

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

TABLE^a

| R ¹ | R ² | Yield, % | |
|--|------------------------------------|--------------|--------------|
| | | (3) | (1) |
| Bu ⁿ | H | 95 | 87 |
| C ₆ H ₁₃ | H | 96 | 82 |
| C ₈ H 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.

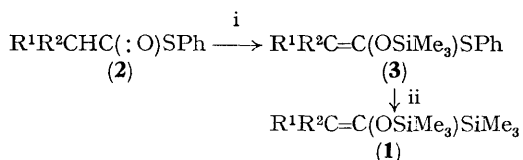
by treatment with lithium di-isopropylamide followed by quenching with trimethylchlorosilane.⁶ Treatment with a reductive silylating system caused the ready and efficient conversion of the carbon-sulphur bond of (**3**) into a carbon-silicon bond. Thus, the silyl ether (**3**) was added to a solution 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.

† 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.

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.



i, $\text{LiNPr}^1_2\text{-Me}_3\text{SiCl}$; ii, $\text{Na-Me}_3\text{SiCl}$

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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**, C1.

⁵ J. F. Biemann 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.