

Rearrangement of Allylic Silylsulphonium Ylides. A Synthesis of $\beta\gamma$ -Unsaturated Aldehydes

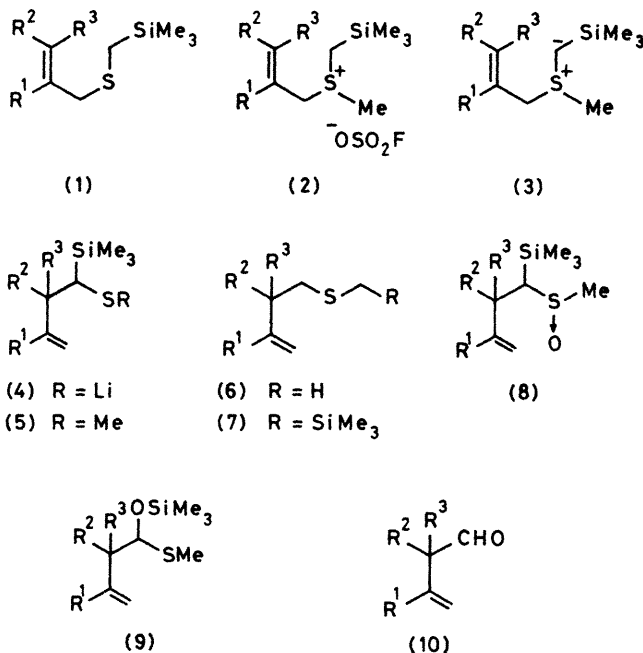
By PHILIP J. KOCIENSKI

(Department of Organic Chemistry, The University, Leeds LS2 9JT)

Summary The ylides derived from the reaction of allylic silylmethylsulphonium salts with *n*-butyl-lithium rearrange to homoallylic α -methylthiosilanes which are precursors to $\beta\gamma$ -unsaturated aldehydes.

SILICON can have a pronounced effect on the chemistry of sulphur compounds. For example carbanions co-operatively stabilized by both elements¹ form readily at low temperature and are stable and moderately nucleophilic. Similarly, silicon-activated Pummerer rearrangement of sulfoxides² proceeds at room temperature or below to give hydrolytically labile *O*-trimethylsilylhemithioacetals. A combination of these advantageous properties was recently used in a new procedure for nucleophilic formylation.^{3,4} We now report a permutation which gives $\beta\gamma$ -unsaturated aldehydes.

When the *S*-allylic thiomethylsilane (**1c**) was metallated at 0 °C with *n*-butyl-lithium in tetrahydrofuran (THF), a [2,3] sigmatropic rearrangement of the resultant carbanion was observed, to give the lithium thiolate (**4c**) which could be alkylated with methyl iodide to give the sulphide (**5c**) in 55% yield accompanied by several minor by-products which were difficult to separate. By contrast, the *S*-allylic *S*-trimethylsilylmethylsulphonium fluorosulphonate salts (**2**), prepared in high yield from the sulphides (**1**)⁵ by reaction with methyl fluorosulphonate in CH_2Cl_2 at 0 °C, reacted with *n*-butyl-lithium in THF at -78 °C to give the ylides derived from selective deprotonation of the carbon bearing silicon and sulphur. The ylides (**3**) underwent a [2,3] sigmatropic rearrangement below -20 °C to give the homoallylic α -methylthiosilanes (**5**) cleanly and in good yield (65–75%). Minor by-products (**6**) and (**7**) (*ca.* 10% each) presumably



arose from rearrangement of alternative ylides generated by deprotonation of the SMe group in the case of (7) and desilylation in the case of (6).

The rearranged α -methylthiosilanes (5) were converted into the aldehydes (10) in 40—60% overall yield *via* the sila-Pummerer reaction. Oxidation of (5) with 1 mol. equiv. of *m*-chloroperbenzoic acid in CH_2Cl_2 at -40°C gave the thermally labile sulfoxides (8) which had rearranged to the *O*-trimethylsilylhemithioacetals (9) after the usual extractive work-up. These were hydrolysed in aqueous THF at 20°C for 18 h in the presence of 1 mol. equiv. of oxalic acid. It is noteworthy that in the synthesis of γ -cyclocitral (10d),

the hydrolysis of (9d) proceeded without rearrangement of the unstable double bond into conjugation with the carbonyl group.

The present work expands the scope of carbon-carbon bond-forming reactions available to nucleophiles stabilized by sulphur and silicon and provides a useful application of silicon-substituted sulphonium ylides about which little is known.⁶

We thank the S.R.C. for support and John Tideswell for technical assistance.

(Received, 18th August 1980; Com. 908.)

¹ D. Peterson, *J. Org. Chem.*, 1958, **33**, 780.

² A. G. Brook, *Acc. Chem. Res.*, 1974, **7**, 77.

³ P. J. Kocienski, *Tetrahedron Lett.*, 1980, **21**, 1559.

⁴ D. J. Ager and R. C. Cookson, *Tetrahedron Lett.*, 1980, **21**, 1677.

⁵ Prepared by reaction of the allylic chloride with trimethylsilylmethanethiol in ethanolic sodium ethoxide. The thiol is known: D. C. Noller and H. W. Post, *J. Org. Chem.*, 1952, **17**, 1393.

⁶ F. Cooke, P. Magnus, and G. L. Bundy, *J. Chem. Soc., Chem. Commun.*, 1978, 714.