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THE PREPARATION OF KETONES WITH 1-PHENYLTHIO-1-TRIMETHYLSILYLETHENE[1]

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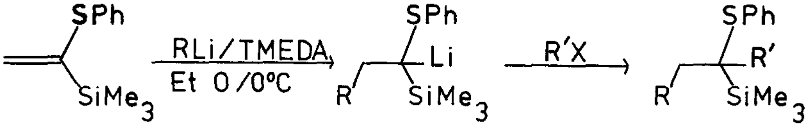
Summary: The ketone equivalents(3) were prepared by the addition of an alkyllithium to 1-phenylthio-1-trimethylsilylmethane(1) followed by reaction with an alkyl halide.

It has already been noted that 1-phenylthio-1-trimethylsilylalkanes cannot be deprotonated to give acyl anion equivalents[3]. This has meant that alternative approaches to the required anions have had to be found.

The addition of an alkyllithium to 1-phenylthio-1-trimethylsilylethene(1) has been used to prepare aldehydes[4]; the required acyl anion equivalent(2) is formed in this reaction and has now been successfully alkylated to give the ketone equivalents(3).



(1) (2) (3)

The olefin(1) was added in ether solution, to a slight excess of the alkyllithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) in ether at 0°C over 1 - 1.5h.. After a further 0.5h., excess alkyl halide was added. Extractive work up gave the required ketone equivalents(3). The yields are given in the table and, as expected, were highest when the alkyl halide was primary; secondary halides gave moderate to no yield. Some experiments were carried out with t-butyllithium as base, but the yields were low which may have been due to this alkyllithium acting as a base with the olefin(1).

The silanes(3) were converted to the corresponding ketones by oxidation, thermal rearrangement and hydrolysis as previously described for aldehydes[5-7].

TABLE

Preparation of ketone equivalents(3) from 1-phenylthio-1-trimethylsilylethene(1).

Alkyllithium R=	Alkyl halide R'X	Yield of (3) (%)	Yield of ketone[a] (%)
Me	MeI	85	70
Me	EtI	79	62
Me	^{n}BuBr	64	63
Me	^{n}BuI	69	63
Me	^{s}BuBr	23	-[b]
Me	$^{n}C_5H_{11}I$	67	67
Me	$^{c}C_6H_{11}Br$	0	-
^{n}Bu	MeI	82	67
^{n}Bu	EtI	80	69
^{n}Bu	^{n}BuBr	70	52
^{n}Bu	^{n}BuI	76	52
^{t}Bu	Me	24	-
^{t}Bu	^{n}Bu	18	-

[a] Isolated as the 2,4-dinitrophenylhydrazone; yield from (3).

[b] Denotes that the reaction was not carried out.

References and Notes

1. Part of this work was carried out at the Department of Chemistry, The University, Southampton, SO9 5NH. An SRC Postdoctoral Fellowship is acknowledged.
2. Present address: Department of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, Ohio 43606.
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7. The thermal rearrangement of sulphoxides derived from (3) is not always straightforward if secondary alkyl centres are present, the formation of vinylsulphides becoming a major pathway. This work will be dealt with in a future paper.

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