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A NOVEL REARRANGEMENT LEADING TO METHOXYCARBONYLMETHYLATED SILYL ENOL ETHERS

Hans-Ulrich Reissig

Institut für Organische Chemie der Universität Würzburg
Am Hubland, D-8700 Würzburg, Germany

Summary: Methyl 2-siloxycyclopropanecarboxylates rearrange smoothly and quantitatively to the corresponding silyl enol ethers (3) by addition of a catalytical amount of iodo trimethylsilane. Scope and limitation of this novel process as well as the synthesis of the electron rich diene (10a) are described.

Silyl enol ethers (1) are extremely useful and versatile compounds in organic synthesis [1]. However, rather few methods exist for the generation of simple silyl enol ethers bearing further functionalized substituents, e.g. methoxycarbonylmethyl groups.

We recently described Lewis acid promoted additions towards methyl 2-siloxycyclopropanecarboxylates (2) giving adducts (5) [2] and a mechanistically interesting cis-trans equilibration for these donor-acceptor cyclopropanes by means of certain Lewis acids [3]. During these investigations we discovered that the thermally stable cyclopropanes (2) rearrange smoothly at room temperature to the corresponding silyl enol ethers (3) within minutes to days, if (2) are activated by a catalytical amount (0.05 - 0.4 equiv.) of iodo trimethylsilane [4] (scheme I). (2) can be prepared efficiently[5] via (1) from the carbonyl compound (4) thereby the synthetically useful overall transformation (4) → (3) is constituted. Whereas (2) reacts with electrophiles providing adducts (5) [6], their regioisomers (6) are now available from the silyl enolethers (3) [1].

Scheme 1:

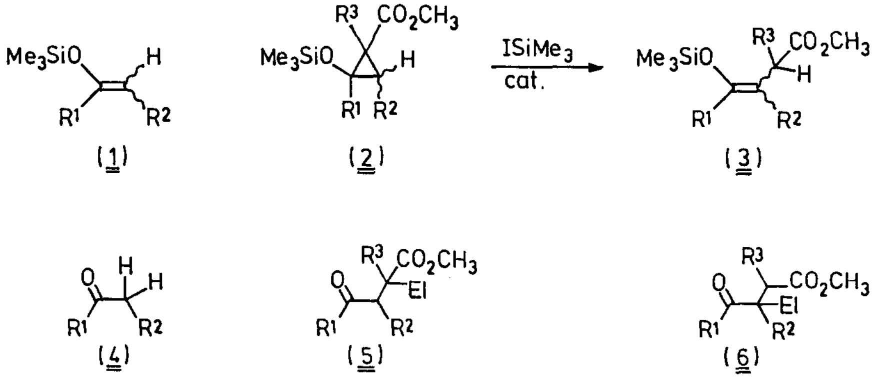
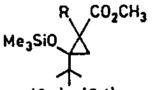
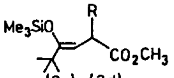
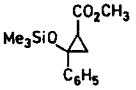
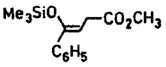
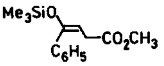
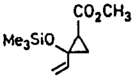
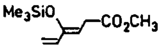
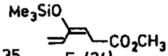
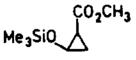
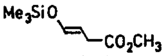
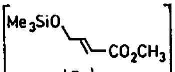
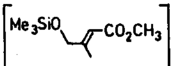
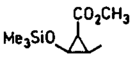
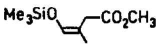
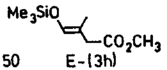
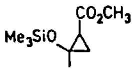
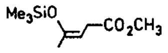
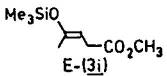
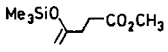


Table 1 demonstrates scope and limitation of this novel rearrangement. Entries a - d show that substituents at C-1 of the cyclopropane, which can even bear further functionality, are tolerated, and that the silyl enol ethers (3a)- (3d) are generated as Z-isomers exclusively[7]. On the other hand compounds (3e)-(3i) are obtained as mixtures of stereoisomers.

Table 1: $ISiMe_3$-catalyzed rearrangement (2) → (3) [a)]

entry	Siloxycyclopropane (2)		ReactionTime	Silyl Enol Ether (3) [b)]	Yield [%] [c)]
a	 (2a) - (2d)	R = H	1d	 (3a) - (3d)	97 (100)
b		R = CH_3	1d		(100)
c		R = SCH_3	4d		(100)
d		R = $CH_2CH=CH_2$	2d		71 (100)
e	 (2e)		5h	 Z-(3e) 90 : 10  E-(3e)	77 (100)
f	 (2f)		30 min	 Z-(3f) 65 : 35  E-(3f)	49 [d)] (100)
g	 (2g)		20 min	 Z-(3g) 80 : 20  E-(3g)	(100)
				 [(7g)]  [(7h)]	
h	 (2h)		30 min	 Z-(3h) 50 : 50  E-(3h)	95 (100)
i	 (2i)		20 min	 Z-(3i)  E-(3i)	89 (100)
				 (8i) Z-(3i):E-(3i):(8i) = 70:20:10	

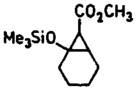
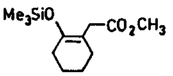
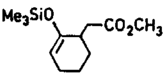
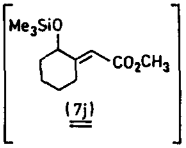
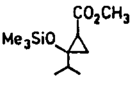
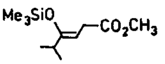
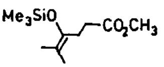
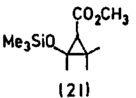
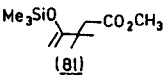
a) All reactions are performed at room temperature in abs. $CHCl_3$ or $CDCl_3$ in the presence of 0.05 - 0.4 eq. $ISiMe_3$ (ALDRICH) and 0.1 - 0.5 eq. $HN(SiMe_3)_2$ (exceptions: entries g, h, j; see text). For a typical procedure see ref. 9.

b) All compounds exhibit the appropriate spectral data. The portion of hydrolysis product (9) in (3) is smaller than 5 %.

c) Yields of distilled isolated compounds (3); in parentheses yields according to ^1H-NMR spectroscopy without isolation.

d) (3f) has a high tendency to polymerize.

Table 1 continued

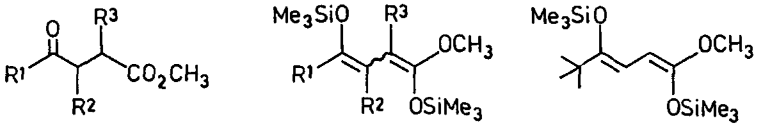
entry	Siloxycyclopropane (2)	Reaction Time	Silyl Enol Ether (3)[b)]	Yield [%][c)]
j	 (2j)	20 min	 (3j) 84 : 16  (8j)  (7j)	72 (100)
k	 (2k)	6h	 (3k) 25 : 75  (8k)	83 (100)
l	 (2l)	8d	 (8l)	70

If, however, enolization of the masked ketone moiety in (2) is possible to the α and α' side (entries i, j, k) mixture of regioisomeres (3) and (8) are formed. Since Miller[8] observed a similar ratio of isomers (3i) and (8i) by reacting levulinic ester with $ISiMe_3$/$HN(SiMe_3)_2$ these mixtures probably reflect the thermodynamic equilibrium. As expected (2l) rearranges to (8l) (entry l).

In most cases it is advisable to have $HN(SiMe_3)_2$ in the reaction mixture - albeit the rearrangement is considerably slower, this additive minimizes the formation of the γ-oxo-esters (9) and facilitates isolation of pure (3). However, in entries g, h and j these conditions provide side products in 5 - 15 %, very likely the α,β-unsaturated esters (7) formed by deprotonation/protonation of (3). Their generation can be avoided by using $ISiMe_3$ without base and adding $HN(SiMe_3)_2$ just before the work up[9].

The mechanistic path leading from (2) to (3) is not at all straightforeward[10]. By ^1H NMR spectroscopy certain intermediates can be detected just after addition of $ISiMe_3$, which, within minutes to hours, give a mixture of compounds (3), (9) and diene (10) (Scheme II). These provide the desired silyl enol ethers (3) exclusively by further standing at room temperature (hours to days). These observations - which will be disclosed with details in a full paper - demonstrate that the "simple" rearrangement (2) → (3) is a cascade of silylgroup and proton shifts finally delivering (3) as thermodynamically most stable compound of the system.

Scheme II:



(9) (10) (10a)

If (2a) is treated with equimolar amounts of $ISiMe_3$ and triethylamine at room temperature in $CHCl_3$ one obtains a nearly quantitative yield (92 % distilled) of the highly donor-substituted diene (10a) [11]. The reactions (cycloadditions) of (10)-type-dienes as well as characteristic transformations of (3) (e.g. cyclopropanation to new donor-acceptor systems) will be reported in near future and demonstrate the synthetic utility of the building block (2) [12].

References and Notes

1. Reviews: E. Colvin, Silicon in Organic Synthesis, Butterworths, London 1981. - W. P. Weber, Silicon Reactions for Organic Synthesis, Springer, Berlin 1983. - P. Brownbridge, Synthesis 1983, 1, 85.
2. H.-U. Reissig, Tetrahedron Lett. 1981, 22, 2981. - H.-U. Reissig, I. Reichelt, Tetrahedron Lett. 1984, 25, 5879. - H.-U. Reissig, H. Lorey to be published.
3. H.-U. Reissig, I. Böhm, Tetrahedron Lett. 1983, 24, 715.
4. For ring opening of cyclopropane derivatives by iodo trimethylsilane see: R. D. Miller, D. R. McKean, J. Org. Chem. 1981, 46, 2412. - U. Hertenstein, S. Hünig, H. Reichelt, R. Schaller, Chem. Ber. 1982, 115, 261. - R. K. Dieter, S. Pounds, J. Org. Chem. 1982, 47, 3174. - M. Demuth, G. Mikhail, Tetrahedron 1983, 39, 991.
5. E. Kunkel, I. Reichelt, H.-U. Reissig, Liebigs Ann. Chem. 1984, 512. - I. Reichelt, H.-U. Reissig, Liebigs Ann. Chem. 1984, 536.
6. See ref. 2 and I. Reichelt, H.-U. Reissig, Liebigs Ann. Chem. 1984, 820.
7. For synthesis and use of stereoselectively prepared silyl enol ethers see: C. H. Heathcock, K. T. Hug, L. A. Flippin, Tetrahedron Lett. 1984, 25, 5973. - M. T. Reetz, K. Kesseler, A. Jung, Tetrahedron 1984, 40, 4327 and references cited therein.
8. R. D. Miller, D. R. McKean, Synthesis 1979, 730.
9. Typical procedure: To 12.2 g (50.0 mmol) (2a) in 20 ml abs. $CHCl_3$ are added under N_2 0.7 g (4.7 mmol) $HN(SiMe_3)_2$ and 0.82 g (4.1 mmol) $ISiMe_3$ (ALDRICH). According to ^1H NMR the rearrangement is complete after 24 h. After evaporation of the solvent the residue is dissolved in petrolether, filtered through a pad of florisil (10 g) and distilled (100-110 ^{o}C/0.3 mm) providing 11.8 g (97 %) (3a) as colorless oil. ^1H NMR ($CDCl_3$): δ=4.75 (t, J = 6.8 Hz, 1H, CH), 3.65 (s, 3H, CO_2CH_3), 2.65 (d, J = 6.8 Hz, 2H, CH_2), 1.20 (s, 9H, tBu), 0.22 (s, 9H, $SiMe_3$). - IR (CCl_4): 1740 (CO_2CH_3), 1660 cm^{-1} (C=C).
10. It is not certain so far whether the actual catalyst is Me_3SiI or HI.
11. The stereochemistry of the diene is tentatively assigned as depicted in formula (10a).
12. Support of this work by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie and the Universitätsbund Würzburg is gratefully appreciated.

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