Efficient Method for the Preparation of Trimethylsilyl Enol Ethers of Acyltrimethylsilanes

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Summary Treatment of trimethylsilyl enol ethers of benzenethiol esters with metallic sodium–trimethylchlorosilane affords the corresponding trimethylsilyl enol ethers of acyltrimethylsilanes in excellent yield.

RECENTLY, we described the synthetic use of trimethylsilyl enol ethers of acyltrimethylsilanes (**1**),[1] for example, in the synthesis of $\alpha\beta$-unsaturated aldehydes *via* β-alkoxyacylsilanes,[2] β-hydroxyalkyl- or β-ketoalkyl-trimethylsilanes *via* α-chloroacylsilanes,[3] and $\alpha\beta$-unsaturated acyltrimethylsilanes *via* α-phenylthioacylsilanes.[4] However, we sometimes encountered difficulties in purifying the silanes (**1**) or in large scale preparations. We report here a novel preparation of the silanes (**1**) which is also applicable in syntheses.

It is well known that reductive removal of sulphur from sulphides can easily be achieved with alkali metals in the presence of a proton source such as secondary amines.[5] We have examined such reactions with trimethylchlorosilane replacing the proton source and have found a new method for carbon–silicon bond formation. The benzenethiol esters (**2**) could be converted into the corresponding trimethylsilyl enol ethers (**3**) in almost quantitative yield by treatment with lithium di-isopropylamide followed by quenching with trimethylchlorosilane.[6] Treatment with a reductive silylating system caused the ready and efficient conversion of the carbon–sulphur bond of (**3**) into a carbon–silicon bond. Thus, the silyl ether (**3**) was added to a solution of trimethylchlorosilane (8 equiv.) in benzene† containing sodium dispersion (9 equiv.) under reflux. After heating for a further 1—2 h, the deposited material was filtered off. Removal of solvent, followed by fractional distillation, afforded the corresponding silyl enol ether of the acyltrimethylsilane (**1**) in excellent yield along with phenyltrimethylsilane, phenylthiotrimethylsilane, and bis(trimethylsilyl) sulphide.

TABLE[a]

R^1	R^2	Yield, % (**3**)	Yield, % (**1**)
Bu^n	H	95	87
C_6H_{13}	H	96	82
C_8H_{17}	H	96	94
$CH_2{=}CH[CH_2]_7$	H	95	88
$PhCH_2$	H	92	82
$-[CH_2]_5-$		92	88

[a] Satisfactory spectral and analytical data were obtained for all new products.

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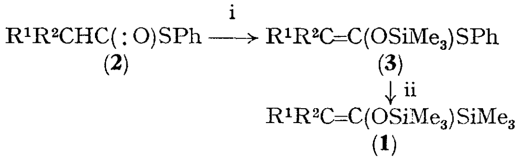
† Less satisfactory results were obtained with tetrahydrofuran as solvent.

In contrast to (**3**), silyl enol ethers of ethanethiol esters were almost inert under these conditions.



$$\begin{array}{ccc} \mathrm{R^1R^2CHC(:O)SPh} & \xrightarrow{\text{i}} & \mathrm{R^1R^2C{=}C(OSiMe_3)SPh} \\ (\mathbf{2}) & & (\mathbf{3}) \\ & & \downarrow \text{ii} \\ & & \mathrm{R^1R^2C{=}C(OSiMe_3)SiMe_3} \\ & & (\mathbf{1}) \end{array}$$

i, LiNPr$^i_2$–Me$_3$SiCl; ii, Na–Me$_3$SiCl

Further, this procedure offers a convenient route to acyltrimethylsilanes, since (**1**) is easily hydrolysed under acidic conditions.[1]

The method can be applied not only to primary esters, but also to secondary esters, which broadens the scope in comparison with methods reported hitherto.

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[1] For the preparation of (**1**), see; I. Kuwajima, M. Arai, and T. Sato, *J. Amer. Chem. Soc.*, 1977, **99**, 4181.

[2] T. Sato, M. Arai, and I. Kuwajima, *J. Amer. Chem. Soc.*, 1977, **99**, 5827.

[3] T. Sato, T. Abe, and I. Kuwajima, *Tetrahedron Letters*, 1978, 259.

[4] N. Minami, T. Abe, and I. Kuwajima, *J. Organometallic Chem.*, 1978, **145**, Cl.

[5] J. F. Bielmann and J. B. Ducep, *Tetrahedron Letters*, 1969, 3707.

[6] For the preparation of trimethylsilyl enol esters by similar procedures, see C. Ainsworth, F. Chen, and Y.-N. Kuo, *J. Organometallic Chem.*, 1972, **46**, 59; M. W. Rathke and D. F. Sullivan, *Synthetic Comm.*, 1973, 67.