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ALDEHYDES FROM ALKYLLITHIUMS WITH 2-CARBON HOMOLOGATION[1]

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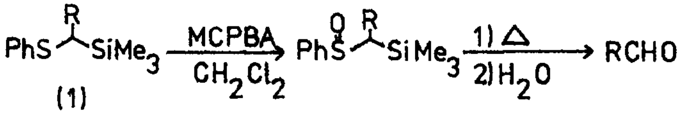
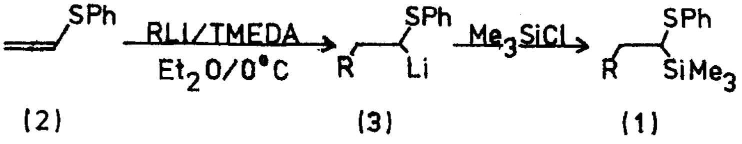
Summary: 1-Phenylthio-trimethylsilylalkanes, which are readily converted to aldehydes, are prepared by the addition of alkyllithiums to phenylthioethene, trimethylsilylethene and 1-phenylthio-1-trimethylsilylethene.

It has already been shown that 1-phenylthio-1-trimethylsilylalkanes (1) can be converted to aldehydes by oxidation to the sulphoxide, thermal rearrangement and hydrolysis[2,3]:



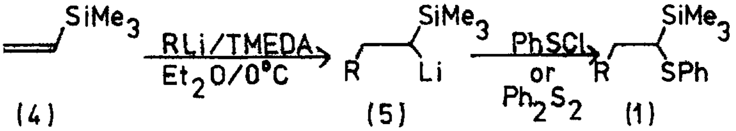
The silanes (1) have been prepared by alkylation of phenylthiotrimethylsilylmethyllithium[2,3], we now wish to report alternative preparations of (1).

Alkyllithiums add to phenylthioethene (2) in diethyl ether at 0°C in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA) to give the lithium derivatives (3) in high yield[4]. Silylation with chlorotrimethylsilane gave (1) (see scheme 1 and table 1).



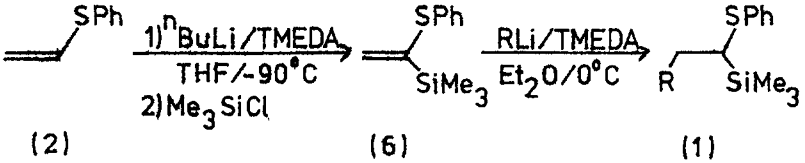
Scheme 1.

In a similar manner, alkyllithiums added to trimethylsilylethene (4)[5] to give (5), which when treated with phenylsulphenyl chloride or diphenyldisulphide gave (1) (see scheme 2 and table 2). The yields were not as high as those obtained using the sequence outlined in scheme 1.



Scheme 2.

Finally, the silanes (1) were prepared by the addition of alkyllithiums to 1-phenylthio-1-trimethylsilylethene (6)[6,7] (see scheme 3 and table 3)[8]. The vinylsilane (6) was prepared by quenching 1-lithio-1-phenylthioethene[9] with chlorotrimethylsilane (scheme 3).



Scheme 3.

Table 1.

$$(2) \xrightarrow[\text{2) } Me_3SiCl]{\text{1) } RLi/Et_2O/TMEDA/0^{o}C} (1)$$

R=	Yield of (1) (%)
Me	81
^{n}Bu	85
Ph	73

Table 2.

$$(4) \xrightarrow[\text{2) } RSX]{\text{1) } RLi/Et_2O/TMEDA/0^{o}C} (1)$$

R=	X=	Yield of (1)(%)
Me	Cl	53
Me	SPh	62
^{n}Bu	Cl	60
^{n}Bu	SPh	67
Ph	Cl	51
Ph	SPh	55

Table 3.

$$(6) \xrightarrow{RLi/Et_2O/TMEDA/0^{o}C} (1)$$

R=	Yield of (1)(%)
Me	89
^{n}Bu	85
Ph	78

References and Notes.

1. Part of this work was carried out at the Department of Chemistry, University of Southampton. An S.R.C. Postdoctoral Fellowship and the help and advice of Professor Richard Cookson are gratefully acknowledged.
2. D.J. Ager and R.C. Cookson, *Tetrahedron Letters*, 1980,21,1677
3. P.J. Kocienski, *Tetrahedron Letters*, 1980,21,1559
4. The reactions were carried out by slowly adding (typically over 1h) a dilute solution of the olefin to an excess of the alkyllithium in diethyl ether containing one equivalent of TMEDA.
5. c.f. P.F. Hudrlik and D. Peterson, *Tetrahedron Letters*, 1974,1133
   L.F. Cason and H.G. Brooks, *J.Org.Chem.*, 1954,19,1278
6. B. Harirchian and P. Magnus, *Chem.Comm.*, 1977,522
7. By using the method described in (4) the yields are much higher than those previously reported for the addition of alkyllithiums to (6).
   M. van der Leij and B. Zwanenburg, *Tetrahedron Letters*, 1978,3383
8. The preparation of ketones by the addition of alkyllithiums to (6) followed by alkyl iodides is well advanced.
9. R.C. Cookson and P.J. Parsons, *Chem.Comm.*, 1976,990.
   See also ref. 6.

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