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# Preparation of Allylsilanes via Cross-Metathesis

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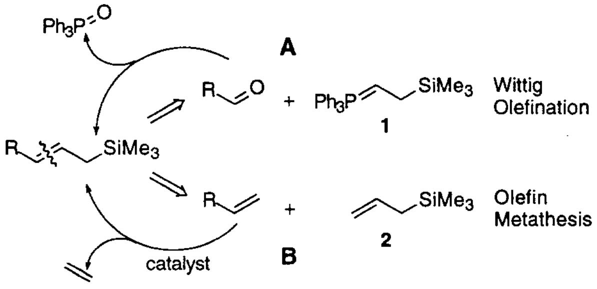
**Abstract:** Allylsilanes are prepared by simple metathetical cross-coupling of terminal olefins with allyltrimethylsilane. Allyltrimethylsilane coupling with $\pi$-substituted terminal olefins (styrenes, 1-phenyl-1,3-butadiene, and acrylonitrile) proceeds in excellent yield and very high selectivity. Lower, but still useful, selectivities are observed for allyltrimethylsilane/alkyl olefin cross-metathesis reactions.

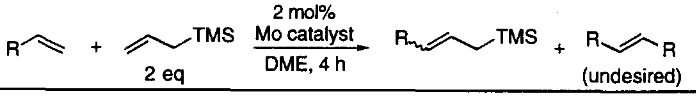
Allylsilanes are an important class of carbon nucleophiles in organic synthesis possessing a number of favorable traits including stability, ease of handling, and versatile reactivity.[1] Olefination (Scheme 1) is an attractive route for allylsilane synthesis if the organosilane component is readily obtained. Allylsilanes can be prepared by Wittig olefination (Scheme 1A) using the Seyferth-Fleming phosphorane,[2] $Ph_3P=CHCH_2SiMe_3$ (**1**), as the organosilane reagent; generation of the phosphorane reagent is reasonably straightforward and the Wittig olefination reaction is fairly general.[3] We report here that allylsilanes can also be prepared by olefin metathesis (Scheme 1B) using allyltrimethylsilane, $CH_2=CHCH_2SiMe_3$ (**2**), as the organosilane reagent. A notable advantage of olefin metathesis is the use of off-the-shelf organosilane reagent (as opposed to *in situ* generated **1**).



**Scheme 1**

The successful application of olefin metathesis to allylsilane synthesis hinges on the cross-metathesis selectivity of the coupling reaction. In previous studies we observed high cross-metathesis selectivity for the coupling of styrenes[4] or acrylonitrile[5] with sterically small, alkyl-substituted olefins. We reasoned that selectivity arose from the preferential reaction of the most stable alkylidene in solution (aryl- or cyano-substituted) with the most nucleophilic olefin. Hyperconjugative C-Si electron donation from the $CH_2SiMe_3$

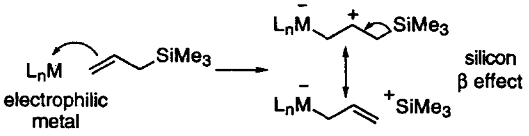
**Table 1.** Cross-Metathesis Reactions of π- and Alkyl-substituted Olefins



| Entry | R | Yield[a] | Trans:Cis[b] | RCH=CHR[a] (%) |
|---|---|---|---|---|
| 1 | Ph | 85 (92)[d] | trans | 0[c] |
| 2 | *p*-$MeC_6H_4$ | 83 | trans | 0[c] |
| 3 | *p*-$MeOC_6H_4$ | 61 | trans | 0[c] |
| 4 | *o*-$NO_2C_6H_4$ | 40 | trans | 0[c] |
| 5 | PhCH=CH | 80 | 4.2:1 | 0[c] |
| 6 | CN | 76[e] | 1:4.7 | 0[c] |
| 7 | $(CH_2)_2CO_2Bn$ | 61 | 3.0:1 | 30 |
| 8 | *o*-$MeOC_6H_4CH_2$ | 73 | 3.2:1 | 7[c] |
| 9 | $(CH_2)_3OPh$ | 72 | 2.6:1 | 5[c] |
| 10 | $(CH_2)_3Br$ | 60 | 3.1:1 | 19 |
| 11 | $(CH_2)_2Br$ | 45 | 2.8:1 | 12 |
| 12 | $(CH_2)_3CH(OMe)_2$ | 55 | 2.7:1 | 5 |
| 13 | $(CH_2)_4OTBS$ | 56 | 2.8:1 | 19 |
| 14 | $(CH_2)_3OTBS$ | 54 | 3.8:1 | 10 |
| 15 | $(CH_2)_2OTBS$ | 62 | 3.2:1 | 23 |
| 16 | $(CH_2)_4OBn$ | 66 | 2.6:1 | 6[c] |
| 17 | $(CH_2)_3OBn$ | 60 | 4.6:1 | 26[c] |
| 18 | $(CH_2)_2OBn$ | 67 | 3.7:1 | 8[c] |
| 19 | $(CH_2)_3CN$ | 62 | 4.9:1 | 14 |
| 20 | $(CH_2)_2CN$ | 37 | 4.4:1 | 15 |
| 21 | $CH_2CN$ | 34 | 4.1:1 | 0[c] |

a) Reported yields are for pure, isolated products. A small amount of the product of allyltrimethylsilane self-metathesis (ca. 5-7% yield) was observable in crude product mixtures. b) Determined by $^1H$ NMR with the aid of homonuclear decoupling. c) Estimated from $^1H$ NMR of crude product mixture. d) Yield in parenthesis is for a reaction run in $Et_2O$ in the presence of 4 mol% $PPh_3$. e) 5 mol% catalyst used ($CH_2Cl_2$ solvent), see reference 5.

substituent of allyltrimethylsilane should enhance olefin nucleophilicity (eq 1) but should have little or no effect on alkylidene stability. Thus, allyltrimethylsilane might be expected to undergo selective cross-metathesis with π-substituted olefins such as styrene or acrylonitrile. When various π-substituted olefins were treated with allyltrimethylsilane in the presence of Schrock's molybdenum catalyst $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ (3, 2-5 mol%)[6] high cross-metathesis selectivity was in fact observed (Table 1, entries 1-6).[7,8]

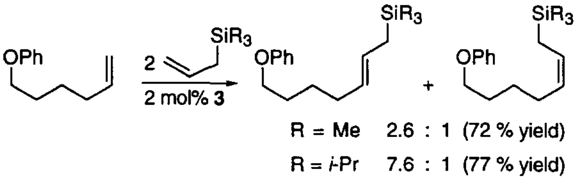


(1)

Metathetical coupling of allyltrimethylsilane with small, alkyl-substituted olefins might not be expected to be highly selective since neither olefin possesses a good alkylidene stabilizing substituent. When alkyl-substituted olefins were reacted with allyltrimethylsilane (2 equiv) in the presence of catalyst **3** (2 mol%) smaller, but still useful, levels of cross-metathesis selectivity were observed as illustrated in Table 1 (entries 7-21).[8] For these reactions we found that a coordinating solvent like dimethoxyethane (DME) was necessary to provide reasonable yield and selectivity.[9, 10] The ratio of cross-metathesis to self-metathesis of the alkyl olefin, ranges from 2.0:1 to 11:1, with a 3:1 ratio being typical.

For allyltrimethylsilane cross-metathesis reactions the crude reaction mixture is composed of up to three additional components which must be separated from the desired cross-metathesis product: self-coupled allyltrimethylsilane (5-7%), self-coupled alkyl olefin (see Table 1), and unreacted alkyl or aryl olefin (5-10%). Unreacted alkyl or aryl olefin has similar polarity to the desired product and often cannot be removed by conventional flash chromatography. We found that the use of silica gel containing 15% (by weight) silver nitrate[11] allowed for easy removal of unreacted starting material, along with the other two reaction byproducts.

In the one example that we examined, we found that increasing the size of the alkyl groups on the allyltrialkylsilane reagent can increase trans selectivity without diminishing the overall yield. Thus, the cross-metathesis of phenyl 4-pentenyl ether with allyltriisopropylsilane gave 7.6 : 1 trans/cis selectivity (eq 2).



(2)

The cross-metathesis selectivity observed in the alkyl olefin/allyltrimethylsilane coupling reactions suggests that the $CH_2SiMe_3$ substituent not only enhances the reactivity of an olefin via electron-donation but also diminishes the reactivity of an alkylidene via steric hindrance.[12] Were this not the case, self-metathesis of allyltrimethylsilane (used in two-fold excess) would be observed to a much larger extent. Cross-metathesis selectivities obtained from the data given in Table 1 give some indication of relative olefin reactivities in the product-forming step. Allyltrimethylsilane appears to be slightly (1.02-7.2 times) more reactive[13] than small, alkyl-substituted olefins and substantially (> 20 times) more reactive than $\pi$-substituted olefins.

In conclusion, we have reported an operationally simple method for conversion of terminal olefins to allylsilanes in good yields using stable, readily available allyltrimethylsilane as the organosilane reagent. The results presented herein demonstrate the potential of electron-rich olefins as cross-metathesis substrates. The cross-metathesis selectivity reported herein may also apply to other allylmetal substrates and perhaps to other classes of electron-rich olefins.[14]

**Acknowledgment.** Support of this work by the Emory University Research Fund and the Petroleum Research Fund is gratefully acknowledged.

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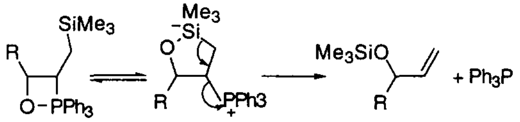
2. (a) Seyferth, D.; Wursthorn, K. R.; Mammarella, R. E. *J. Org. Chem.* **1977**, *42*, 3104. (b) Seyferth, D.; Wursthorn, K. R.; Lim, T. F. O.; Sepelak, D. J. *J. Organomet. Chem.* **1979**, *181*, 293-304. (c) Fleming, I.; Paterson, I. *Synthesis* **1979**, 446-448.

3. A yield-limiting side reaction which sometimes occurs is:



   See: (a) Tsukamoto, M.; Iio, H.; Tokoroyama, T. *Tetrahedron Lett.* **1985**, *26*, 4471-4474. (b) Tsukamoto, M.; Iio, H.; Tokoroyama, T. *J. Chem. Soc., Chem. Commun.* **1986**, 880-882. (c) Hughes, L. R.; Schmid, R.; Johnson, W. S. *Bioorg. Chem.* **1979**, *8*, 513-518.
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5. Crowe, W. E.; Goldberg, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 5162-5163.
6. (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373-1374. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. B. *J. Am. Chem. Soc.* **1990**, *112*, 3875-3886. (c) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287-2289.
7. A representative procedure: To a mixture of 80 mg of 4-methylstyrene (0.68 mmol) and 155 mg (1.36 mmol) of allyltrimethylsilane in 2 mL of DME was added 10 mg (0.01 mmol) of $Mo(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ (**3**). The resulting mixture was stirred at room temperature for 4 hours in an uncapped vial, then passed through a pad of silica gel and rinsed with methylene chloride. The solvent was removed under reduced pressure, and the crude residue was chromatographed on silica gel containing 15% (by weight) $AgNO_3$ (hexane eluent) to provide 116 mg (83%) of trimethyl[3-(4-methylphenyl)-2-propenyl]silane as a clear, colorless liquid. A similar reaction run with 5.0 g (42 mmol) of 4-methylstyrene, 9.66 g (84 mmol) of allyltrimethylsilane, 324 mg (1 mol%) of catalyst afforded 7.8 g (89%) of trimethyl[3-(4-methylphenyl)-2-propenyl]silane and 0.44g (9%) of unreacted 4-methylstyrene.
8. All new compounds were characterized spectroscopically by $^1H$ NMR, $^{13}C$ NMR, and IR spectroscopy and gave satisfactory combustion analysis and/or high-resolution mass spectrometric data.
9. DME has been shown to stabilize methylene complexes formed as reactive intermediates in and products of molybdenum-catalyzed olefin metathesis reactions: (a) Fox, H. H.; Lee, J. K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759-768. (b) Fox, H. H.; Schrock, R. R.; Odell, R. *Organometallics* **1994**, *13*, 635-639.
10. In allyltrimethylsilane/styrene cross-metathesis, we found that addition of 4 mol% $PPh_3$ increases the reaction yield from 85% to 92%. A possible explanation for this intriguing result is that $PPh_3$ extends catalyst life by stabilizing the methylene complex[9] formed as reactive intermediate in the coupling reaction.
11. Gupta, A. D.; Dev, S. J. *J. Chromatogr.* **1963**, *12*, 189-195.
12. Alkylidene reactivity has been shown to be strongly dependent on the size of the alkylidene substituent. See, for example: (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423-35. (b) Feldman, J. Ph.D. Thesis, Massachusetts Institute of Technology, 1989; pp 59-63. (c) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004.
13. This probably reflects a counterbalance of increased electron-richness (increasing reactivity) and greater steric bulk (decreasing reactivity) of allyltrimethylsilane compared to a small, alkyl-substituted olefin.
14. Preliminary experiments show that allyltributylstannane can be selectively cross-metathesized with substituted styrenes. Crowe, W. E.; Goldberg, D. R.; Zhang, Z. J., work in progress.

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