

ANIONIC REARRANGEMENTS STARTING WITH 1-LITHIO-2-PROPYNYL SILYL ETHERS

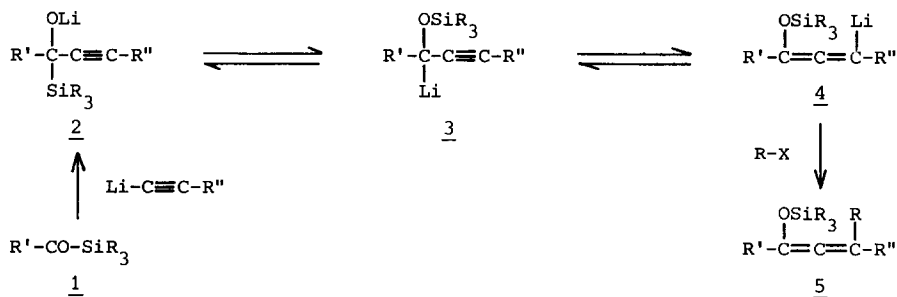
A ROUTE TO ( $\beta$ -TRIMETHYLSILYL VINYL) SILYL KETONES

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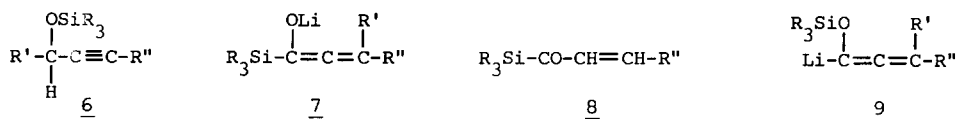
**Abstract** The title compounds undergo silyl-Wittig rearrangement at low temperature and lead to allenolates at room temperature.

The mobility of both silicon and lithium in the system  $2 \rightleftharpoons 3 \rightleftharpoons 4$  forms the basis of syntheses of siloxyallenes 5 (and the corresponding  $\alpha, \beta$ -unsaturated ketones) from silyl ketones 1.



We have studied three cases in which  $\text{R}' = \text{H}$  and have found that

- (a) this system can be entered at 3 through lithiation of 2-propynyl trialkyl silyl ethers (6 a-c);  
 (b) yet another mode of mobility in propargylic-allenic lithium compounds - 1,3-migration of hydrogen<sup>2</sup> - leads to a fourth type of tautomer, the allenolates 7 a-c.



- a:  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{SiMe}_3$ ,  $\text{R}_3 = t\text{-Bu, Me, Me}$   
 b:  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{CH}_3$ ,  $\text{R}_3 = t\text{-Bu, Me, Me}$   
 c:  $\text{R}' = \text{H}$ ,  $\text{R}'' = \text{SiMe}_3$ ,  $\text{R}_3 = \text{Me, Me, Me}$

The transformation  $\underline{6} \rightarrow \underline{7}$  is effected most advantageously in the case of 6a. Under the same circumstances (*vide infra*) slower deprotonation of 6b and faster silyl ether cleavage of 6c cause lower yields (15% and 30%, respectively) of the final products 8b and 8c

derived from 7b and 7c by hydrolysis.

Treatment of 6a with *n*-BuLi at  $-30^{\circ}\text{C}$  in ether-hexane (3:1) led to 2a. Standing at room temperature overnight converted this alkoxide into the allenolate 7a. Hydrolysis of 7a yielded a 85:15 mixture of the *Z/E* isomers of 8a (73%, based on 6a)<sup>3</sup>. The isomers can be separated by column chromatography on silica. The main product *Z*-8a isomerizes to *E*-8a on treatment with acid or on standing in  $\text{CDCl}_3$ .

7a is attacked at oxygen by alkyl halides and by trimethylchlorosilane, respectively. The resulting allenol ethers can be hydrolyzed with acid to give *E*-8a. The mode of formation of 7 has not yet been established. However, a likely route involves reversion of 2 ( $\text{R}' = \text{H}$ ) to its type-3 or type-4 isomer, which can undergo 1,3-migration of hydrogen<sup>2</sup> to give 9. Silyl-Wittig rearrangement of 9 gives 7. Lithium 3-trimethylsilyl-2-propynoxide did not undergo 1,3-migration of hydrogen when subjected to the conditions of formation of 7a.

8a and 8c have the interesting feature of being both an acylsilane and a vinylsilane and thus can be expected to be prone to selective modification at either carbon-silicon moiety by nucleophilic or electrophilic agents, respectively<sup>4</sup>.

#### References

- I. Kuwajima and M. Kato, *Tetrahedron Letters*, 623 (1980);  
H.J. Reich and M.J. Kelly, *J. Am. Chem. Soc.*, **104**, 1119 (1982).
- See J. Klein, in *The Chemistry of the Carbon-Carbon Triple Bond*, S. Patai, Ed., John Wiley and Sons, 1978, part 1, p. 343.  
Recent example: P.E. van Rijn, R.H. Everhardus, and L. Brandsma, *Recl. Trav. Chim. Pays-Bas*, **99**, 179 (1980).
- Z*-8a: *IR* ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ): 1620, 1540;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 7,32 (d,  $J=13,5$  Hz, 1H), 6,05 (d,  $J=13,5$  Hz, 1H), 0,94 (s, 9H), 0,22 (s, 6H), 0,14 (s, 9H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 237,9 (s), 144,8 (d), 144,4 (d), 26,4 (q), 16,8 (s), -0,7 (q), -7,1 (q); *MS* (70 eV, m/e): 227 (0.1%), 186 (1%), 73 (100%).  
*E*-8a: *IR* ( $\text{CCl}_4$ ,  $\text{cm}^{-1}$ ): 1620, 1590, 995;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 6,86 (d,  $J=19,6$  Hz, 1H), 6,72 (d,  $J=19,6$  Hz, 1H), 0,93 (s, 9H), 0,24 (s, 6H), 0,14 (s, 6H);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ,  $\delta$ ): 236,3 (s), 147,0 (d), 145 (d), 26,6 (q), 16,6 (s), -1,8 (q), -5,9 (q). *MS* (70 eV, m/e): 227 (0,2%), 186 (3%), 73 (100%).  
In the cases of 8b and 8c the *Z/E*-ratios were 90:10. Analytical data of these compounds were in complete agreement with the structures assigned to them.
- For nucleophilic attack on acylsilanes cf. ref. 1 and: D. Schinzer and C.H. Heathcock, *Tetrahedron Letters*, 1881 (1981).  
For electrophilic attack on vinylsilanes cf. T.H. Chan and I. Fleming, *Synthesis*, 761 (1979).

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