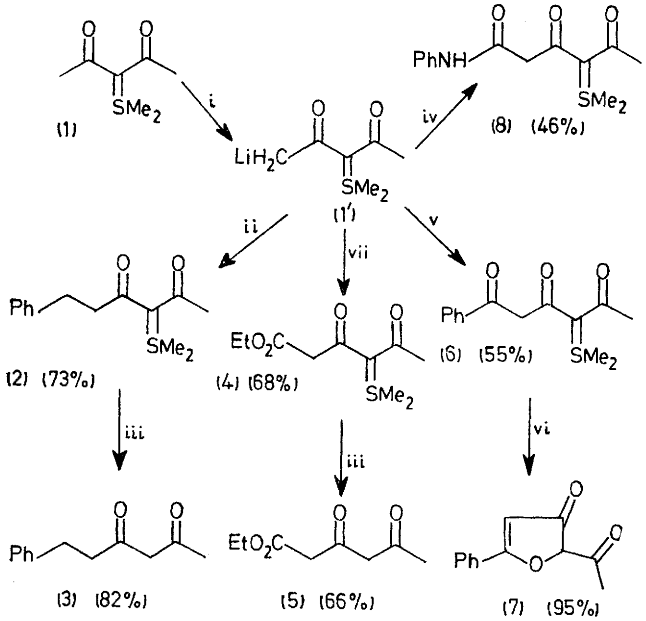
† A small amount of the *S*-methyl lithiated compound was also formed under these conditions, as shown by the reaction of (**1**) with benzyl bromide which gave (**2**) (73%) and methylphenethylsulphonium diacetylmethylide (13%).



Reagents: i, $\mathrm{Bu^nLi}$, THF; ii, $\mathrm{PhCH_2Br}$; iii, Zn–AcOH; iv, PhNCO; v, PhCOCl; vi, refluxing $\mathrm{C_6H_6}$; vii, $\mathrm{ClCO_2Et}$.

The lithiated sulphonium ylide (**1′**) was not formed below −30 °C; however above −25 °C (**1′**) was obtained as a white precipitate in THF or DME. Compound (**1′**) is stable below 0 °C for several hours under nitrogen, but at > 30 °C it gradually decomposes.

The ylide (**1′**) reacted with benzyl bromide (1 equiv.) to give the alkylated product (**2**) (73%) which underwent reductive elimination of $\mathrm{Me_2S}$ on treatment with Zn–AcOH in dioxan at room temperature to give the corresponding β-diketone (**3**) (82%). The copper chelate of (**3**), m.p. 160—161 °C, was identical to that of an authentic sample.[4]

Compound (**1′**) reacted with ethyl chloroformate (0·5 equiv.) to give the ylide ester (**4**) (68%),‡ yield based on ethyl chloroformate, which also underwent reductive elimination of $\mathrm{Me_2S}$ to give the diketoester (**5**) (66%). The structure of (**5**) was confirmed by comparison of its n.m.r. spectrum with that of an authentic sample.[5]

Reaction of the ylide (**1′**) with benzoyl chloride (0·5 equiv.) afforded the triketosulphonium ylide (**6**) (55%). Heating of compound (**6**) in refluxing benzene for 1 h afforded the furanone (**7**), m.p. 200—201 °C, quantitatively, possibly *via* initial proton transfer from the active methylene group to the ylide carbon atom in (**6**), followed by attack of the resulting enolate anion at the ylide carbon atom.[6] $\mathrm{Me_2S}$ is then displaced concertedly to give the furanone (**7**).

Phenyl isocyanate also reacted with (**1′**) (2 equiv.) to give the new ylide (**8**) (46%).

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‡ The lithium–hydrogen exchange (1) was assumed to occur in solution, so a molar ratio of 2 : 1 was used.

$$(4) + (1') \rightarrow (1) + \mathrm{EtOCO\bar{C}HCOC(COMe){=}SMe_2Li^+} \qquad (1)$$

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[5] S. N. Huckin and L. Weiler, *Tetrahedron Letters*, 1972, 2405.
[6] For a proton transfer reaction of a sulphonium ylide see: J. W. Batty, P. D. Howes, and C. J. M. Stirling, *Chem. Comm.* 1971, 534.