ORGANIC LETTERS

2001
Vol. 3, No. 6
937−939

Synthesis of (*Z*)-Vinylsilanes with High Diastereoselectivity by Using Samarium Diiodide

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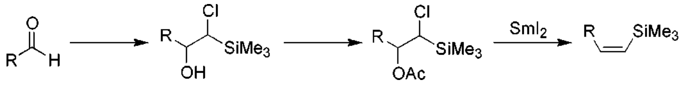
Received January 23, 2001

ABSTRACT



β-Elimination of *O*-acetyl 1-chloro-1-trimethylsilylalkan-2-ols 1 was achieved by using samarium diiodide as a metaling reagent and afforded the corresponding (*Z*)-vinylsilanes with high stereoselectivity. The starting compounds 1 were easily prepared by treatment of different aldehydes with (chlorolithiomethyl)trimethylsilane and further acetylation.

Alkenylsilanes serve as important intermediates in organic synthesis.[1] In the literature, there are various methodologies for their preparation.[2] These methods utilize, generally, alkynes,[3] alkenyl halides,[4] or carbonyl compounds[5] as starting materials. More specifically, using carbonyl compounds as starting materials. several methodologies have been published to promote the elimination reaction, but the use of samarium diiodide remain unreported.

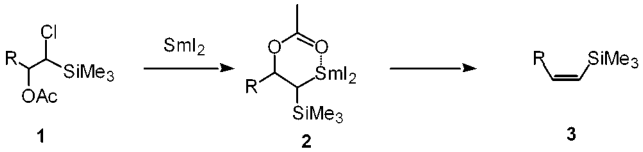
Recently, we have reported the preparation of (*Z*)-vinyl halides with high stereoselectivity (ed >80%) from *O*-acetyl 1,1-dihaloalkan-2-ols[6] and the synthesis of (*E*)-α,β-unsaturated esters with total stereoselectivity from the corresponding 2-halo-3-hydroxy esters.[7] In both cases, elimination reactions were promoted by samarium diiodide at room temperature, the methodology being easy, simple, and general. Here, we wish to report a new synthesis of (*Z*)-vinylsilanes with high stereoselectivity by treatment of the easily available *O*-acetyl 1-chloro-1-trimethylsilylalkan-2-ols with samarium diiodide.

The reaction of several *O*-acetyl 1-chloro-1-trimethylsilylalkan-2-ols **1** with SmI_2 in THF at reflux gave the corresponding (*Z*)-vinylsilane with high stereoselectivity and in high yield (Scheme 1, Table 2).[8]

The starting material **1** can be easily prepared by reaction of different aldehydes with (chlorolithiomethyl)trimethylsilane at −65 °C and further O-acetylation with acetic anhydride (Scheme 2, Table 1).

The α-silyl carbanion was generated by lithiation of (chloromethyl)trimethylsilane with *sec*-butyllithium and tet-

Scheme 1. Synthesis of (*Z*)-Vinylsilanes



1 **2** **3**

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10.1021/ol015601p CCC: $20.00

Table 1. Yields of Starting Compounds **1** and **5**

entry	R	isomeric composition	yield (%)	
			5[b]	**1**[c]
1	Bu	71/29	82	86
2	Bu[c]	75/25	81	85
2	*i*-Bu	68/32	81	86
4	Ph	67/33	79	84
5	*p*-ClC_6H_4	71/29	85	88
6	*p*-$MeOC_6H_4$	74/26	78	85
7	cyclohexyl	85/15	77	84
8	C_7H_{15}	69/31	84	87
9	MeCH(Ph)	80/20	79	88
10	$Me_2CH(CH_2)_2CH(Me)CH_2$	37/3613/12	81	90

[a] Isomeric composition determined by ^{13}C NMR of the crude products. [b] Yield based on starting aldehyde **4**. [c] Yield based on chlorohydrin **5**.

ramethylethylenediamine (TMEDA) at temperatures ranging between −78 and −65 °C.[9]

The diastereoisomeric excess was determined on the crude reaction products by ^1H NMR spectroscopy (200 or 300 MHz) and GC−MS. The results are summarized in Table 2. The *Z* stereochemistry in the double bond C=C of products **3** was assigned on the basis of the value of the ^1H NMR coupling constant between the olefinic protons[10] and by comparison of their NMR spectra with those previously reported (**3a**,[3d] **3d**,[3e,11b] **3g**[11a]).

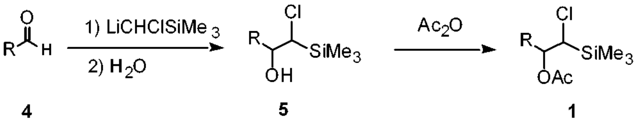
Several comments are worth noting. (1) Although the elimination reaction was carried out using a mixture of diastereoisomers (roughly 1:1) of **1**, the corresponding vinylsilanes **3** were obtained with high diastereoisomeric excess (de). (2) The reaction was general to obtain vinylsilanes derived from aliphatic (linear, branched or cycic) aldehydes. (3) The synthesis of vinylsilanes can be carried out at higher scale: 89% of **3h** was obtained starting from 1 mmol of **1h**. (4) Substitution at the silicon atom of **3** could also be changed using a different α-silyl carbanion to prepare compound **1** (entry 2). (5) Elimination took place with moderate stereoselectivity when aromatic aldehydes were used. (6) When 1-chloro-1-trimethylsilylalkan-2-ols (no *O*-acetylated) were utilized no elimination reaction was detected. (7) When the reaction was performed at room temperature, neither β-elimination was observed.

Table 2. Synthesis of (*Z*)-Vinylsilanes **3**

entry	**3**[a]	R	*Z*/*E*[b]	yield (%)
1	**3a**	Bu	>98/−	96
2	**3b**	Bu[c]	>98/−	94
3	**3c**	*i*-Bu	97/3	95
4	**3d**	Ph	80/20	95
5	**3e**	*p*-ClC_6H_4	68/32	95
6	**3f**	*p*-$MeOC_6H_4$	15/85	94
7	**3g**	Cyclohexyl	97/3	95
8	**3h**	C_7H_{15}	>98/−	96
9	**3i**	MeCH(Ph)	>98/−	92
10	**3j**	$Me_2C{=}CH(CH_2)_2CH(Me)CH_2$	95/5	94

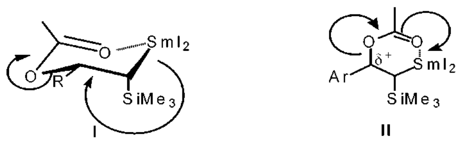
[a] Yield based on the starting crude acetate **1**; all vinylsilanes were fully characterized by spectroscopy methods (IR, NMR and MS). [b]Diastereoisomeric excess determined by GC/MS and 200 or 300 MHz ^1H and ^{13}C NMR analysis of the crude products. [c](*Z*).-1-hexenyldimethylphenylsilane obtained using (chlorolithiomethyl)dimethylphenylsilane.

Scheme 2. Synthesis of Starting Compounds



The observed stereochemistry and the high *Z*-selectivity of the elimination reaction can be explained by the formation of the intermediate **2**, in which the oxophilic Sm (III) center is chelated with the carbonyl oxygen atom of the acetoxy group producing a six-membered ring (Scheme 2).[12] This chelation increases the ability of the acetoxy group as a leaving group. We surmise that the chairlike transition-state model **I** (Scheme 3) might be involved with an equatorial R group (to avoid 1,3-diaxial interactions) and an axial trimethylsilyl group (to avoid interactions with the samarium coordination sphere and taking into account that no 1,3-diaxial interactions are present). Elimination from **I** gives (*Z*)-vinylsilanes **3**.

Scheme 3. Proposed Mechanism



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(8) Representative procedure for the synthesis of (*Z*)-vinylsilanes **3**: A solution of SmI_2 (2 mmol) in THF (24 mL) was added, under nitrogen atmosphere, to a solution of the corresponding *O*-acetyl 1-chloro-1-trimethylsilylalkan-2-ol **1** (0.4 mmol) in THF (4 mL). After being stirred at reflux for 3.5 h, the mixture was treated with aqueous HCl (0.1 M, 10 mL), and after usual workup, the corresponding crude vinylsilanes **3** were obtained, which were examined by ^1H NMR and GC/MS to give the diastereoisomeric excess reported in Table 2. Distillation at reduced pressure provided pure (*Z*)-vinylsilanes **3**.

(9) Representative procedure for the synthesis of staring compounds **1**: To a stirred solution of (chloromethyl)trimethylsilane (14.95 mL, 14 mmol) in THF (21 mL) were successively added *sec*-butillithium (11.9 mL of 1.3 M solution in cyclohexane, 15.4 mmol) and TMEDA (2.1 mL, 14 mmol) at −78 °C under nitrogen atmosphere. Stirring was continued for 40 min, allowing the temperature to rise to −65 °C, and then a solution of the corresponding carbonyl compound (10 mmol) in THF (3 mL) was added. The resulting mixture was stirred for 2 h at temperature ranging between −60 and −45 °C. The reaction was treated with a saturated aqueous solution of NH_4Cl (25 mL), and after usual workup, the corresponding crude 1-chloro-1-trimethylsilylalkan-2-ol was obtained. This alcohol (8 mmol) was treated with pyridine (25 mL), acetic anhydride, and 4-(dimethylamino)-pyridine (5 mg). After being stirred for 12 h, the mixture was treated with ice, and after usual workup, the corresponding crude *O*-acetyl 1-chloro-1-trimethylsilylalkan-2-ol **1** was obtained. The crude products **1** were used without further purification.

To explain the synthesis of **3** with high stereoselectivity from a mixture of diastereoisomers, we assume that after metalation by samarium(II) initially two diastereoisomers are obtained. Of the two, the diastereoisomer in which the coordination of the samarium(III) center with the carbonyl oxygen atom is the most favored could eliminate directly, while the other diastereoisomer epimerizes[13] before the elimination.

The lower stereoselectivity observed when aromatic aldehydes were used can be explained by assuming a nonconcerted elimination reaction: the stabilization of the positive charge by resonance would induce prior cleavage of the C−O bond **II** (Scheme 3). Indirect support for this is provided by the lower *Z*-selectivity obtained from an aromatic aldehyde with an electron-releasing substituent (entry 6), since the presence of this substituent favored the formation of the carbocation intermediate.

In conclusion, we have described a simple, general synthesis of vinylsilanes, which takes place in high yield and with high stereoselectivity from easily available starting compounds.

Acknowledgment. We thank II Plan Regional de Investigación del Principado de Asturias (PBP-PGI99-01) and the Ministerio de Educación y Cultura (PB97-1278) for financial support. E.B. thanks the Universidad de Oviedo for a predoctoral fellowship.

Supporting Information Available: Spectroscopic data for all new compounds **1** and **3**, ^{1}H NMR spectra of **1** and **3**, GC of compounds **3**, and representative procedure for the synthesis of compounds **1** by using 1 mmol of starting material. This material is available free of charge via the Internet at http://pubs.acs.org.

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