changed to 40:60 with 2 equiv Et_3B. Further, use of 1 equiv of R_3B produces **3** either exclusively or predominantly (method C). Presumably, excess R_3B removes PhSeLi from **6** to afford $R_3BSePhLi$ and the corresponding allylic borane, and hence use of excess R_3B facilitates the allylic migration. The regioselectivity for the formation of **3** from aliphatic aldehydes is not so high at the present time. Various kinds of primary alkyl groups as R may be tolerated both in the linear and branched alcohols. This is especially important, since the preparation of the allylic organometallic compounds with a long alkyl chain, in turn the preparation of **2** and **3** with such a substituent,[3] is not so easy. Furthermore, combination between organoselenium chemistry[8] and the boron migration reaction,[9] nowadays rather old chemistry, may provide a new synthetic reaction. Further work along this line is now under active investigation.

Registry No. **2** (R = Et, R′ = Ph) (isomer 1), 87999-70-0; **2** (R = Et, R′ = Ph) (isomer 2), 87999-71-1; **2** (R = Bu, R′ = Ph) (isomer 1), 87999-72-2; **2** (R = Bu, R′ = Ph) (isomer 2), 87999-73-3; **2** (R = Et, R′ = p-$CH_3C_6H_4$) (2somer 1), 87999-74-4; **2** (R = Et, R′ = p-$CH_3C_6H_4$) (isomer 2), 87999-75-5; **2** (R = Et, R′ = p-$CH_3OC_6H_4$) (isomer 1), 87999-76-6; **2** (R = Et, R′ = p-$CH_3OC_6H_4$) (isomer 2), 87999-77-7; **2** (R = Et, R′ = p-$O_2NC_6H_4$) (isomer 1), 87999-78-8; **2** (R = Et, R′ = p-$O_2NC_6H_4$) (2somer 2), 87999-79-9; **2** (R = Et, R′ = Pr) (isomer 1), 87999-80-2; **2** (R = Et, R′ = Pr) (isomer 2), 87999-81-3; **2** (R = Et, R′ = n-C_9H_{19}) (isomer 1), 87999-82-4; **2** (R = Et, R′ = n-C_9H_{19}) (isomer 2), 87999-83-5; (E)-**3** (R = Et, R′ = Ph), 58927-86-9; (Z)-**3** (R = Et, R′ = Ph), 58927-85-8; (E)-**3** (R = Et, R′ = p-$CH_3C_6H_4$), 87999-84-6; **3** (R = Et, R′ = p-$CH_3OC_6H_4$), 87999-85-7; **3** (R = Et, R′ = p-$O_2NC_6H_4$), 87999-86-8; Et_3B, 97-94-9; Bu_3B, 122-56-5; C_6H_5CHO, 100-52-7; p-$CH_3C_6H_4CHO$, 104-87-0; p-$CH_3OC_6H_4CHO$, 123-11-5; p-$O_2NC_6H_4CHO$, 555-16-8; n-C_3H_7CHO, 123-72-8; n-$C_9H_{19}CHO$, 112-31-2; allyl phenyl selenide, 14370-82-2.

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(5) The formation of ate complexes suppresses such rearrangment. See: Mikhailov B. M. *Organomet. Chem. Rev., Sec. A.* **1972**, *8*, 1.

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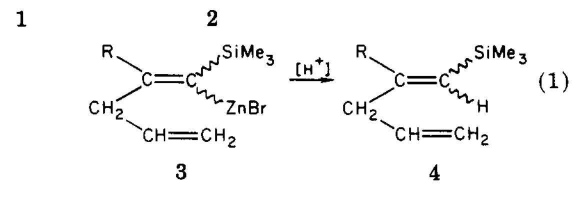
Allylmetalations. The Allylzincation of 1-(Trimethylsilyl)-1-alkynes

Summary: Allylzinc bromide (**1**) reacts with a variety of 1-(trimethylsilyl)-1-alkynes **2** to provide regio- and stereoselective carbometalated products **3**, the zinc atom being placed at the carbon bearing the silicon. Under the conditions of the reaction, the stereochemistry of the products is highly dependent on the structure of **2**.

Sir: Carbometalation reactions provide an extremely attractive method for the synthesis of organic molecules.[1] Certainly one of the greatest advantages in this approach is that at the same time a carbon–carbon bond has formed a new organometallic reagent is generated that can be carried on through further reactions. As a consequence, very rapid construction of organic molecules is feasible.

Although allylzincations of terminal alkynes[2] (presumably through the corresponding alkynylzinc halides) and alkynylmetallics[3] utilizing allylzinc halides are known, internal alkynes have been reported to be unreactive.[2a,e,g,3a] Thus the presence of electropositive atoms on the triple bond appears to be a prerequisite for efficient reaction.

We were intrigued by the possibility of utilizing **2** as substrates for the allylzincation reaction for several reasons. Silicon, being more electropositive than carbon, might be expected to facilitate the carbometalation and allow functionalization on what is formally an internally substituted alkyne. In addition to providing some insight on the stereochemical nature of the addition and the mechanism of the reaction,[2i] the products of such a reaction would provide useful synthons for further transformations. In analogy to reactions of **1** with other alkynylmetallics, we anticipated that the regiochemical outcome of the carbometalation reaction would be such as to place the zinc on the same carbon as the silicon. A regio- and stereoselective allylzincation would provide 1,1-dimetalloalkenes **3**[4] in which the two metals were *chemically differentiable* (eq 1). These reagents could be utilized to generate a



(1)

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Table I. Allylzincation of 1-(Trimethylsilyl)-1-alkynes 2 with Allylzinc Bromide[a] (1)

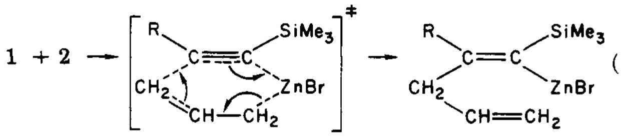
alkynylsilane	product[b]	% GC yield (isolated)	stereochemical purity[c]
1-(trimethylsilyl)-1-hexyne (**2a**)	1-(trimethylsilyl)-2-(2-propenyl)-1-hexene (**4a**)	85 (70)	85[e]
1-(trimethylsilyl)-5-chloro-1-pentyne (**2b**)	1-(trimethylsilyl)-2-(3-chloropropyl)-1,4-pentadiene (**4b**)	88 (63)	81[e]
1-(trimethylsilyl)-2-phenylethyne[d] (**2c**)	1-(trimethylsilyl)-2-phenyl-1,4-pentadiene (**4c**)	78	>95[e]
1-(trimethylsilyl)-3-(benzyloxy)-1-hexyne (**2d**)	1-(trimethylsilyl)-2-(2-propenyl)-3-(benzyloxy)-1-hexene (**4d**)	74	>95[f]
1-(trimethylsilyl)-3-(trimethylsiloxy)-1-hexyne (**2e**)	1-(trimethylsilyl)-2-(2-propenyl)-3-(trimethylsiloxy)-1-hexene (**4e**)	52	>95[f]
4-(trimethylsilyl)-2-methyl-1-buten-3-yne (**2f**)	1-(trimethylsilyl)-2-isopropenyl-1,4-pentadiene (**4f**)	57	>95[f]
1-(trimethylsilyl)-3,3-dimethyl-1-butyne (**2g**)	no reaction	0	

[a] Unless otherwise indicated, reactions were performed in refluxing THF for 16–25 h by using 2.5 equiv of 1 per equiv of 2 and then quenched with saturated NH_4Cl. [b] Satisfactory ^1H NMR, ^{13}C NMR, IR, and mass spectral data were obtained for all products. [c] Determined by ^{13}C NMR. [d] Reaction was run at room temperature for 2 days in THF. [e] Predominant net cis carbometalation. [f] Predominant net trans carbometalation.

variety of regio- and stereodefined di-, tri-, and tetrasubstituted olefins. Selective reaction at the more nucleophilic zinc center with electrophiles (e.g., protonolysis, halogenolysis,[5] or carbon–carbon bond formation[6]) would provide the corresponding alkenylsilanes. Alkenylsilanes themselves have been shown to be useful intermediates, and those produced by this methodology could thus be utilized in still further transformations.[7]

Allylzinc bromide (**1**) was utilized in conjunction with a variety of alkynylsilanes in this study and proved to be an effective carbometalating reagent (Table I). The standard procedure adopted involved reaction of **2** with 2.5 equiv of **1** in THF for 16–48 h. After protonolysis of the reaction mixture, the alkenylsilanes **4** could be isolated. Gas chromatographic yields of the products varied from 0% to 90%, depending on the structure of **2**. The only other major compounds found by gas chromatography were the starting materials. The conversions were nearly 100% on the basis of reacted starting material. Curiously, yields of **4** could not be increased by further increases in the ratio of **1** to **2** nor by longer reaction times.

The reaction was found to be completely regiospecific, placing the zinc on the carbon bearing the silicon as anticipated. Under the conditions of the reaction, 80% to virtually 100% stereoselectivity was observed. Perhaps not surprisingly, the stereochemistry of the resultant products, **4**, was highly dependent on the structure of **2** and on the reaction conditions. Although other mechanisms (e.g., S_E2[2i]) cannot be ruled out completely for all substrates, we believe that the reaction proceeds through a cyclic transition state to initially provide the products resulting from cis addition (eq 2). Thus the reaction between **1** and the highly reactive **2c**, which occurs at room temperature, provides the product **4c** as a result of complete cis addition to the triple bond. The less reactive substrates **2a** and **2b** require heating overnight in THF with excess **1**. Under these conditions, a mixture of stereoisomers results. We postulate that the initially formed alkenylzincs isomerize to provide these isomeric mixtures (eq 3).[8] Finally, substrates **2d–f**, with sterically more demanding secondary propargylic centers, provide exclusively those products resulting from a net trans addition to the alkyne (eq 4).



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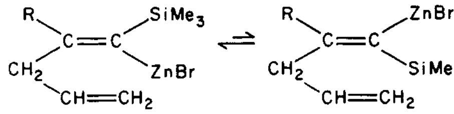

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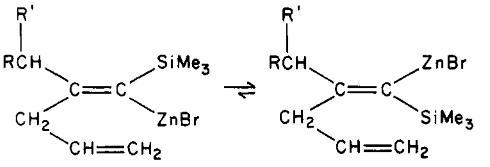

(4)

The regiochemistry of addition was determined by comparison of the ^1H NMR spectra of **4a** and **4c** to published spectra[9] or to spectra obtained in our laboratories of authentic samples of the regioisomers.[10] For all substrates, the stereochemistry of addition was established and the regiochemistry confirmed by NOE difference spectra experiments.[11]

Thus, the allylmetalation reaction of alkynylsilanes would appear to be a viable synthetic procedure for the regiospecific synthesis of a number of alkenylsilanes. Although the process is not totally stereoselective in all cases, for some applications this is not necessary. Thus we envision many instances in which this methodology may be useful in organic synthesis.

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Note Added in Proof: Professor E. Negishi has informed us of their study of allylmetalations of alkynylsilanes. Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761.

Registry No. 1, 18925-10-5; **2a**, 3844-94-8; **2b**, 77113-48-5; **2c**, 2170-06-1; **2d**, 88083-69-6; **2e**, 62896-55-3; **2f**, 18387-60-5; **2g**, 14630-42-3; (*E*)-**4a**, 88083-70-9; (*Z*)-**4a**, 88083-71-0; (*E*)-**4b**, 88105-48-0; (*Z*)-**4b**, 88083-72-1; **4c**, 88083-73-2; **4d**, 88083-74-3; **4e**, 88083-75-4; **4f**, 88083-76-5.

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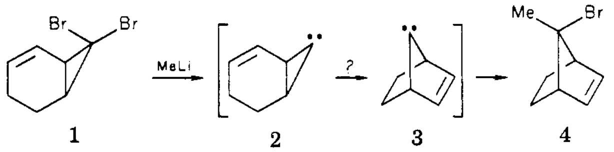
Skattebol-Type Rearrangement of Lithium Carbenoids at Low Temperatures

Summary: The Skattebol rearrangement of carbenoids with well-defined stereochemistry at low temperatures is discussed.

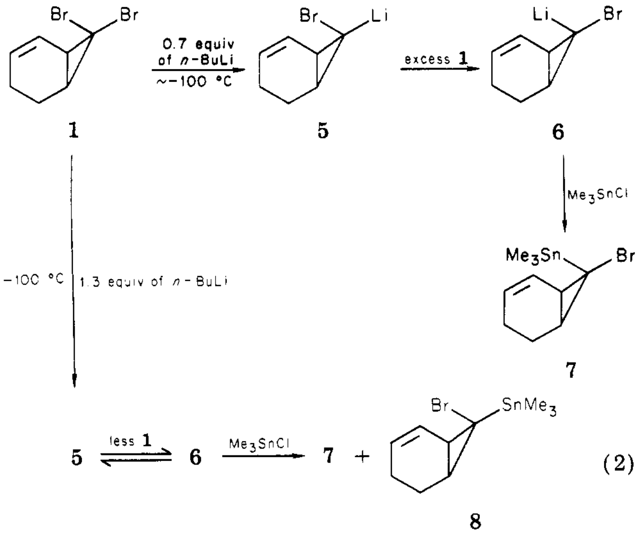
Sir: In contrast to the situation for carbonium ions, carbanions, and radicals, the direct rearrangement of one carbene to another has not been compellingly demonstrated.[1,2] Perhaps the earliest proposal of a direct carbene–carbene rearrangement involves the vinylcyclopropylidene to cyclpentenylidene rearrangement (Skattebol rearrangement), as exemplified in eq 1.[3] However, we[4]



(1)

demonstrated, utilizing a tricyclic analogue of 1, that this rearrangement involves carbenoids rather than free carbenes. In 1981, Brinker[5] showed that passing 1 over MeLi-coated glass chips in the gas phase at ≥24 °C produced the same products as obtained from **3** generated from 7-norbornenyltosylhydrazone.[6] It may thus be tempting to conclude that **2** did indeed rearrange to **3**. As is demonstrated herein, such need not be the case at all.

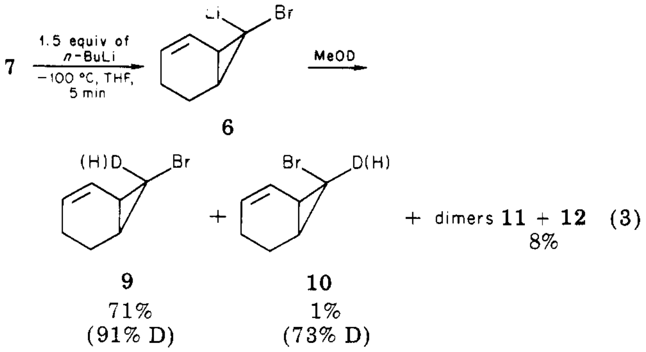
Our investigation of the carbenoids derived from **1** originated with the isomeric organotin compounds **7** and **8**,[5,7] which were themselves made by stannylation of the lithiocarbenoids derived from **1** at ca. −100 °C. As shown (eq 2), the carbenoids present, as reflected by the stannanes



(2)

formed, were dependent upon the conditions utilized. With a deficiency of *n*-BuLi (excess of **1**), the initial carbenoid **5**, was rapidly transformed into the more stable **6**. When *n*-BuLi was present in excess, the **5** to **6** conversion became incomplete, thereby affording both **7** and **8**. Importantly, this demonstrated that **6** is thermodynamically more stable than **5**. This pattern is the same as Seyferth found for the saturated counterparts of **5** and **6**.[7b]

When **7** and **8** were separately treated with 1.5 equiv of *n*-BuLi/THF at ca. −100 °C for 5 min, followed by MeOD quenching, the products[8] were as shown in eq 3 and 4.[9]



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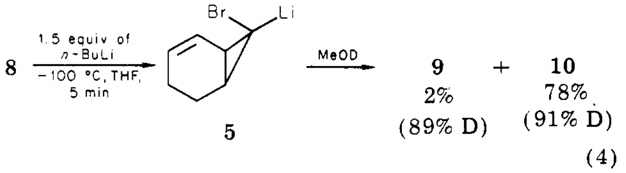

(4)

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