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A NEW METHOD FOR PREPARING 1-PHENYLTHIO-1-TRIMETHYLSILYLALKANES: THE PREPARATION OF α-SILYLCARBANIONS AND OLEFINS.

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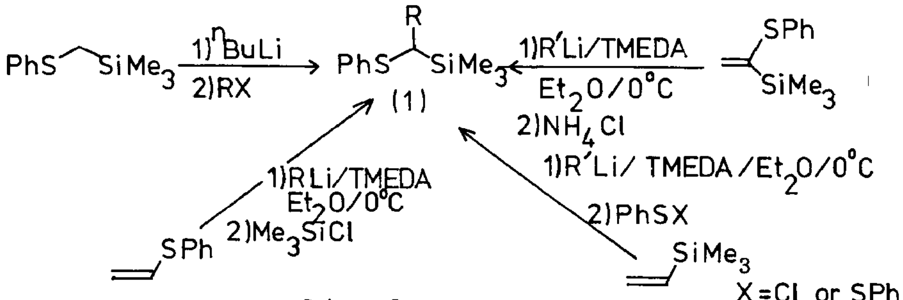
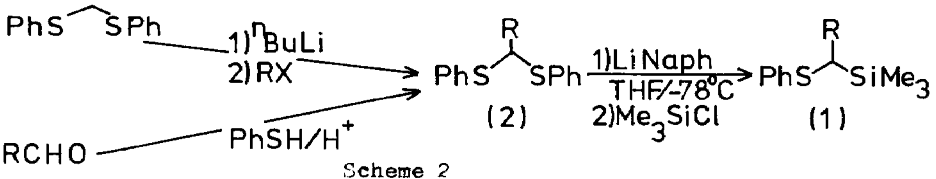
Summary: 1-Phenylthio-1-trimethylsilylalkanes(1) are prepared in high yield from 1,1-bis(phenylthio)acetals(2) by reaction with lithium naphthalenide(3) followed by chlorotrimethylsilane. α-Silylcarbanions are formed from the alkanes(1) and lithium naphthalenide(3). Subsequent reaction with carbonyl compounds gave the olefins(4) via the Peterson reaction.

The preparation of 1-phenylthio-1-trimethylsilylalkanes(1) has been described previously[1-3]. They are readily available from phenylthiotrimethylsilylmethane(2) by alkylation of the anion[1,2] or by the addition of alkyllithiums to appropriately substituted olefins[3] (scheme 1).



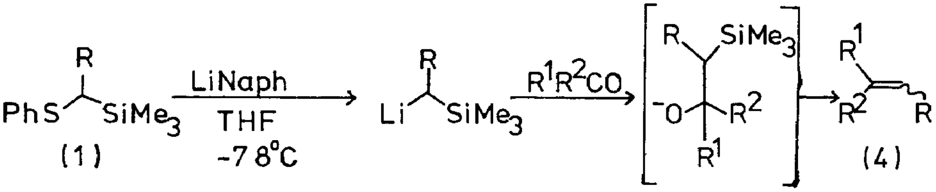
Scheme 1

In addition to the above methods, 1-phenylthio-1-trimethylsilylalkanes may be prepared from bis(phenylthio)acetals(2) by the method of Screttas[4] and Cohen[5]. The acetal(2) was added to a solution of lithium naphthalenide(Li Naph)(3)(2.2 equivalents) at -78°C and stirred at this temperature for 0.25h.. Quenching the reaction with chlorotrimethylsilane gave, after work-up, the alkane(1)(see table 1 and scheme 2). As bis(phenylthio)acetals(2) can be prepared from aldehydes and thiophenol in the presence of an acid[6], besides alkylation of bis(phenylthio)methane[7], the above reaction formally describes the use of 1-phenylthio-1-trimethylsilylalkanes(1) as an aldehyde protecting group because these alkanes(1) have already been converted to their corresponding aldehydes[1,2]. Although this is feasible, the reaction's main use is to provide a new, high yielding method for preparing the alkanes(1) when the R group is not a straight alkyl chain.



Scheme 2

Unlike the Wittig reaction[8], the Peterson reaction[9] has not found such a widespread use to prepare olefins[10]. One of the reasons for this is the α-silylcarbanions are not readily available. α-Silylcarbanions have been prepared by the addition of alkyllithiums to vinylsilanes[11], substitution of selenium[12] or directly from the silane[13], although this last method gives low yields. The major class of α-silylcarbanion has another anion stabilising group present[14] but these, of course, give rise to substituted olefins[15]. The reaction of 1-phenylthio-1-trimethylsilylalkanes(1) with lithium naphthalenide(3) is, therfore, a useful general method for preparing α-silylcarbanions. These anions were reacted with aldehydes or ketones[17] to give, via the Peterson reaction[9], the corresponding olefins(4)(see table 2 and scheme 3)



Scheme 3

This method of preparing olefins is novel as 1-phenylthio-1-trimethylsilylalkanes(1) are masked aldehydes[1,2] and retrosynthetically the olefin is formed by joining two carbonyl groups together:-

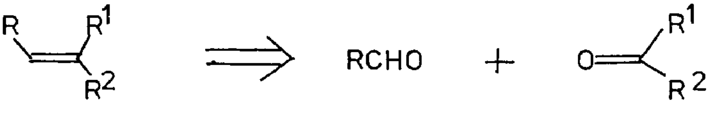


TABLE 1

The preparation of 1-phenylthio-1-trimethylsilylalkanes(1) from bis(phenylthio)acetals by reaction with lithium naphthalenide followed by chlorotrimethylsilane.

(2),R=	Yield of (1)(%)
H	86
Me	90
^{n}Pr	82
^{i}Pr	87
^{n}Bu	75
^{s}Bu	79
$^{n}C_5H_{11}$	72
Ph	84

TABLE 2

The preparation of olefins from 1-phenylthio-1-trimethylsilylalkanes(1) by reaction with lithium naphthalenide followed by the carbonyl compound.

	Yield of olefin(4)(%)					
(1),R=	MeCHO	^{n}PrCHO	PhCHO	Me_2CO	PhCOMe	Ph_2CO
H	-[a]	64	77	-	83	71
Me	-	74	75	-	79	80
^{n}Bu	82	78	86	61	76	74
Ph[16]	71	85	76	70	69	59

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14)The use of one or more phenyl groups or a second silyl group has been included in this group.

15)For examples of groups used see a)H. Sakurai, K.-i. Nishiwaka and M. Kira, Tetrahedron Letters, 1973,4193, b)I. Ojima and M. Kumagai, Tetrahedron Letters, 1974,4005, c)K. Sachdev and H.S. Sachdev, Tetrahedron Letters, 1976,4223, d)K. Sachdev, Tetrahedron Letters, 1976,4041, e)K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto and H. Nozaki, J.Amer.Chem.Soc., 1974,96,1620, f)F. Cooke and P. Magnus, J.Chem.Soc.,Chem.Commun.,1977,513, g)F.A. Carey and A.S. Court, J.Org.Chem., 1972,37,939, h)F.A. Carey and O. Hernandez, J.Org.Chem., 1973,38,2670, and references 1, 2, 9, 10b, 11a and 16.

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17)Other electrophiles are under active investigation.

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