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THE PREPARATION OF PHENYL KETONES USING (PHENYLTHIO)PHENYL(TRIMETHYLSILYL)METHYL-LITHIUM[1]

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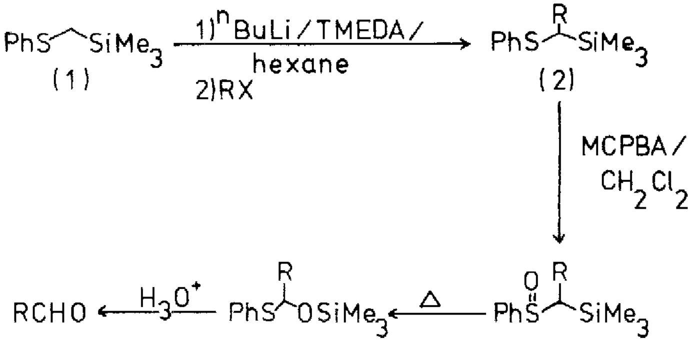
Summary: Phenyl ketones are prepared by alkylation of (phenylthio)phenyl(trimethylsilyl)methyl-lithium followed by oxidation and rearrangement.

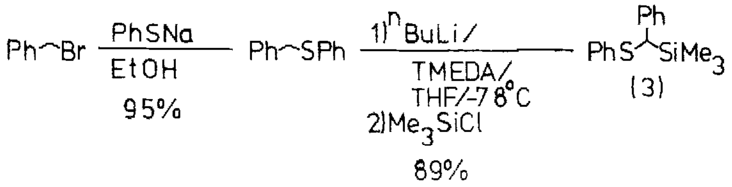
We have previously reported that phenylthiotrimethylsilylmethane (1) can be used to prepare aldehydes (scheme 1)[2].



Scheme 1.

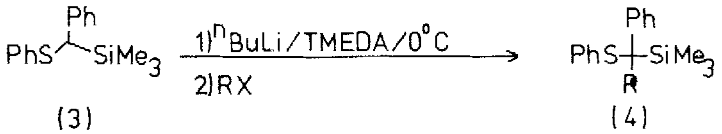
The alkylated products (2), have, so far, defied attempts to carry out the second alkylation[3,4]. This is not the case, however, when R = Ph.

It is not possible to prepare (phenylthio)phenyl(trimethylsilyl)methane (3) by the route given in scheme 1. (3) was prepared by the method given in scheme 2.

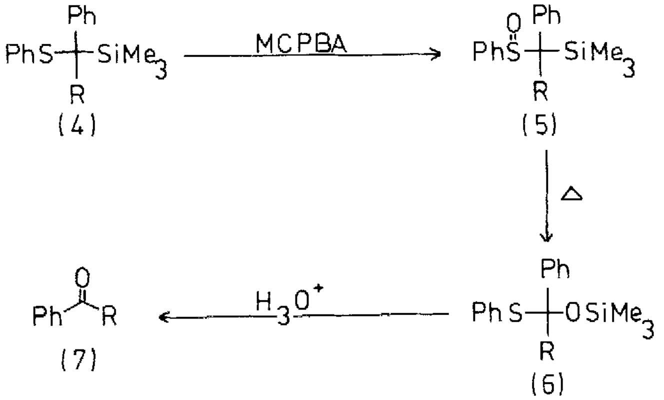


Scheme 2.

The adduct (3) was lithiated using n-butyllithium-N,N,N',N'-tetramethylethylenediamine (TMEDA) complex in hexane at 0°C. The results of the subsequent alkylations are given in the table.



These products (4) were converted to the sulphoxides (5) by oxidation with m-chloroperoxybenzoic acid (MCPBA) in dichloromethane, followed by heating in dry benzene to give the O-trimethylsilylphenylthioacetal (6)[2,5]. Conversion to the ketone (7) was completed by aqueous acid[6].



Table

$$(3)\xrightarrow[\text{2)RX}]{\text{1)}{}^{n}\text{BuLi/TMEDA}}(4)\xrightarrow[\text{2)}\ \Delta]{\text{1)MCPBA}}(6)\xrightarrow{H_3O^+}(7)$$

Yield (%)[a]

RX	(4)	(6)[b,c]	(7)[d]
MeI	94	85	82
EtI	85	78	74
^{n}PrI	86	77	69
^{s}PrI	34	-	53
^{n}BuBr	75	81	75
^{n}BuI	85		
${}^{c}C_6H_{11}Br$	0	-	-
${}^{n}C_{12}H_{25}Br$	64	75	70
allyl - Br	73	79	72[e]
$PhCH_2Br$	71	72	69

a. All new compounds have been characterised. Ketones were characterised as their 2,4-dinitrophenylhydrazones.

b. Overall yield of (6) from (4).

c. n.m.r. yield.

d. Overall yield from (4)

e. The double bond moved into conjugation during hydrolysis.

References and Notes.

1. Part of this work was carried out at the department of Chemistry, The University, Southampton SO9 5NH. 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. The alkylated products (2) have proven to be resistant to ^{n}BuLi and LDA. The use of additives (such as TMEDA, HMPA etc) gave at best only trace amounts of the required lithiated species, direct attack on the silyl group, usually, being the major pathway. Alternative methods for making the required anions are well advanced.
4. P.J. Kocienski, Tetrahedron Letters, 1980,21,1559
5. A.G. Brook and D.G. Anderson, Canad.J.Chem., 1968,46,2115
   E. Vedejs and M. Mullins, Tetrahedron Letters, 1975,2017
6. T.H. Chan and B.S. Ong, Tetrahedron Letters, 1976, 319

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