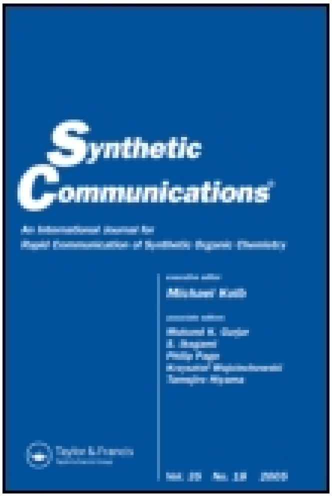


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A Convenient Synthesis of Allyltrimethylsilanes from Allylic Phosphates

Janice Gorzynski Smith [a] , Susan L. Henke [a] , Elizabeth M. Mohler [a] , Linda Morgan [a] & N. Ivy Rajan [a]

[a] Department of Chemistry, Carr Laboratory , Mount Holyoke College , South Hadley, Massachusetts, 01075

To cite this article: Janice Gorzynski Smith , Susan L. Henke , Elizabeth M. Mohler , Linda Morgan & N. Ivy Rajan (1991) A Convenient Synthesis of Allyltrimethylsilanes from Allylic Phosphates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 21:20, 1999-2006, DOI: 10.1080/00397919108019805

To link to this article: http://dx.doi.org/10.1080/00397919108019805

SYNTHETIC COMMUNICATIONS, 21(20), 1999-2006 (1991)

A CONVENIENT SYNTHESIS OF ALLYLTRIMETHYLSILANES FROM ALLYLIC PHOSPHATES

Janice Gorzynski Smith,*,[1] Susan L. Henke, Elizabeth M. Mohler, Linda Morgan, and N. Ivy Rajan

Department of Chemistry, Carr Laboratory,
Mount Holyoke College, South Hadley, Massachusetts 01075

Abstract: Treatment of an allylic phosphate with trimethylsilyllithium or trimethylsilylcopper [prepared from one equivalent of trimethylsilyllithium and copper(I) iodide] affords allyltrimethylsilanes in good - excellent yields with high stereoselectivity.

The use of unsaturated organosilanes in organic synthesis has seen a growing popularity in recent years. In particular, allylsilanes are known to undergo a wide variety of reactions with predictable regiospecificity,[2] and this has prompted the need for mild and controlled methods for the introduction of this functional group into a molecule.

We have recently reported a new method for synthesizing allyltrimethylsilanes from allylic halides using trimethylsilylmetal reagents,[3] and have used this method in the regio- and stereoselective synthesis of two isomeric allyltrimethylsilanes from a single allylic halide by appropriate choice of reaction conditions.[4,5] Herein we report that allylic

---

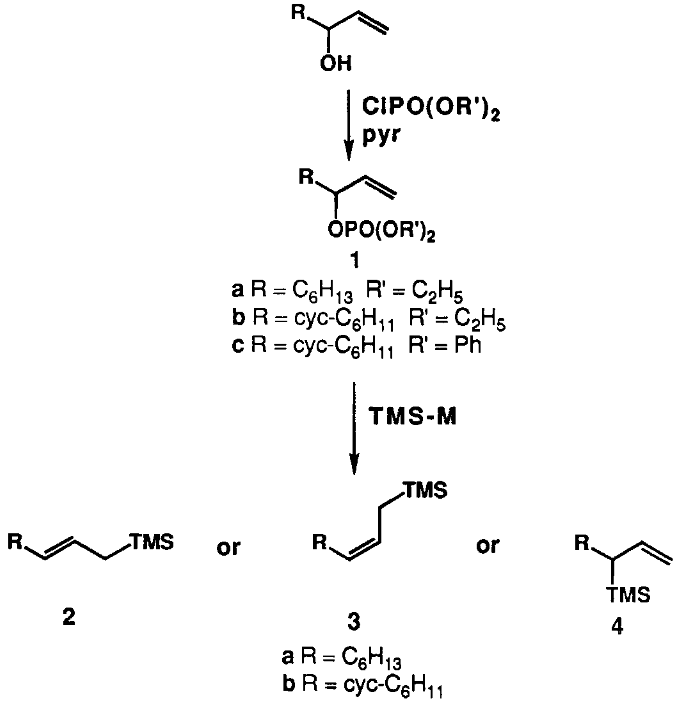
*To whom correspondence should be addressed *phosphates react with these same silyl metal reagents to form allyltrimethylsilanes* stereoselectively in high yield. Although there are now several examples of the reaction of trialkylsilyl- or arylalkylsilylmetal reagents with allylic halides and allylic acetates,[6] the use of allylic phosphates as precursors to allylsilanes has remained largely unexplored.[7]

Specifically, we have examined the reaction of a variety of 1° and 2° allylic phosphates such as **1** with trimethylsilyllithium (TMSLi),[8] trimethylsilylcopper [TMSCu, formed from one equivalent each of trimethylsilyllithium and copper(I) iodide],[5] and lithium bis(trimethylsilyl)cuprate [$(TMS)_2CuLi$, formed from two equivalents of trimethylsilyllithium and one equivalent of copper(I) iodide] in hexamethyl-

TMS-Li **TMS-Cu** **$(TMS)_2CuLi$**

phosphoramide (HMPA):ether (1:3) at -60 - -50° C. The allylic phosphates **1** were prepared in high yield from the corresponding allylic alcohols using diethyl chlorophosphate or diphenyl chlorophosphate in pyridine using known methods.[9] The results are summarized in the Table.

Although a 2° allylic phosphate such as **1** could in theory afford three isomeric *allylsilanes* **2**, **3**, *or* **4** *by reaction with a trimethylsilylmetal reagent (Equation I), we have* found that treatment of a substrate such as **1** with either TMSLi or TMSCu affords only allylsilanes **2** and **3** having an internal carbon-carbon double bond, with **2** being the predominant if not exclusive product formed. For example, when **1b** was treated with trimethylsilylcopper in HMPA:ether (1:3) at -60 - -50°C the **E** isomer **2b** was formed in 81% isolated yield (Entry 2). With TMSLi, this same product was formed exclusively in 59% yield (Entry 5). With these 2° allylic phosphates it is generally true that yields are higher with TMSCu, and when mixtures of stereoisomers result the reactions are more stereoselective with this silyl metal reagent (Entries 1 and 4). It was likewise noted that using a reagent prepared from two equivalents of TMSLi and one



1

a R = C_6H_{13} R' = C_2H_5
b R = cyc-C_6H_{11} R' = C_2H_5
c R = cyc-C_6H_{11} R' = Ph

2 **3** **4**

a R = C_6H_{13}
b R = cyc-C_6H_{11}

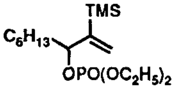
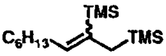
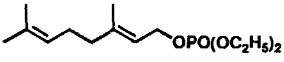
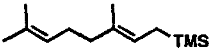
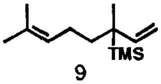
(I)

equivalent of copper(I) iodide gave reasonable yields of allylsilanes but with poorer stereoselectivity (Entry 7).

With 1° allylic phosphates this reaction was likewise successful (Entries 9 and 10). Treatment of **7** with TMSCu afforded a mixture of allylsilanes in 92% yield, with the isomer **9** having a terminal double bond and the trimethysilyl group at the 3-position formed predominantly. Moreover, in this case TMSLi gave complementary results, with the isomeric allylsilane **8** formed exclusively in 69% yield.

It should likewise be noted that we found that it was not necessary to isolate the allylic phosphate prior to reaction with a trimethylsilylmetal reagent (Entry 8). In cases where the allylic phosphate appeared to be unstable or could only be isolated cleanly in

Table: Conversion of Allylic Phosphates to Allylsilanes

Entry	Compound	Reagent	Product[a]	Yield[b]
1	**1a**	TMSCu	**2a**:**3a** (88:12)	84%
2	**1b**	TMSCu	**2b** only	81%
3	**1c**	TMSCu	**2b** only	67%
4	**1a**	TMSLi	**2a**:**3a** (69:31)	71%
5	**1b**	TMSLi	**2b** only	59%
6	**1c**	TMSLi	**2b** only	61%
7	**1a**	$(TMS)_2CuLi$	**2a**:**3a** (55:45)	80%
8	 **5**	TMSCu	 (Z:E, 55:45) **6**	34%[c]
9	 **7**	TMSCu	 + **8**  9 (**8**:**9**, 25:75)	92%
10	**7**	TMSLi	**8** only	69%

---

[a] Ratios were determined by gas chromatography using an OV-17 column.

[b] Yields refer to products isolated and purified by column chromatography.

[c] The phosphate was formed *in situ* from the allylic alcohol.

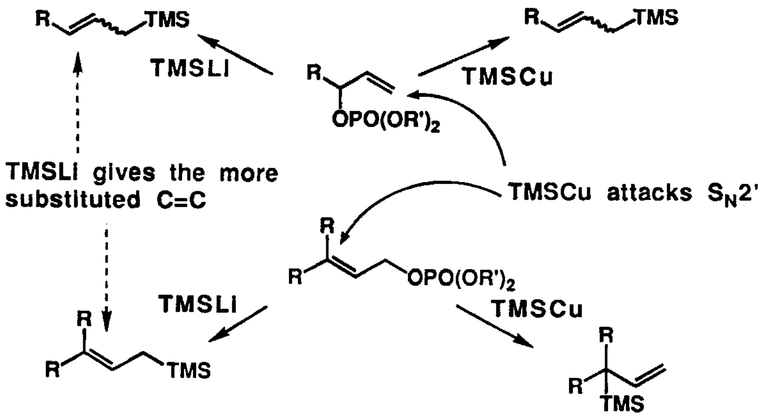


FIG I

low yield, it was possible to prepare the allylic phosphate from the allylic alcohol using a dialkyl chlorophosphate and methyllithium in ether at -78°, and add this intermediate to the trimethylsilylmetal reagent directly. This "one-step" conversion of an allylic alcohol to an allylsilane (*via* an allylic phosphate formed *in situ*) provides an attractive alternative to existing methodology.

From these results the following conclusions can be drawn. Reaction of an allylic phosphate with either TMSCu or TMSLi affords allyltrimethylsilanes stereoselectively in high yield. In general it has been observed that when an allylic phosphate is treated with TMSCu, the major or exclusive product is formed from what is formally an S_N2'-like reaction. With TMSLi, however, the major product is always the isomeric allylsilane having a more substituted internal double bond (FIG I). This reaction complements existing methodology in that with allylic halides as starting materials, the major allylsilane formed using TMSCu as reagent is usually the isomer having a terminal double bond with the trimethylsilyl group at the 3-position.[5] Since most allylic phosphates are stable substrates and readily available from allylic alcohols in high yield, this reaction should provide a valuable new method for the synthesis of allylsilanes.

Experimental

Allylic phosphates: Allylic phosphates **1** were in general prepared from the corresponding allylic alcohols using diethyl (or diphenyl) chlorophosphate in pyridine at 0° for 1 h. The crude products were purified using silica gel column chromatography to afford the desired material **1a-1c** and **7** in high yield.[9] Allylic phosphate **5** was prepared from 2-trimethylsilyl-1-nonen-3-ol by treatment with 1.0 equiv of methyllithium-lithium bromide complex and 1.0 equiv of diethyl chlorophosphate in ether at -78° for 3 h. It was used directly without isolation.

Typical procedure for the preparation of (E)-1-trimethylsilyl-2-nonene 2b with TMSCu: To a vigorously stirred solution of TMSCu (2.5 mmol), prepared as previously described[5] from TMSLi[8] (2.5 mmol) and copper(I) iodide (2.5 mmol) in dimethyl sulfide (1 mL) and HMPA (3 mL) at 0 - 5° under argon was added 7 mL of ether. The black reaction mixture was stirred for 1 min, cooled to -60 - -50° and stirred 2-3 min. Allylic phosphate **1b** (1mmol) was added in 1 mL of ether and the reaction mixture was stirred 1 h at this temperature. The cold mixture was poured into petroleum ether and saturated ammonium chloride solution (buffered to pH 8 by addition of ammonium hydroxide) and the two-phase mixture was stirred for 1 h. The aqueous phase was extracted with petroleum ether and the combined organic extracts were washed with water, dried and concentrated. The crude product was purified by silica gel column chromatography with petroleum ether as eluent to afford **2b** in 81% yield. Spectral data for **2b** have been previously reported.[5]

Typical procedure for the preparation of 2b with TMSLi: To a vigorously stirred red solution of TMSLi (2.5 mmol) in HMPA (3 mL) at 0 - 5° under argon was added 7 mL of ether. The reaction mixture was cooled to -60 - -50° and stirred 2-3 min, and the allylic phosphate **1b** was added in 1 mL of ether. The reaction mixture was stirred 1 h at this temperature and the cold mixture was poured into petroleum ether and saturated ammonium chloride solution. The aqueous phase was extracted with petroleum ether, and **2b** was isolated in 59% yield exactly as described above.

Acknowledgment

We gratefully acknowledge financial support from the Biomedical Research Division of American Cyanamid, the Petroleum Research Fund, and Mount Holyoke College (Skinner Fellowship to N. Ivy Rajan) for support of this work. We also thank the National Science Foundation and the Pew Memorial Trust for funds used to purchase the GC/MS used for product analysis in this work.

References

1. Recipient of an American Cyanamid Academic Award, 1990.
2. (a) Fleming, I. and Dunogues, J., *Org. Reactions*, **1989**, *37*, 57; (b) Colvin, E. "Silicon Reagents in Organic Synthesis," Academic Press, Boston, **1988**.
3. Smith, J.G., Quinn, N.R., and Viswanathan, M, *Synth. Commun.*, **1983**, *13*,1.
4. Smith, J.G., Quinn, N.R., and Viswanathan, M, *Synth. Commun.*, **1983**, *13*, 773.
5. Smith, J. G., Drozda, S.E., Petraglia, S. P., Quinn, N. R., Rice, E.M., Taylor, B. S., and Viswanathan, M., *J. Org. Chem.*, **1984**, *49*, 4112.
6. See for example: (a) Trost, B.M. and Chan, D.M.T., *J. Am. Chem. Soc.*, **1982**, *104*, 3733; (b) Fleming, I. and Marchi, D., Jr., *Synthesis*, **1981**, 560; (c) Negishi, E., Luo, F.T., and Rand, C.L., *Tetrahedron Lett.*, **1982**, *23*, 27.
7. There is one report of the reaction of a silyl aluminum reagent with an allylic phosphate to give a mixture of isomeric allylsilanes: Okuda, Y., Sato, M., Oshima, K., and Nozaki, H., *Tetrahedron Lett.*, **1983**, *24*, 2015.

8. Still, W.C., *J. Org. Chem.*, **1976**, *41*, 3063.

9. Araki, S. and Butsugan, *J. Chem. Soc. Perkin Trans. I*, **1984**, 969.

(Received in USA 22 May, 1991)