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## Cohalogenation of Allyl and Vinylsilanes using Polymer-bound Haloate(I)-Reagents<sup>‡</sup>

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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<sup>-</sup>-form) vinyl silanes are converted into epoxy silanes.

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

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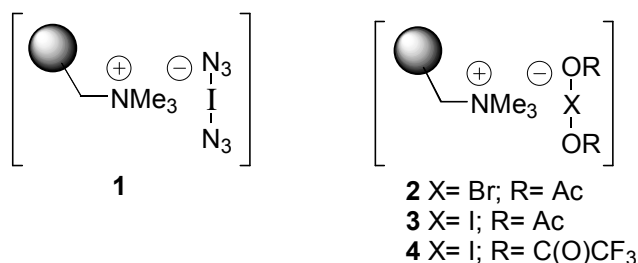
### Introduction

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, IBF<sub>4</sub>, 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  $\beta$ -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].

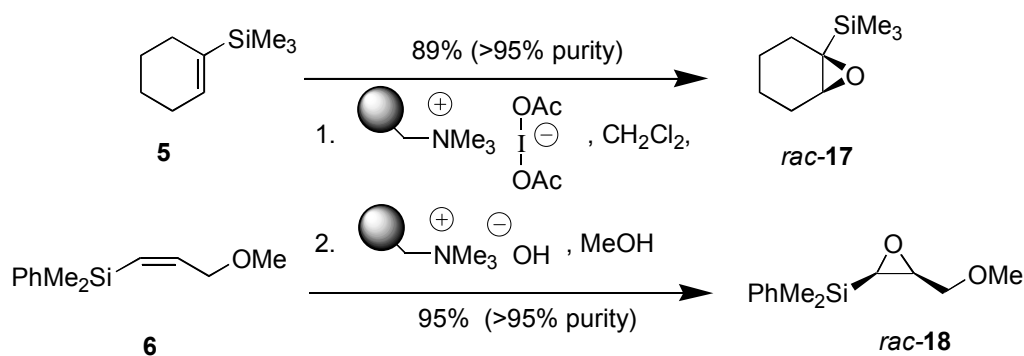
In contrast to these results, we observed formation of the 1,2-addition products (**11**)-(13) when vinylsilanes (**5**) and (**6**) were treated with polymer-supported reagents (**2**) and (**3**) in dichloromethane (Table 1). In fact, dimethylphenylsilyl-substituted alkene (**6**) reacted much slower 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<sup>-</sup>- 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 <sup>a</sup> (eq.) <sup>b</sup>	Product	Yield %, <sup>c</sup> 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) <sup>d</sup>
7		→ 3 (4), 6h		14 62 (75), >95
8		→ 3 (3), 6h		15 67 (80), >95
9		→ 3 (5), 2.5h		16 83, >95
10		→ 3 (8), 8d	-----	no reaction

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

$^1\text{H}$ - and  $^{13}\text{C}$ -NMR spectra were measured with 200 MHz (50 MHz) using tetramethylsilane as the internal standard.  $\text{CDCl}_3$  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<sub>P254</sub> and detected either by UV-absorption or by staining with  $\text{H}_2\text{SO}_4$ / 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  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$  (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  $\text{CH}_2\text{Cl}_2$  (1.5 ml / mmol) at rt. Completion of the reaction was monitored by tlc. Filtration terminated the reaction. The resin was washed with  $\text{CH}_2\text{Cl}_2$  (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;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{OCH}_3$ ), 1.91 (s, 3H,  $\text{OAc}$ ), 0.49 [s, 6H,  $\text{Si}(\text{CH}_3)_2$ ];  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 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,  $\text{OCH}_3$ ), 20.9 (q,  $\text{OAc}$ ), 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;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  = 7.60 and 7.30 (m, 5H, Ph), 4.79 (dddd, 1H,  $J$ = 8.3, 5.6, 5.0, 5.0 Hz,  $\text{CHOAc}$ ), 3.33 and 3.18 (2dd, 2H,  $J$ = 10.4, 5.0 Hz,  $\text{CH}_2\text{-I}$ ), 1.87 (s, 3H,  $\text{OAc}$ ), 1.36 (dd, 1H,  $J$ =

14.8, 8.3 Hz, CH<sub>2</sub>Si), 1.24 (dd, 1H, *J*= 14.8, 5.6 Hz, CH<sub>2</sub>-Si), 0.35, 0.34 [2s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>]. - <sup>13</sup>C NMR (CDCl<sub>3</sub>): 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, CH<sub>2</sub>Si), 20.9 (q, OAc), 12.4 (t, CH<sub>2</sub>-I), -2.5 and -2.7 [q, Si(CH<sub>3</sub>)<sub>2</sub>]; Anal. Calcd. for C<sub>13</sub>H<sub>19</sub>IO<sub>2</sub>Si: 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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