

Cohalogenation of Allyl and Vinylsilanes using Polymer-bound Haloate(I)-Reagents[‡]

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Abstract: Polymer-supported electrophilic halogenate(I) complexes **2** and **3** promote smooth addition to vinyl and allylsilanes without loss of the silyl group. In conjunction with Amberlyst A26 (OH⁻-form) vinyl silanes are converted into epoxysilanes.

Keywords: Cohalogenation, allylsilane, vinylsilane, polymer-supported reagent.

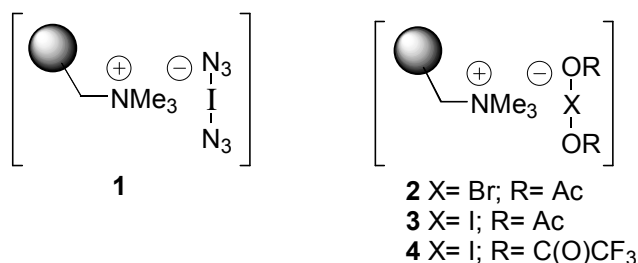
Introduction

Recently, the development and applications of polymer-supported reagents have seen a dramatic increase in interest [1]. Functionalized matrices can be used in excess to drive reactions in solution to completion and are finding application in high throughput, automated parallel syntheses [2]. In some cases major differences between reactions on polymer supports and their low-molecular mass analogues have been observed [3]. Apart from differences in reaction rates, altered regio- and stereoselectivity has been described in some cases using functionalized polymers. *E. g.* Patchornik and

coworkers encountered that crosslinked poly(maleimide) in which 70% of the repeat units were *N*-brominated gave a different set of bromination products in reactions with cumene than *N*-bromosuccinimide [4]. These properties give polymer-supported reagents additional attraction. Thus, in this communication we report on the unexpected clean cohalogenation of allyl and vinylsilanes which is promoted by functionalized polymers with electrophilic properties.

Results and Discussion

Recently, our interest in new electrophilic halogen-ate(I) complexes [5] has led to the development of the first polymer-bound iodine azide source (**1**) [6] as well as of functionalized polymers (**2**)-(4) which are loaded with synthetic equivalents of acylated hypohalites [7]. All of these electrophilic reagents promote 1,2-cohalogenations of various alkenes [8,9] under very mild conditions and with high efficiency [7].



In this paper, we disclose reactions of vinyl and allylsilanes with polymer-supported electrophilic reagents (**2**) and (**3**) which instead to the expected desilylation lead to 1,2-addition products. In fact, numerous methods [10] are known for effecting iododesilylation of vinyl and allylsilanes using different iodonium sources like ICl, IBr, IBF₄, and NIS [11]. It is generally accepted that the reaction is initiated by attack of the electrophilic iodonium source to the double bond to form a cyclic iodonium ion and formation of β -silicon stabilized cation. After rotation around the C-C-bond a planar orientation between the empty p-orbital and the C-Si bond is achieved which allows facile removal of the silyl group by a nucleophile. In some instances, additional stabilization of the intermediate carbocation by the solvent was accounted [11].

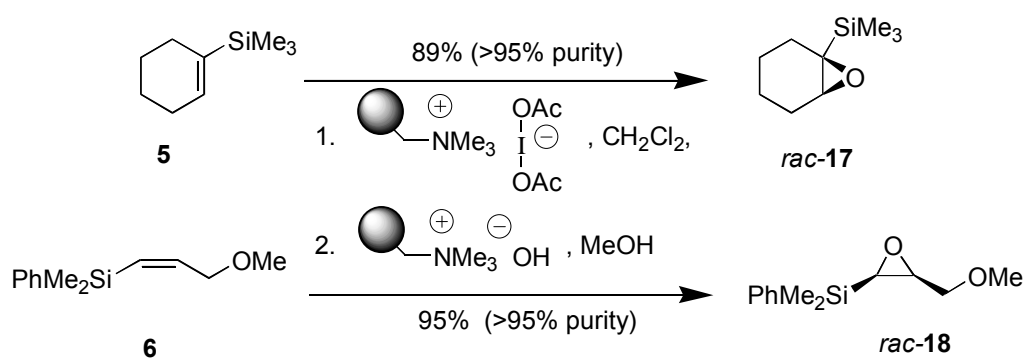
In contrast to these results, we observed formation of the 1,2-addition products (**11**)-(13) when vinylsilanes (**5**) and (**6**) were treated with polymer-supported reagents (**2**) and (**3**) in dichloromethane (Table 1). In fact, dimethylphenylsilyl-substituted alkene (**6**) reacted much slower than 1-trimethylsilylcyclohexene (**5**). In a similar manner the even more reactive allylsilanes (**7**)-(9) gave 1,2-cohalogenation products (**14**)-(16) in moderate yield [12]. Only alkynylsilane (**10**) was unreactive under the conditions typically employed [13]. This latter result is in sharp contrast to the treatment of terminal alkynes with functionalized polymer (**3**) which affords alkynyl iodides [7b].

As an extensions of these studies, we utilized iodate(I) reagent (**3**) and Amberlyst A26 (OH⁻- form) for developing a simple addition/cyclization protocol. Starting from vinylsilanes (**5**) and (**6**), crude 1,2-cohalogenation products (**11**) and (**12**) were further transformed under basic conditions to the corresponding epoxysilanes (**17**) and (**18**) in good yield and with high purity (Scheme 1).

Table 1. Haloacetoxylation of vinyl and allyl silanes.

	Alkene	Reagent ^a (eq.) ^b	Product	Yield %, ^c Purity %
5		→ 3 (4), 5h		11 76 (80), >99
6		→ 3 (6), 60h 2 (4), 40h	 X= I X= Br	12 84 (98), >99 13 77 (90) ^d
7		→ 3 (4), 6h	 Nu= OAc	14 62 (75), >95
8		→ 3 (3), 6h	 Nu= OAc	15 67 (80), >95
9		→ 3 (5), 2.5h		16 83, >95
10		→ 3 (8), 8d	-----	no reaction

^a Refer to Experimental Section. ^b All reagents are employed in excess with reference to the amount of polymer-bound halide specified by the commercial provider [13]. ^c All yields refer to isolated pure products. Yields in parentheses refer to crude products. ^d Formation of the 1,2-*cis*-addition byproduct was proven by ¹H-NMR-spectroscopy of the crude product.



Scheme 1.

In conclusion, polymer-supported haloate(I)-complexes promote cohalogenation of allyl and vinylsilanes under very mild conditions without exerting substantial desilylation. These reagents allow easy product isolation, are conveniently recycled [14] and finally are potentially useful for automated solution phase synthesis.

Experimental

General Methods

^1H - and ^{13}C -NMR spectra were measured with 200 MHz (50 MHz) using tetramethylsilane as the internal standard. CDCl_3 is the solvent for all NMR experiments. All solvents used were of reagent grade and were further dried. Reactions were monitored by TLC on silica gel 60_{P254} and detected either by UV-absorption or by staining with H_2SO_4 / 4-methoxybenzaldehyde in ethanol. Flash column chromatography was performed on silica gel 60 (230-400 mesh).

General Procedure for the Preparation of Polymer-Bound Reagents 2 and 3

A suspension of polymer bound halide (available from Fluka; 3.5 mmol/g bromide and 2.9 mmol/g) and $\text{PhI}(\text{OAc})_2$ (1.8 eq.) in dry CH_2Cl_2 (2.5 mL/mmol halide anion) under nitrogen was shaken at 300 rpm for 24 h at room temperature. The yellowish suspension was protected from light. Filtration and washing of the resin with CH_2Cl_2 (3x) and drying in vacuo afforded the light yellow reagents.

General procedure for the 1,2-cohalogenation of silylated alkenes

A mixture of alkene (1 eq.) and resin (for number of eq. refer to Table 1) were shaken at 300 rpm under light protection in dry CH_2Cl_2 (1.5 ml / mmol) at rt. Completion of the reaction was monitored by tlc. Filtration terminated the reaction. The resin was washed with CH_2Cl_2 (3x) and the combined organic washings and filtrate were concentrated under reduced pressure. In some cases, further purification by column chromatography was necessary. Selected physical and spectroscopic data for cohalogenation products **12** and **14** (final purification by flash column chromatography on silica gel: petroleum ether/ethyl acetate 50:1).

12: colourless oil; ^1H NMR (CDCl_3): δ = 7.58 and 7.35 (m, 5H, Ph), 4.50 (ddd, 1H, J = 6.5, 5.4, 3.1 Hz, 2-H), 3.67 (d, 1H, J = 3.1 Hz, 3-H), 3.42 (dd, 1H, J = 9.3, 5.4 Hz, 1-H), 3.35 (dd, 1H, J = 9.3, 6.5 Hz, 1'-H), 3.25 (s, 3H, OCH_3), 1.91 (s, 3H, OAc), 0.49 [s, 6H, $\text{Si}(\text{CH}_3)_2$]; ^{13}C NMR (CDCl_3): δ = 189.5 (s, $\text{C}=\text{O}$), 135.5 (s, *ipso* Ph), 133.9, 127.7 (d, *ortho* and *meta* Ph), 129.6 (d, *para* Ph), 74.2 (t, C-1), 70.2 (d, C-2), 58.8 (q, OCH_3), 20.9 (q, OAc), 20.1 (d, C-3), -2.38 and -3.13 [q, $\text{Si}(\text{CH}_3)_2$]; Anal. Calcd. for $\text{C}_{14}\text{H}_{21}\text{IO}_3\text{Si}$: C, 42.86; H, 5.40; I, 32.35. Found: C, 42.59; H, 5.21; I, 30.99.

14: colourless oil; ^1H NMR (CDCl_3): δ = 7.60 and 7.30 (m, 5H, Ph), 4.79 (dddd, 1H, J = 8.3, 5.6, 5.0, 5.0 Hz, CHOAc), 3.33 and 3.18 (2dd, 2H, J = 10.4, 5.0 Hz, $\text{CH}_2\text{-I}$), 1.87 (s, 3H, OAc), 1.36 (dd, 1H, J =

14.8, 8.3 Hz, CH₂Si), 1.24 (dd, 1H, *J*= 14.8, 5.6 Hz, CH₂-Si), 0.35, 0.34 [2s, 6H, Si(CH₃)₂]. - ¹³C NMR (CDCl₃): δ = 170.1 (s, C=O), 137.8 (s, *ipso* Ph), 133.5, 127.9 (d, *ortho* and *meta* Ph), 129.2 (d, *para* Ph), 70.6 (d, CHOAc), 22.4 (t, CH₂Si), 20.9 (q, OAc), 12.4 (t, CH₂-I), -2.5 and -2.7 [q, Si(CH₃)₂]; Anal. Calcd. for C₁₃H₁₉IO₂Si: C, 43.10; H, 5.29; I, 35.03. Found: C, 42.91; H, 5.40; I, 34.15.

Acknowledgements

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13. This fact, may either be rationalized by assuming that only a proportional amount of immobilized halide was transformed into the haloate(I)-species or that only the most accessible haloate(I) anions are involved in the cohalogenation process. If acylated hypohalites are the active species after release from the polymer (see also reference [12]), their degradation prior to the reaction with alkenes may also contribute to the need for a formal excess of reagent.
14. The functionalized polymers were recycled to the halide form without loss of activity by treatment with concentrated aqueous HBr or HI for 1 h at rt.

Sample Availability: Samples of compounds **1**, **2**, **3**, **4**, **11**, **12**, **17** are available from the authors.

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