

REGIOSELECTIVE PREPARATION OF KINETIC TRIMETHYLSILYL ENOL ETHERS
FROM β -KETO SILANES

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Kinetic trimethylsilyl enol ethers were prepared regioselectively by the two-step method, i.e., trimethylsilyl triflate catalyzed rearrangement of β -keto silanes which were prepared from trimethylsilylmethylcopper and acid chlorides.

Trimethylsilyl enol ethers have been used for a variety of synthetic reactions and several methods have been developed to prepare them regioselectively.¹⁾ For example, two methods were communicated quite recently; rhodium catalyzed isomerization of β -trimethylsilyl allyl alcohols²⁾ and thermal isomerization of β -keto silanes prepared from trimethylsilylmethyl lithium and esters.³⁾

During our research on the regioselective introduction of substituents into heteroaromatics, kinetic trimethylsilyl enol ethers were required.⁴⁾ And we found that one of the most convenient route should be to use β -keto silanes, which would generally be available from trimethylsilylmethylcopper and acid chlorides as was suggested by Kishi et al. in a footnote.⁵⁾ In this communication, we report a simple procedure to β -keto silanes and facile regioselective rearrangement to trimethylsilyl enol ethers with catalytic trimethylsilyl triflate.

For the preparation of the β -keto silanes, the most convenient procedure is as follows; Trimethylsilylmethylmagnesium chloride (60 mmol) was added to the suspension of an acid chloride (50 mmol) and cuprous iodide (55 mmol) in ether at -78 °C and after the mixture was allowed to warm to 0 °C, it was quenched with 1 equiv. of aq NH_4Cl .⁶⁾ The extracted crude product was pure enough for further use. The results are summarized in Table 1. In every case the products (**3**) were obtained in high yields and it is noteworthy that the above method can be applied even in the presence of an ester group in the acid chloride (entry 5).

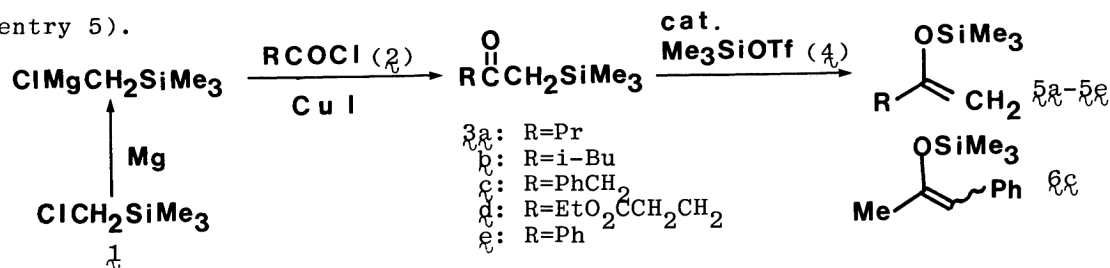


Table 1. Synthesis of kinetic trimethylsilyl enol ethers ($\bar{5}$) by the rearrangement of β -keto silanes ($\bar{3}$)

Entry	$\bar{3}$	R	Yield/% ^{a)}	$\bar{5}$	Yield/% ^{b)}	React. cond. ^{c)} (at rt) $\bar{4}$ (mol%) min quench	
1	$\bar{3a}$	Pr	91	$\bar{5a}$	0	10	5 aq NaHCO ₃
2					77	10	5 Et ₃ N
3	$\bar{3b}$	i-Bu	94	$\bar{5b}$	81	10	30 Et ₃ N
4	$\bar{3c}$	PhCH ₂	79 (92)	$\bar{5c}$	98 ^{d)}	5	1 Et ₃ N
5	$\bar{3d}$	EtO ₂ CCH ₂ CH ₂	72 (91)	$\bar{5d}$	91	5	1 Et ₃ N
6	$\bar{3e}$	Ph	- (99)	$\bar{5e}$	quant	5	1 Et ₃ N

a) Yield after distillation (crude yield in parenthesis). b) Yield not distilled. c) Pentane was used as a solvent. d) This compound contained 1.2% of $\bar{6c}$.

Emde et al. observed that symmetrical β -keto silanes were rearranged to trimethylsilyl enol ethers with trimethylsilyl triflate in an NMR tube,⁷⁾ we also tried the rearrangement of $\bar{3a}$ to $\bar{5a}$ in CCl₄, and ¹H NMR showed that $\bar{5a}$ was cleanly produced. But when it was quenched by 5% NaHCO₃ at 0 °C, we isolated not $\bar{5a}$ but 2-pentanone only. Therefore, triethylamine was used as a quenching reagent. The results are also cited in Table 1. Only in the case of $\bar{5c}$, $\bar{6c}$ was significantly produced (25%) after treatment with $\bar{4}$ for 30 min but this isomerization was suppressed by quick quenching (1 min). In other cases no isomerization was detected. Thus, unsymmetrical β -keto silanes ($\bar{3}$) could generally be converted to the corresponding trimethylsilyl enol ethers ($\bar{5}$) by treatment with a catalytic amount of trimethylsilyl triflate. The relatively lower yields of $\bar{5a}$ and $\bar{5b}$ were probably due to the loss during evaporation of solvent because of the lower bp of these compounds.

As α -silyl carbanions can be easily obtained by a number of procedure,¹⁾ this method can potentially be used for the regioselective synthesis of β -keto silanes and silyl enol ethers.

References

- 1) For reviews, E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981); W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer-Verlag, Berlin (1983).
- 2) I. Matsuda, S. Sato, and Y. Izumi, *Tetrahedron Lett.*, **24**, 2787 (1983).
- 3) G. L. Larson, I. M. de López-Cepero, and L. E. Torres, *Tetrahedron Lett.*, **25**, 1673 (1984).
- 4) For example, K. Akiba, T. Kobayashi, and Y. Yamamoto, *Heterocycles*, **22**, 1519 (1984); K. Akiba, Y. Nishihara, and M. Wada, *Tetrahedron Lett.*, **24**, 5269 (1983); M. Wada, M. Nakatani, and K. Akiba, *Chem. Lett.*, **1983**, 39; K. Akiba, M. Nakatani, M. Wada, and Y. Yamamoto, *J. Org. Chem.*, **50**, in press (1985).
- 5) B. A. Perlman, J. M. McNamara, I. Hasan, S. Hatakeyama, H. Sekizaki, and Y. Kishi, *J. Am. Chem. Soc.*, **103**, 4248 (1981).
- 6) When the reaction mixture was quenched by a large excess of ammonium chloride, significant amount of desilylated product was obtained.
- 7) H. Emde, A. Götz, K. Hofmann, and G. Simchen, *Liebigs Ann. Chem.*, **1981**, 1643.
- 8) Partial support of this work is acknowledged for Grant-in-Aid for Scientific Research (No. 58740231) from the Ministry of Education, Science, and Culture.

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