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Unexpected Products from the Reaction of Alkynylstannanes with 9-Borabicyclo[3.3.1]nonane

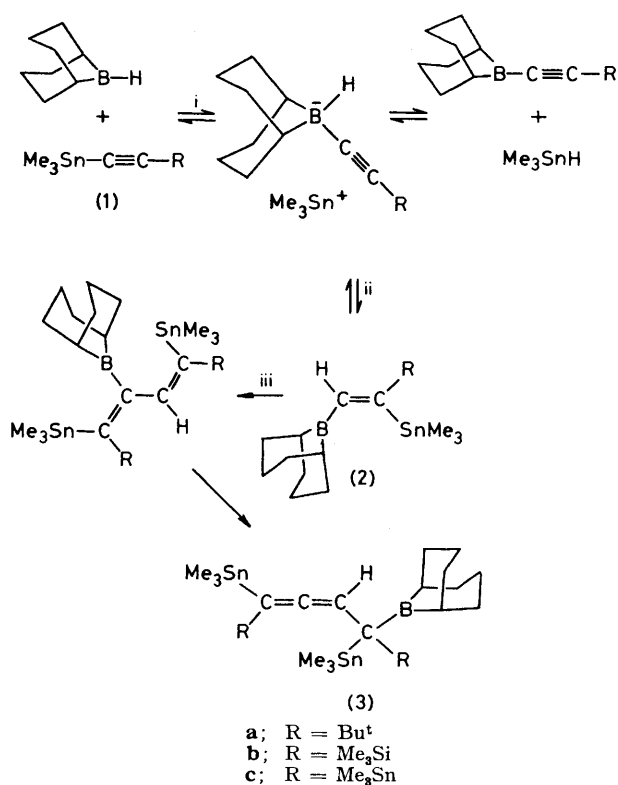
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Summary The reaction of 9-borabicyclo[3.3.1]nonane with alkynyltrimethylstannanes ($\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{R}$) yields a new alkene ($\text{R} = \text{Bu}^t$) and new allenes ($\text{R} = \text{Me}_3\text{Si}$ or Me_3Sn); the formation of both types of compounds is not consistent with hydroboration but involves exchange reactions, alkynyl borate intermediates, and organoboration.

THE hydroboration of alkynes leads to alkenylboranes which are useful in organic synthesis.¹ In this connection the hydroboration products of alkynylstannanes would be of interest. Our current interest in alkynylstannanes² prompted us to study their reaction with 9-borabicyclo[3.3.1]nonane (9-BBN).

We have isolated and characterized the products (**2**) and (**3**) from the reaction of alkynyltrimethylstannanes (**1**) with 9-BBN (Scheme) and neither product is consistent with the expected *cis*-addition of the B-H bond to the $\text{C}\equiv\text{C}$ triple bond in (**1**). Instead we have proof that cleavage of the $\text{Sn}-\text{C}\equiv$ bond occurs as is evident from the formation of trimethylstannane. In the case of (**1a**) the alkynyl-borane³ was isolated from the reaction mixture. In the case of (**1b**) the exchange reaction is accompanied by rapid formation of (**2b**) followed by organoboration to give the allene (**3b**).⁴⁻⁶ The reaction was monitored by ^{119}Sn n.m.r. spectroscopy which showed the formation of trimethylstannane [δ (^{119}Sn) -103 p.p.m. to low frequency of Me_3Sn], a broad signal at -56.0 p.p.m. due to the alkene intermediate (**2b**), and typical ^{119}Sn resonances⁵ at -11.4 , -11.7 ($\geq\text{Sn}-\text{C}=\text{C}$) and -3.6 , -2.7 p.p.m. ($\geq\text{Sn}-\text{C}\leq$) with $^{117}/^{119}\text{Sn}$ satellites corresponding to 5J (^{119}Sn , ^{119}Sn) 27.07 and 251.4 Hz, respectively, for the two diastereomeric allenes (**3b**). In the case of (**1c**) no ^{119}Sn resonance for trimethylstannane was found and a



SCHEME. Reagents and conditions: i, tetrahydrofuran, 20–25 °C; ii, 20–25 °C, 0.2 h ($\text{R} = \text{Me}_3\text{Sn}$); 60 °C, 0.2 h ($\text{R} = \text{Me}_3\text{Si}$), 60 °C, 12 h ($\text{R} = \text{Bu}^t$); iii, $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{R}$; 20–25 °C, 0.2 h ($\text{R} = \text{Me}_3\text{Sn}$); 60 °C, 0.2 h ($\text{R} = \text{Me}_3\text{Si}$); no reaction for $\text{R} = \text{Bu}^t$.

decrease in the intensity of the ^{119}Sn resonance of (**1c**) was accompanied by an increase in the intensity of the ^{119}Sn -resonances of the allene (**3c**) [-9.6 ($\geq\text{Sn}-\text{C}=\text{C}$), $+9.0$ p.p.m. ($\leq\text{Sn}-\text{C}\leq$)], $^{117,119}\text{Sn}$ satellites correspond to 1J ($^{119}\text{Sn}^{119}\text{Sn}$) 353.0 Hz and 2J ($^{119}\text{Sn}^{117}\text{Sn}$) 335.0 ($\text{Sn}_2\text{C}=\text{C}$) and 502 Hz ($\text{Sn}_2\text{C}\leq$).

The reaction conditions and the selective formation of compounds (**2**) are not in agreement with a mechanism involving hydrostannation of alkynes.⁷ Therefore we suggest that the compounds (**2**) result from hydride transfer of an alkynyl borate intermediate. Since compounds (**3b** and **c**) are readily obtained from the mixture of (**1**) and 9-BBN, irrespective of the stoichiometry dehydroboration of (**2b** and **c**) to give (**1b** and **c**) and 9-BBN *via* the alkynyl borate intermediate must be considered. We propose the intermediacy of a butadiene prior to irreversible rearrangement to the allene (**3**) in agreement with the results for other organoborations leading to allenes.^{2,4-6}

Compound (**2a**) is a colourless liquid (b.p. 93 °C at 0.1 Torr) and the structural assignment is based on ^1H , ^{11}B (δ 84.0 p.p.m.), ^{13}C , and ^{119}Sn n.m.r. spectroscopy (δ -35.5 p.p.m.). The ^{13}C n.m.r. spectra show that one olefinic carbon (δ 145.5 p.p.m.) is linked to boron and hydrogen as is apparent from the linewidth [partially relaxed scalar coupling $^1J(\text{CB})$] and from the coupling $^1J(\text{CH})$ of 124.5 Hz. The other olefinic carbon (δ 160.9 p.p.m.) is linked to tin

[$^1J(\text{SnC})$ 493.2 Hz] and to the *t*-butyl group. The magnitude of $^3J(\text{SnH})$ (122.0 Hz) indicates that the SnMe_3 group and hydrogen (δ_{H} 6.4) are *trans*.

Compounds (**3b** and **c**) are colourless solids [m.p. 90 °C (decomp.) for (**3b**) and 112.5 °C for (**3c**)] which can be recrystallized from pentane. The presence of the allene unit was shown by strong sharp i.r. bands at 1887 cm^{-1} for (**3b**) and 1880 cm^{-1} for (**3c**). These assignments were proved by the ^{13}C and ^{119}Sn n.m.r. spectra which were analogous to published spectra for similar allene derivatives.⁵ The allenic ^1H resonance was at δ 4.87 for (**3b**) and δ 4.9 p.p.m. for (**3c**), with $^{117/119}\text{Sn}$ satellites indicating $^3/4J(\text{SnH})$ values of 47.0 Hz for (**3b**) and 49.0 Hz for (**3c**). Mass spectra as well as elemental analyses are in complete agreement with the proposed structures for (**2**) and (**3**).

The access to compounds of the types (**2**) and (**3**) is clearly of interest for further synthetic work. Although the choice of the group R appears to be rather restricted at present a systematic study of the reaction conditions using different solvents and/or different boranes will help to overcome this obstacle.

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