A synthesis of multisubstituted vinylsilanes *via* ynolates: stereoselective formation of β-silyl-β-lactones followed by decarboxylation†

Mitsuru Shindo,* Kenji Matsumoto and Kozo Shishido

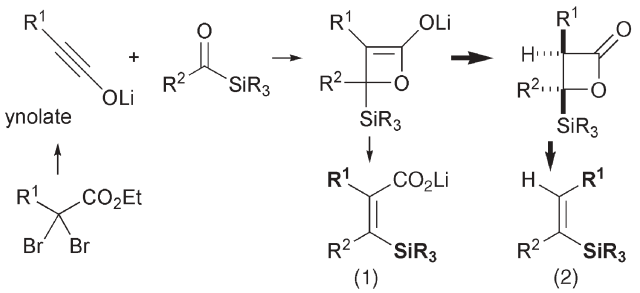
Received (in Cambridge, UK) 7th December 2004, Accepted 10th March 2005
First published as an Advance Article on the web 29th March 2005
DOI: 10.1039/b418310j

(*Z*)-Selective synthesis of multisubstituted vinylsilanes was achieved by stereoselective protonation or alkylation of β-silyl-β-lactone enolates, prepared by cycloadditions of acylsilanes with ynolates, followed by decarboxylation.

Vinylsilanes are important synthetic tools in organic chemistry.[1] Although various methodologies for their preparation have been reported, there have been few reports on a successful, widely useful stereoselective olefination of acylsilanes.[2] Recently, we reported a stereoselective olefination of acylsilanes, *via* torquoselective electrocyclic ring-opening of β-lactone enolates derived from ynolates, giving (*Z*)-β-trialkylsilyl-α,β-substituted acrylates, that is, multisubstituted vinylsilanes [Scheme 1 (1)].[3] Herein, we report a new strategy for the stereochemically complementary olefination of acylsilanes with ynolates *via* a stereoselective β-silyl-β-lactone formation–decarboxylation sequence [Scheme 1 (2)].

In our previous communication, we reported the cycloaddition of the acylsilane **2a** with the ynolate **1a**[4] to furnish the β-lactone enolate, which is ring-opened *at room temperature* to provide the (*Z*)-β-silylacrylate without stereoisomers. When this reaction was carried out *at −78 °C*, the corresponding β-lactone **3a** was isolated in 91% yield after protonation (Scheme 2). The diastereomeric ratio of **3a** was found to be very high and the minor isomer could not be detected by ^{1}H-NMR spectroscopy. After recrystallization, **3a** underwent thermal decarboxylation[5] under reflux in benzene in the presence of silica gel, to provide the (*Z*)-vinylsilane **4a** in 88% yield without any detectable (*E*)-isomer.

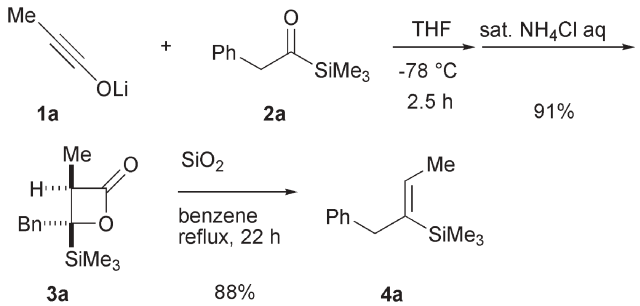
Encouraged by this excellent result, we next examined the generality of this synthesis of vinylsilanes. Due to the instability of some of the β-lactones **3** toward silica gel, decarboxylation was carried out without purification of **3**.[6] Table 1 shows the results of



Scheme 1

† Electronic supplementary information (ESI) available: representative procedures and spectral data for compounds **2** and **4**. See http://www.rsc.org/suppdata/cc/b4/b418310j/

*shindo@ph.tokushima-u.ac.jp



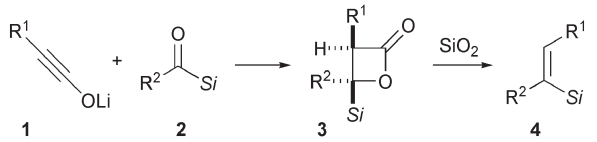
Scheme 2

the reactions of various combinations of acylsilanes **2**[7] and ynolates **1** to furnish the disubstituted vinylsilanes **4**. The methyl, ethyl, isopropyl, and phenyl-substituted ynolates afforded the vinylsilanes in good yield with high *Z*-selectivities (entries 1–4). Although the minor isomer could not be detected by ^{1}H-NMR spectroscopy at the β-lactone stage,[8] a few percent of the minor (*E*)-isomers were detected by ^{1}H-NMR spectroscopy and HPLC (entries 1–3). While the *tert*-butyl substituted ynolate did not give the desired product (entry 5), presumably due to steric reasons, the trimethylsilyl substituted ynolate afforded bis(trimethylsilyl)alkenes in moderate yield with (*E*)-selectivity (entry 6). According to the ^{1}H-NMR spectrum of the intermediate, the first step of the cycloaddition should have proceeded cleanly, but gave instead an almost 1:1 mixture of stereoisomers. At the decarboxylation step, the route to the (*Z*)-isomer suffers from steric compression and took place very little. Benzoylsilanes and functionalized acylsilanes provided vinylsilanes in good yields with Z selectivities (entries 8–13). The acryloylsilane, however, did not give the desired product but rather a complex mixture at the first stage (entry 14). As for substituents on the silane, triethylsilyl, *tert*-butyldimethylsilyl, and benzyldimethylsilyl groups could also be used (entries 7, 9, 12, and 13). In the case of the benzyldimethylsilyl group, the *Z*/*E* ratio decreased slightly (entry 12) compared with that of the trimethylsilyl one (entry 11).

Instead of protonation, alkylation of the β-lactone enolates was attempted. As shown in Scheme 3, methylation by MeI assisted with HMPA, followed by decarboxylation, provided the trisubstituted vinylsilane **4o** in good yield with excellent *Z*-selectivity. The aldol reaction, followed by decarboxylation, was also performed with benzaldehyde to afford the desired vinylsilane **4p** with good *E*-selectivity. In both cases, the electrophiles were introduced *trans* to the silyl group.

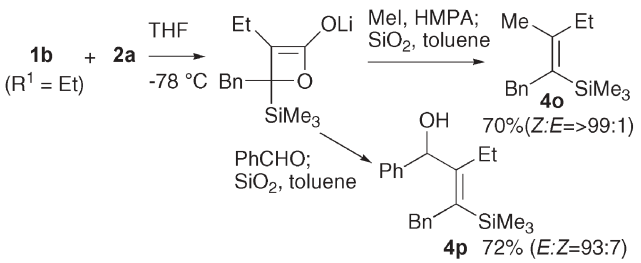
The *E*/*Z* selectivity is determined in the protonation (or alkylation) of the β-lactone enolates, because the decarboxylation

Table 1 Synthesis of vinylsilanes *via* decarboxylation of β-lactones derived from cycloaddition of acylsilanes with ynolates



		2				4		
Entry	R^1	R^2		*Si*	Decarboxylation[a]	Yield (%)		*Z*:*E*[b]
1	Me	**2a**	$PhCH_2$	Me_3Si	A, 21 h	**4a**	72	98:2
2	Et	**2a**	$PhCH_2$	Me_3Si	A, 28 h	**4b**	74	95:5
3	*i*Pr	**2a**	$PhCH_2$	Me_3Si	A, 22 h; B, 6 h	**4c**	78	94:6
4	Ph	**2a**	$PhCH_2$	Me_3Si	B, 4 h	**4d**	60	>99:1
5	*t*Bu	**2a**	$PhCH_2$	Me_3Si	—	**4e**	0[c]	—
6	Me_3Si	**2a**	$PhCH_2$	Me_3Si	B, 10 h	**4f**	46	19:81[d]
7	Me	**2g**	$PhCH_2$	Et_3Si	A, 21 h	**4g**	78	95:5
8	Me	**2h**	Ph	Me_3Si	A, 2 h	**4h**	62	92:8[e]
9	Me	**2i**	Ph	Et_3Si	A, 15 h	**4i**	71	88:12[e]
10	Me	**2j**	4-(PivO)C_6H_4	Me_3Si	A, 18 h	**4j**	64	92:8[e]
11	Me	**2k**	CH_2=$CH(CH_2)_3$	Me_3Si	A, 17 h	**4k**	72	94:6
12	Me	**2l**	CH_2=$CH(CH_2)_3$	$BnMe_2Si$	B, 4 h	**4l**	69	86:14
13	Me	**2m**	$CH_3O(CH_2)_2$	*t*-$BuMe_2Si$	A, 17 h	**4m**	84	93:7
14	Me	**2n**	CH_2=CH	$PhMe_2Si$	—	**4n**	0[c]	—

[a] Condition A: refluxed in benzene. Condition B: refluxed in toluene. [b] The stereochemistry was determined by NOE experiments except for entries 8, 9 and 10. [c] The cycloaddition gave a complex mixture. [d] At the β-lactone stage, the diastereomeric ratio was 55:45, as judged by ^{1}H-NMR spectroscopy. [e] After protodesilylation with HI, the coupling constant between the vinylic protons of the resulting alkenes was 15.6 Hz, which shows *trans* relationship of the protons.[9]



Scheme 3

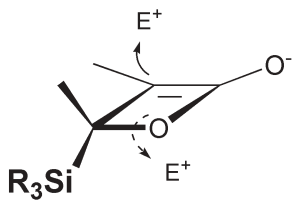
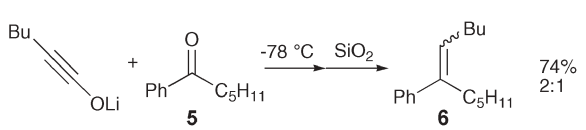


Fig. 1

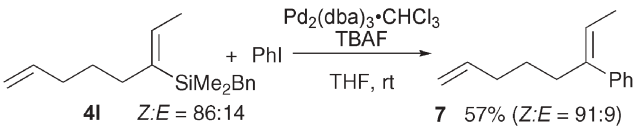
is supposed to be a *syn*-elimination (retention).[10] When the phenyl pentyl ketone **5** was reacted according to the same protocol, the resulting trisubstituted olefin **6** was a 2:1 mixture of geometrical isomers (Scheme 4).[11] This remarkable difference in the stereoselectivity would be due to the steric and stereoelectronic effects of the trialkylsilyl group, that is, the kinetically controlled protonation (or alkylation) of the β-lactone enolates leads to preferential introduction of the proton (or an electrophile) *anti* to the trialkylsilyl group (Fig. 1). These results are in good agreement with Fleming's reports on the protonation/alkylation of β-silyl ester enolates.[12] For example, the selectivity of alkylation is higher than that of protonation, and the selectivity does not depend on the substituents on the silicon.



Scheme 4

These results show the high generality of this synthetic method for multisubstituted vinylsilanes, and it should be regarded as a complementary method to our previous olefination, since R^1 has a *cis* relationship with the silyl group here and a *trans* relationship in the previous case. To demonstrate the synthetic utility of this process, the benzyldimethylvinylsilane **4l** (Trost's vinylsilane) was coupled with iodobenzene, catalyzed by palladium, to afford the trisubstituted alkene **7** (Scheme 5).[13]

In conclusion, we have developed a stereoselective synthesis of di- and trisubstituted vinylsilanes *via* protonation or alkylation of β-silyl-β-lactone enolates derived from the cycloaddition of ynolates with acylsilanes, followed by decarboxylation. The stereoselectivity was determined in the protonation or alkylation of β-lactone enolates, which is governed by the steric and stereoelectronic effects of the trialkylsilyl group. The geometry is complementary to our previous olefination of acylsilanes *via*



Scheme 5

electrocyclic ring-opening. This methodology would be useful for the stereoselective construction of multisubstituted alkenes.

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan. K. M. thanks the Japan Society for the Promotion of Science (JSPS) for a research fellowship.

Mitsuru Shindo,* Kenji Matsumoto and Kozo Shishido
Institute of Health Biosciences, The University of Tokushima Graduate School, Shomachi 1, Tokushima 770-8505, Japan.
E-mail: shindo@ph.tokushima-u.ac.jp; Fax: (+81)88 633 7294;
Tel: (+81)88 633 7294

Notes and references

1 For recent reviews, see: (*a*) I. Fleming, A. Barbero and D. Walter, *Chem. Rev.*, 1997, **97**, 2063; (*b*) M. A. Brook, *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, 2000.
2 (*a*) J. A. Soderquist and C. L. Anderson, *Tetrahedron Lett.*, 1988, **29**, 2425; (*b*) G. L. Larson, J. A. Soderquist and M. R. Claudio, *Synth. Commun.*, 1990, **20**, 1095; (*c*) P. Jankowski, K. Plesniak and J. Wicha, *Org. Lett.*, 2003, **5**, 2789.
3 M. Shindo, K. Matsumoto, S. Mori and K. Shishido, *J. Am. Chem. Soc.*, 2002, **124**, 6840.
4 For reviews, see: (*a*) M. Shindo, *Synthesis*, 2003, 2275; (*b*) M. Shindo, *J. Synth. Org. Chem. Jpn.*, 2000, **58**, 1155; (*c*) M. Shindo, *Yakugaku Zasshi*, 2000, **120**, 1233; (*d*) M. Shindo, *Chem. Soc. Rev.*, 1998, **27**, 367.
5 W. Adam and L. A. A. Encarnacion, *Synthesis*, 1979, 388.
6 Some of the β-lactones can be purified by recrystallization to remove minor isomers.
7 Acylsilanes were prepared from silyl thioacetals, like 2-silyl-1,3-dithianes. See ESI.
8 Due to the overlap of peaks in the ^{1}H-NMR spectrum.
9 K. Utimoto, M. Kitai and H. Nozaki, *Tetrahedron Lett.*, 1975, 2825.
10 For a review, see: A. Pommier and J.-M. Pons, *Synthesis*, 1993, 441.
11 (*a*) M. Shindo, Y. Sato and K. Shishido, *J. Am. Chem. Soc.*, 1999, **121**, 6507; See, also: (*b*) R. L. Danheiser and J. S. Nowick, *J. Org. Chem.*, 1991, **56**, 1176; (*c*) J. Mulzer and A. Chucholowski, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 777.
12 R. A. N. C. Crump, I. Fleming, J. H. M. Hill, N. L. Reddy and D. Waterson, *J. Chem. Soc., Perkin Trans. 1*, 1992, 3277.
13 B. M. Trost, M. R. Machacek and Z. T. Ball, *Org. Lett.*, 2003, **5**, 1895.