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Vinylborane and Vinylchalcogenide Mediated Syntheses of Tri- and Tetrasubstituted Olefins from 1-Alkynes.

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Abstract: The title olefins have been prepared with high regio- and stereocontrol from 1-alkynes through vinyl boranes / vinyl chalcogenides; the reaction sequences involved protonolysis or transmetallation - alkylation of the boranes followed by an Ni(0) catalyzed coupling reaction. © 1998 Elsevier Science Ltd. All rights reserved.

Among the numerous methods for assembling olefinic structures[1] the most versatile ones are those taking advantage of the availability of regio- and stereodefined vinylmetals[2] having one or more metallic and/or heteroatomic moieties attached to the double bond. Many of these heterosubstituted vinylic intermediates are accessible *inter alia* by the transition metal catalyzed, as well as by the uncatalyzed, additions to alkynes of various main group metal derivatives.[3]

Herein we report our first results on the synthesis and further transformations of chalcogen substituted vinylboranes obtained from 1-alkynylboron «ate» complexes[4] or by hydroboration of 1-chalcogeno-1-alkynes. We show that these diheterosubstituted alkenes can lead to the title olefins with good to excellent regio- and stereocontrol.

Although the rearrangements of 1-alkynylborates induced by a number of electrophilic reagents have been described,[4,5] it is the first time that this reaction is extended to tellurenyl halides as electrophiles. Both phenyl- and *n*-butyltellurenyl bromides[6] react smoothly with lithium 1-alkynyl-trialkylborates, respectively to give the corresponding tetrasubstituted alkenes **2** in good yields (Scheme 1, entries 3, 5, 6).

As the **1** -> **2** conversion is completely stereoselective,[7] alkenes **2** should allow elaboration of the title olefins. One possible way of doing this is to carry out Suzuki couplings on these intermediates followed by the well known nickel catalyzed coupling of the so obtained vinyl chalcogenides **3** with Grignard reagents. We have found that this strategy fails to produce the desired tetrasubstituted alkenes in all of the cases tried. Thus, the very crowded vinyldicyclohexylboranes **2** (R_2 = c-Hex)[8] led mainly to the elimination products **4** when subjected to the usual Suzuki coupling conditions in the presence of PhI / $Pd(PPh_3)_4$ / aq. NaOH or Na_3PO_4, DMF (Scheme 1, entries 1-3). The diethyl analogues **2** (R_2 = Et) gave predominantly the hydrolysis products **5** under the same conditions. As expected[9] vinyldicyclohexylboranes **2** also appeared very reluctant towards protonolysis. However, vinyl primary dialkylborane derivatives **2** could be transformed into the disubstituted vinyl chalcogenides **5** in good yield using acetic acid at room temperature (Scheme 1, entries 4-6).[10] In turn, these disubstituted vinyl chalcogenides **5** underwent nickel ($NiCl_2(PPh_3)_2$ or $NiCl_2$(dppe)) catalyzed couplings with Grignard reagents to give trisubstituted alkenes **6** with excellent regio- and stereocontrol (Scheme 1, entries 4,5).

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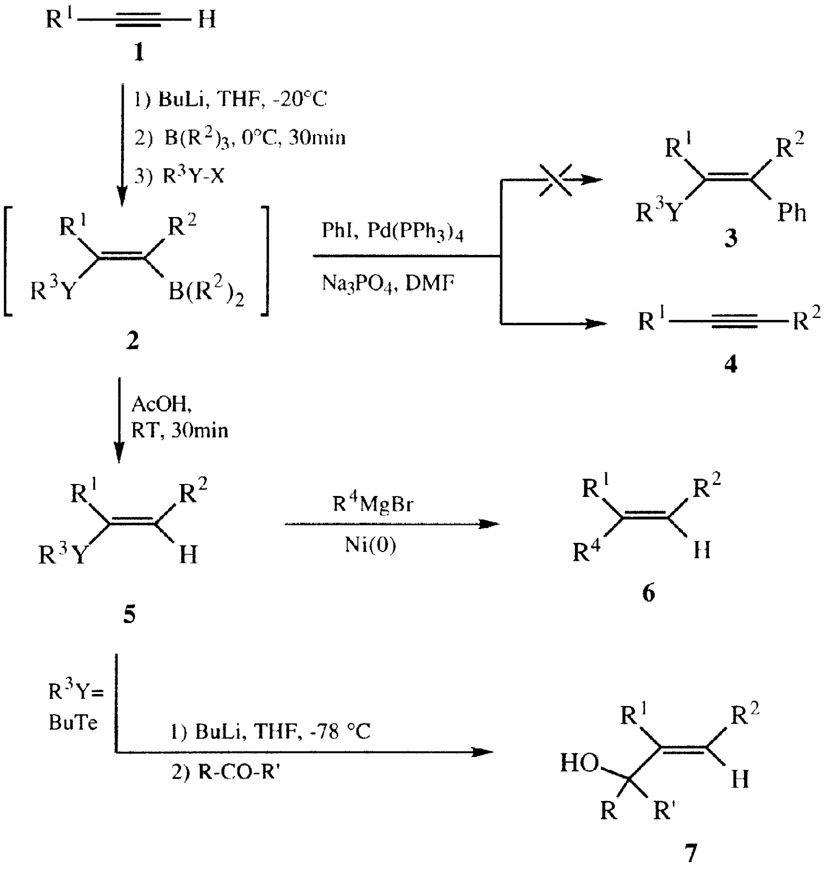
Scheme 1



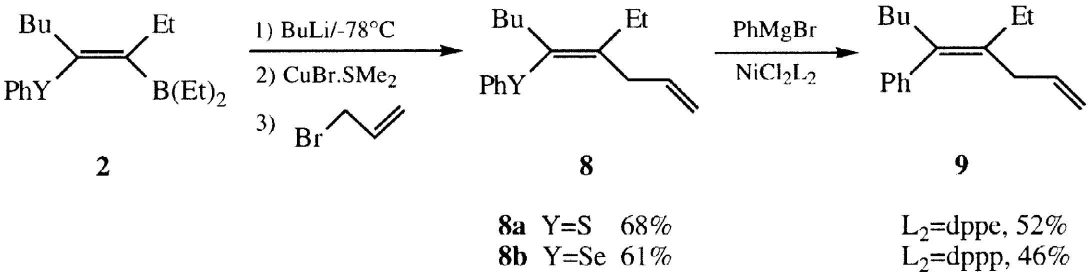
Entry	R^1	R^2	R^3YX	R^4	Product, yield (%)				
					2	4	5	6	7
1	Bu	c-Hex	PhSCl		67	50[a]	55[b]		
2	Pent	c-Hex	PhSeBr		69	82			
3	Pent	c-Hex	PhTeBr		69	88			
4	Bu	Et	PhSCl	Ph	78		74[c]	83	
5	Pent	Et	PhTeBr	Ph			52	77	
6	Bu	Et	BuTeBr				72		70, 68[d]

[a]) 33% of **3** was also formed; [b]) obtained from **2** with 2 equiv. MeLi, then CuI, then MeOH; [c]) Z/E isomeric ratio of 3/97 was established by ^{1}H NMR/DIFNOE ; [d]) yields for R,R'= -$(CH_2)_5$- and Ph,H, respectively

It is known that while the cleavage with butyllithium of phenylvinyl tellurides gives mixtures of phenyl- and vinyllithiums, the latter are formed cleanly from alkylvinyl tellurides.[6,11] This was confirmed in our case by the conversion of a butylvinyltelluride **5** into allylic alcohols **7** in good yields (Scheme 1, entry 6).

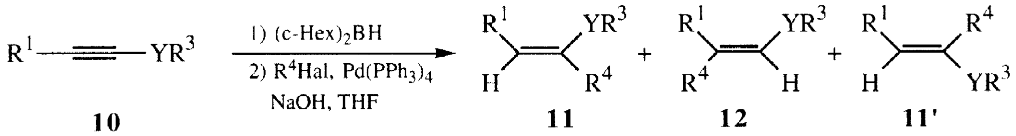
Faced with the failure of the Suzuki-Miyaura couplings we have investigated an alternative way of activating vinylboranes **2** as illustrated in Scheme 2. While the B -> Li -> Cu transmetallation / alkylation of vinylboranes is a known process,[5c, 12] the success of a subsequent coupling was by no means warranted because of the considerable steric crowding present in compounds **8**. Indeed, the reaction of **8** -> **9** displayed modest yields of 52 and 46% (Scheme 2, for Y=S and Se, respectively) even when 10 mol% of catalyst was used.[13]

Scheme 2



We have also studied the potential of the little explored 1-chalcogeno-1-alkenylboranes produced by hydroboration of 1-chalcogeno-1-alkynes **10**. Due to the operation of both steric and electronic effects the hydroboration prefentially places boron *alpha* to sulfur in the case of hydroboration of 1-thio-1-alkynes[9]. The preliminary results displayed in Scheme 3 show that the highest selectivities were obtained on hydroboration of 1-phenylthio-1-heptyne with dicyclohexylborane, followed by palladium-mediated cross-coupling.

Scheme 3



Entry	R^1	YR^3	R^4Hal	**11 : 12 : 11'**	Yield (%)
1	n-Dec	SMe	PhI	71 : 22 : 7	76[a]
2	n-Pent	SPh	PhI	95 : 3 : 2	76[a]
3	n-Pent	SPh	$PhCH_2Cl$	97 : 3 : 0	46[a]
4	n-Pent	TePh	PhI	60 : 14 : 26	25[a]

[a]) The corresponding Z-vinyl chalcogenides arising from the hydrolysis (protodeboronation)[14b] during Suzuki coupling of the intermediary vinyl boranes were also formed in 21, 17, 38 and 70% in entries 1-4, respectively.

In sharp contrast to compounds **2**, subjecting the intermediate 1-(phenylthio)-1-heptenylborane to *in situ* Suzuki coupling led to **11** (YR_3=SPh, R_4=Ph) in good yields.[14] This phenylvinylsulfide also underwent further coupling using $PhMgBr/NiCl_2(dppp)/Et_2O$, rt (84% yield based on consumed vinylsulfide)[15] to produce 1,1-diphenyl-1-heptene, another type of trisubstituted olefin related to alkene **6**.

Work is underway with a view to establishing the scope and limitations of the above methodologies, as well as to solving the problems of proto-deborylation and catalyst poisoning[13,15] (Schemes 2 and 3).

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References and Notes

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7. With a few exceptions this type of reaction is believed to be stereoselective (ref. 4a, p291). Hooz and Mortimer have reported[5a] the non-stereoselective reaction of **1** (R_1= *n*Bu, R_2=Et) with PhSCl. In our case all of the compounds **2** appeared to have *E* stereochemistry.
8. All three phenylchalcogenovinylboranes **2** (Y=S, Se, Te) have been isolated by column chromatography (SiO_2, eluent pentane).
9. Hoshi, M., Masuda, Y., and Arase, A., *Bull. Chem. Soc. Jpn.*, **1990**, *63*, 447.
10. Compounds **5** represent stereoisomeric counterparts of analogues obtained through Pd(0) catalyzed thioboration of 1-alkynes: Ishiyama, T., Nishijima, K., Miyaura, N., and Suzuki, A., *J. Am. Chem. Soc.*, **1993**, *115*, 7219.
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12. Uchida, K. Utimoto, K., and Nozaki, H., *Tetrahedron*, **1977**, *33*, 2987.
13. Yields are based on unrecovered **8**. Premature termination of the reaction seems to be due to poisoning of the catalyst (possibly by the vinylthiolate arising from insertion of Ni(0) into the Ph-Y bond).
14. Regioisomeric analogues of vinylsulfides **11** have been prepared using a catalytic hydroboration-coupling sequence: a) Gridnev, I. D., Miyaura, N., and Suzuki, A., *Organometallics*, **1993**, *12*, 589; b) Gridnev, I. D., Miyaura, N., and Suzuki, A., *J. Org. Chem.*, **1993**, *58*, 5351.
15. The conversion in this latter reaction was only about 50%, possibly due to the poisoning of the nickel catalyst.