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

By MAKOTO YAMAMOTO

(*Department of Chemistry, Saga University, Saga-shi* 840, *Japan*)

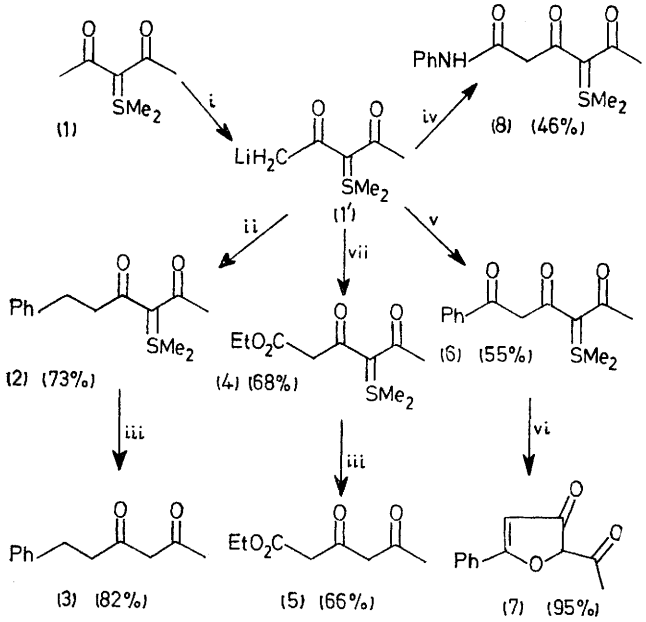
Summary The lithio-derivative prepared from dimethylsulphonium diacetylmethylide and n-butyl-lithium, reacted with a series of electrophiles to give alkylated and/or cyclic products.

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.†

---

† 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, Bu^nLi, THF; ii, $PhCH_2Br$; iii, Zn–AcOH; iv, PhNCO; v, PhCOCl; vi, refluxing C_6H_6; vii, $ClCO_2Et$.

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 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 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] 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%).

This work was supported by the Scientific Research Fund of Ministry of Education, Japanese Government.

(*Received*, 11*th February*, 1975; *Com.* 172.)

---

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

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

[1] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, 1966, **31**, 1689.
[2] H. Nozaki, M. Takaku, Y. Hayashi, and K. Kondo, *Tetrahedron*, 1968, **24**, 6563.
[3] A. W. Johnson and R. T. Amel, *J. Org. Chem.* 1969, **34**, 1240.
[4] K. G. Hampton, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, 1965, **30**, 61.
[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.