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A NEW SYNTHETIC METHOD FOR α-KETOSILANES EMPLOYING METHOXY(PHENYLTHIO)TRIALKYLSILYLMETHANE AS AN α-SILYLACYL ANION EQUIVALENT

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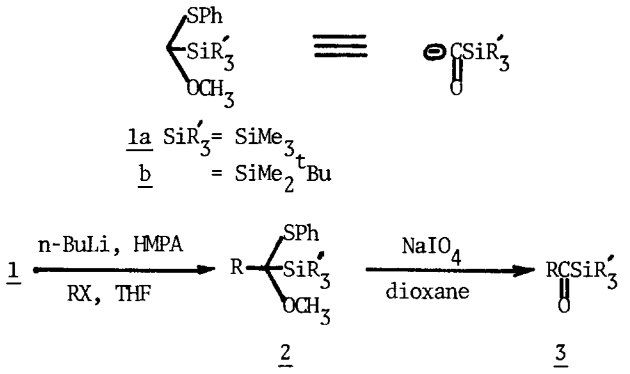
Summary: Development of a new synthetic method for α-ketosilanes can be achieved by a sequence of alkylation of methoxy(phenylthio)trialkylsilylmethane and oxidation with $NaIO_4$.

Due to their unique spectral behaviors1) and versatility as synthetic tools,2) a number of synthetic methods for α-ketosilanes3) have been developed so far. From a synthetic point of view, however, more convenient and practical methods still seem to be desired. In our continuous efforts to utilize methoxy(phenylthio)methane as a reagent for one carbon homologation, we have revealed an excellent transformation of alkylated methoxy(phenylthio)methanes to aldehydes4) by treatment with m-CPBA under nearly neutral conditions.

We wish to report here that a successful synthesis of α-ketosilanes can be realized by a sequence of alkylation of methoxy(phenylthio)trialkylsilylmethane (1)5) and oxidation with $NaIO_4$ as shown in Scheme.

Scheme

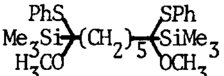


The notable features of the present method are: i) an excellent total yield, ii) simplicity of its manipulation, iii) mildness of the reaction conditions, and iv) availability of a variety of α-ketosilanes with useful functionalities as summarized in Table. A general procedure is as follows. Successive treatment of 1 in THF with n-BuLi (1.2 eq) at -40 °C for 0.5 h followed by HMPA (1.2 eq) and alkyl halide (1.2 eq) at -40 °C for 0.5 h afforded 2 in good yield. Then, conversion of 2 into 3 was achieved by treatment with $NaIO_4$ (1.2 eq) in dioxane-water (5:1) at room temperature for 1 h. Although m-CPBA is also effective for this oxidation, $NaIO_4$ proved to be superior to m-CPBA.

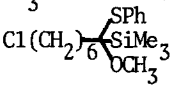
Table Conversion of 1 into α-ketosilanes 3

entry	1	RX	Yield (%)[a]	
			2	3
1	1a	n-C_4H_9I	81	88
2	1a	$THPO(CH_2)_5Cl$	73	98
3	1a	n-$C_9H_{19}Br$	82	93
4	1a	$Br(CH_2)_5Br$[b]	84[c]	97[d]
5	1a	$Cl(CH_2)_6Cl$[e]	71[f]	89[g]
6	1b	n-$C_6H_{13}Br$	90	88
7	1b	$THPO(CH_2)_3Br$	89	87
8	1b	$THPO(CH_2)_5Cl$	17[h]	91
9	1b	$THPO(CH_2)_5I$	84	91

a) Isolated yield after column chromatography (silica gel). b) RX/1a (molar ratio)=0.5.

c) 

d) $Me_3SiCO(CH_2)_5COSiMe_3$ e) RX (3.0 eq/1a) was added in one portion.

f) 

g) $Cl(CH_2)_6COSiMe_3$ h) Reaction conditions, -40 °C, 6 h.

References

1) For the most recent paper on this subject: A. G. Brook, F. Abdesaken, G. Gutekunst, and N. Plavac, Organometallics, 1, 994 (1982).

2) (a) I. Kuwajima, K. Atsumi, T. Tanaka, and T. Inoue, Chem. Lett., 1239 (1979).
(b) I. Kuwajima and M. Kato, Tetrahedron Lett., 21, 623 (1980).
(c) H. J. Reich, J. J. Rusek, and R. E. Olson, J. Am. Chem. Soc., 101, 2225 (1979).
(d) H. J. Reich, R. E. Olson, and M. C. Clark, J. Am. Chem. Soc., 102, 1423 (1980).

3) (a) I. Kuwajima, T. Abe, and N. Minami, Chem. Lett., 993 (1976), and references cited therein.
(b) I. Kuwajima, M. Kato, and T. Sato, J. Chem. Soc., Chem. Commun., 478 (1978).
(c) I. Kuwajima, A. Mori, and M. Kato, Bull. Chem. Soc. Jpn., 53, 2634 (1980).
(d) T. Cohen and J. R. Matz, J. Am. Chem. Soc., 102, 6900 (1980).
(e) K. Yamamoto, S. Suzuki, and J. Tsuji, Tetrahedron Lett., 21, 1653 (1980).
(f) S. Murai, I. Ryu, J. Iriguchi, and N. Sonoda, J. Am. Chem. Soc., 106, 2440 (1984), and references cited therein.

4) T. Mandai, K. Hara, T. Nakajima, M. Kawada, and J. Otera, Tetrahedron Lett., 24, 4993 (1983).

5) The compounds 1a and 1b were prepared in 91% and 94% yields, respectively by adding Me_3SiCl (3.0 eq) and $^tBuMe_2SiCl$ (1.2 eq) in one portion at -78 °C to the carbanion of methoxy(phenylthio)methane in THF generated by n-BuLi at -40 °C for 0.5 h. cf: A. de Groot and B. J. Jansen, Syn. Commun., 985 (1983). S. Hackett and T. Livinghouse, Tetrahedron Lett., 25, 3539 (1984).

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