# Hydrostannation of Conjugated Enynes

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*Received December 21, 1982*

Hydrostannation of three conjugated enynes is reported. The reaction was found to be catalyzed by AIBN and inhibited by galvinoxyl. The addition of trimethyltin hydride takes place preferentially at the triple bond. The initial product is one of anti addition. However, extensive isomerization, catalyzed by trimethyltin radicals, occurs at both double bonds of the dienyl system, resulting in a mixture of geometrical isomers. In each case the thermodynamically more stable isomer was the predominant product. It was also observed that trimethyltin radicals cause isomerization of the enyne prior to addition. Diaddition products were found for two of the three enynes, but telomers were absent. $^1$H NMR data are reported for both mono- and diaddition products.

## Introduction

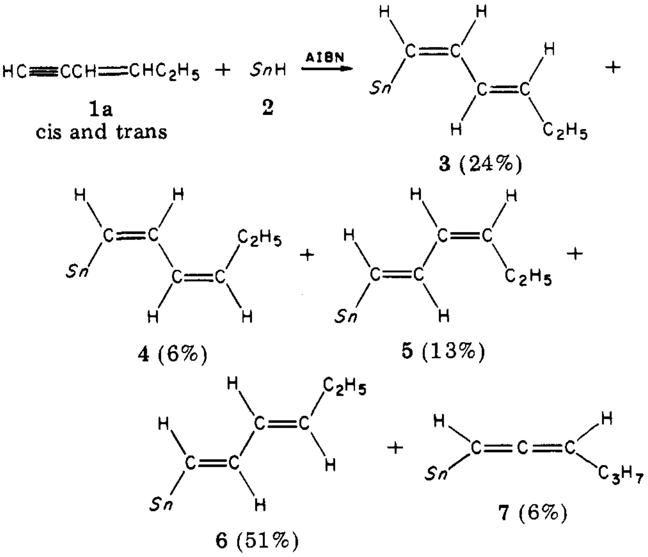
Free radical addition of hydrogen and a trialkyltin group to carbon–carbon and carbon–hetero multiple bonds has been studied for some time, both in this laboratory and elsewhere. Conjugated enynes present a four $\pi$-electron conjugated system as well as an orthogonal two $\pi$-electron system in the "yne" portion of the molecule.[2] In an elegant study, Poutsma and Ibarbia[3] reported that the hydrostannation of conjugated enynes is facilitated by free radical initiators and retarded by free radical scavengers. Earlier Russian workers[4] reported the hydrostannation of conjugated enynes at 80–120 °C, but they did not present conclusive evidence for a free radical mechanism for the reaction. Juenge and co-workers[5] also studied the free radical catalyzed hydrostannation of vinylacetylene and found only 1,4 addition. However, their evidence for the allene as the single product was based only on infrared data.

The reaction is complicated by a number of factors. First is the relative reactivity of the carbon–carbon triple bond compared to the double bond. Second, attack of the trialkyltin radical on $\pi$ systems has been shown to be reversible and thus results in geometrical isomerization of the olefinic portion of the enyne.[6] Third, the initial products of the hydrostannation reaction themselves undergo geometrical isomerization in the presence of trialkyltin radicals. Finally in all reported cases, higher boiling fractions have been obtained. These constitute primarily telomers and/or diaddition products. The presence of these substances in the product mixture distorts any simple stoichiometric relationship between reactants and products.

## Results

**3-Hexen-1-yne.** The neat reaction of this enyne **1a** with trimethyltin hydride (**2**) was carried out under nitrogen at 60–65 °C with AIBN as a catalyst. The catalyst was added in about 2 mol % at the beginning of the reaction, and then during the course of the reaction, further portions of about 2 mol % were added. In the absence of AIBN, the reaction was very slow except in the presence of air. The effect of galvinoxyl as an inhibitor of the reaction was determined by addition of about 2 mol % once the reaction had reached about 30% completion. The initial isomeric composition of **1a** was varied from 100% trans isomer to 71% cis isomer. The ratio of enyne to tin hydride was varied from 2:1 to 1:1. Scheme I shows the structures of the monoaddition products. The structures were assigned from $^1$H NMR spectra of samples collected by gas chromatography. The measured coupling constants and chemical shifts were further refined and the structures confirmed by computer simulation of the spectra and comparison with their experimentally obtained counterparts. Table I summarizes these data.

Scheme I[a]



[a] The percentage values are the relative amounts of each product when the mixture had reached equilibrium. $Sn \equiv$ $Me_3Sn$.

The structure assignments are based on the relative magnitude of the olefinic proton couplings and their chemical shifts. For the $H_a$–$H_c$ coupling there are two sets of values, about 13 and 18.5 Hz, corresponding to the cis and trans geometry at the double bond proximate to the trimethyltin. Also for $H_b$–$H_d$ coupling there are two sets of values, approximately 10.7 and 15.0 Hz corresponding to the cis and trans geometry at the double bond remote to the trimethyltin group. The chemical shifts show that $H_a$ is more shielded when it is cis to the tin than when it is trans, the $\Delta\delta_{ct}$ being about 0.46 ppm, while the $\Delta\delta_{ct}$ values for $H_b$, $H_c$, and $H_d$ are internally consistent on the

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[2] For recent review see: Miginiac, L. *J. Organomet. Chem.* **1982**, *238*, 235.

[3] Poutsma, M.; Ibarbia, P. A. *J. Am. Chem. Soc.* **1973**, *95*, 6000.

[4] (a) Mal'tseva, E. N.; Zavgorodnii, V. S.; Maretino, I. A.; Petrov, A. A. *Zh. Obshch. Khim.* **1968**, *38*, 203. (b) Mal'tseva, E. N.; Zavgorodnii, V. S.; Petrov, A. A. *Ibid.* **1969**, *39*, 152. (c) Mal'tseva, E. N.; Zavgorodnii, V. S. *Ibid.* **1970**, *40*, 2060.

[5] Juenge, E. C.; Hawkes, S. J.; Snider, T. E. *J. Organomet. Chem.* **1973**, *51*, 189.

[6] Kuivila, H. G.; Sommer, R. *J. Am. Chem. Soc.* **1967**, *89*, 5616.

0276-7333/83/2302-1099$01.50/0

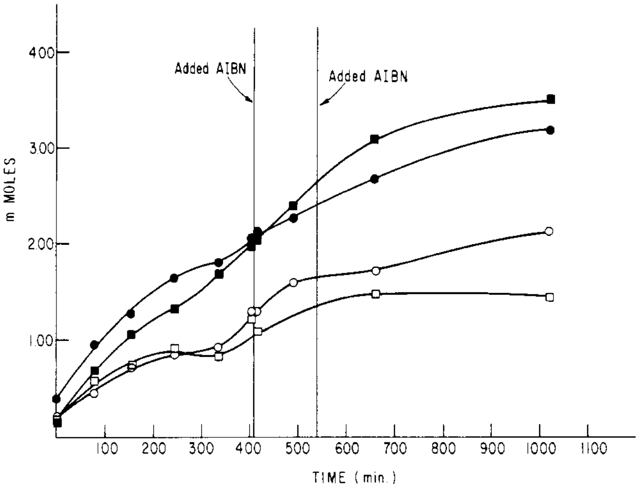

**Figure 1.** Reaction of **1a** with **2** at 60–65 °C, catalyzed by AIBN: ●, *cis,trans*-**3** and allene **7**; □, *cis,cis*-**4**; ○, *trans,cis*-**5**; ■, *trans,trans*-**6**.

basis of the structure assignments. The data are also consistent with previous structure assignments in similar systems from this laboratory[7] and from the work of Kuivila, Rahman, and Fish.[8]

Since it was possible to separate, by gas chromatography, all of the isomeric products except **3** and **7**, it was possible to follow their production as a function of time. Figure 1 shows a plot of the molar amounts of compounds **3**–**7** as the hydrostannation reaction progressed. It can be seen that initially the relative amounts of **3** and **4** are high and that, as the products remain in the presence of trimethyltin radicals, an isomerization reaction takes place at both double bonds leading to the predominance of the thermodynamically most stable product **6**. Isomerization of addition products has been reported previously from this laboratory.[9] This suggests that the initial addition of the tin hydride to the triple bond is anti leading to a cis geometry for the incipient double bond. Also from Figure 1 there is an indication that isomerization of the double bond proximate to tin is faster than isomerization of the double bond remote from tin. The fact that isomerization takes place at both double bonds can be seen from Figure 2. When compounds **4** and **6** were heated separately in the presence of trimethyltin hydride and AIBN, an equilibrium mixture of the four isomeric conjugated dienes was formed. Compound **7** was not present in either product mixture, and thus dehydrostannation of the dienes is not a factor in the isomerization process. Also the absence of the allene in these product mixtures provides an independent determination of the relative amounts of **3** and **7** at equilibrium in the hydrostannation product mixture (Scheme I).

Further information on the hydrostannation and isomerization reactions can be obtained from the effect of galvinoxyl as seen in Figure 3. When small amounts (about 2 mol %) of galvinoxyl are added to the reaction mixture, the addition reaction continues while the isomerization reaction is inhibited. This indicates that the isomerization reaction has a greater dependence on the concentration of trimethyltin radicals than the hydrostannation reaction. Also, after the addition of galvinoxyl, compounds **3** and **4** are the ones which continue to be

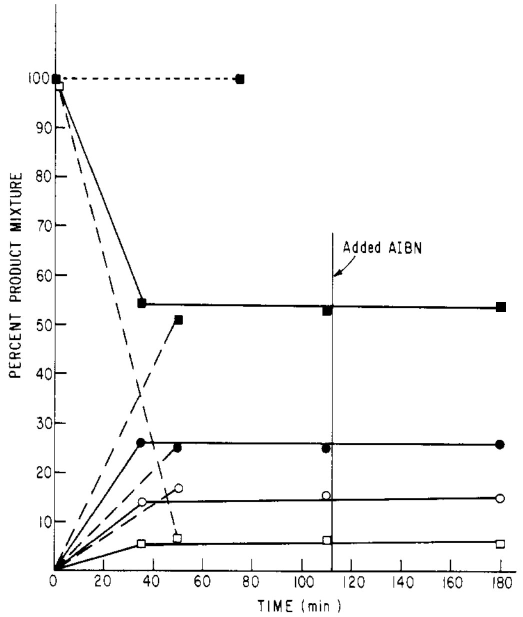

**Figure 2.** Isomerization of **6** by limited **2** plus AIBN (—); isomerization of **4** by limited **2** plus AIBN (– – –); treatment of **6** with limited **2** plus galvinoxyl (- - -): ●, *cis,trans*-**3**; □, *cis,cis*-**4**; ○, *trans,cis*-**5**; ■, *trans,trans*-**6**.

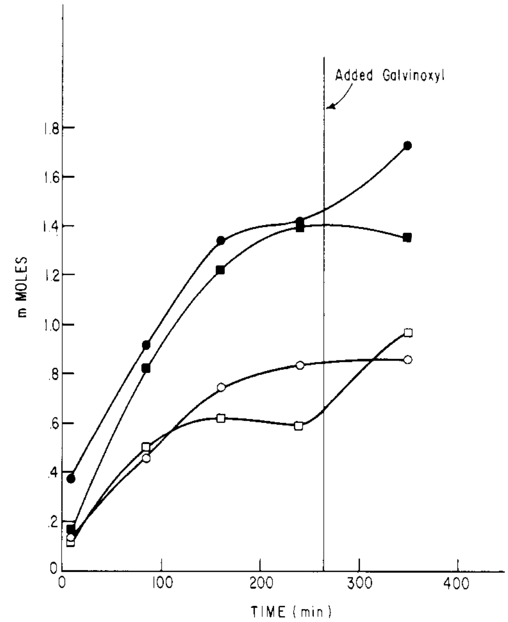

**Figure 3.** Effect of galvinoxyl on the AIBN-catalyzed reaction of **1a** with **2**: ●, *cis,trans*-**3** and allene **7**; □, *cis,cis*-**4**; ○, *trans,cis*-**5**; ■, *trans,trans*-**6**.

produced. This provides further evidence for anti addition to the triple bond.

Isomerization of the enyne can be seen from Figure 4. Pure *trans*-3-hexen-1-yne was allowed to reaction with trimethyltin hydride at 60–65 °C in the presence of AIBN. The reaction mixture was sampled periodically and analyzed by gas chromatography. Very rapidly *cis*-3-hexen-1-yne appeared and the relative amount increased with time to about 30%. This effect was not observed by Poutsma and Ibarbia[3] in the reaction of 3-penten-1-yne with trimethyltin hydride, catalyzed by AIBN in benzene. However they did observe isomerization of the 2-hexen-4-yne.

**2-Methyl-1-buten-3-yne.** When the enyne **1b** was allowed to react neat with trimethyltin hydride (**2**) at 60–65 °C, under an atmosphere of nitrogen and catalyzed by

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[7] Leusink, A. J.; Marsman, J. W.; Budding, H. A. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 689.

[8] Kuivila, H. G.; Rahman, W.; Fish, R. H. *J. Am. Chem. Soc.* **1965**, *87*, 2835.

[9] Leusink, A. J.; Budding, H. A.; Drenth, W. *J. Organomet. Chem.* **1968**, *11*, 541.

Table I. $^1$H NMR Assignments for Products of Reaction between 1a and 2 (Scheme I)

$SnCH_c{=}CH_aCH_b{=}CH_dCH_{2e}CH_3$

| compd | chem shifts, ppm, from $Me_4Si$ | | | | coupling constants, Hz | | | | | | | | | | compd | Δδ ct | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $J_{ab}$ | $J_{ac}$ | $J_{ad}$ | $J_{ae}$ | $J_{bc}$ | $J_{bd}$ | $J_{be}$ | $J_{cd}$ | $J_{ce}$ | $J_{de}$ | | $H_a$ | $H_b$ | $H_c$ | $H_d$ |
| 3 | 6.84 | 5.92 | 5.81 | 5.69 | 10.0 | 12.9 | 0.6 | 0.5 | 0.8 | 15.0 | 2.0 | 0.6 | 0.0 | 6.5 | 3-6 | 0.47 | | −0.19 | |
| 4 | 7.16 | 5.80 | 5.96 | 5.41 | 10.5 | 12.5 | 0.9 | 0.5 | 0.8 | 10.8 | 1.5 | 1.3 | 0.0 | 6.8 | 4-5 | 0.46 | | −0.17 | |
| 5 | 6.70 | 5.85 | 6.13 | 5.31 | 10.4 | 18.5 | 1.3 | 0.2 | 0.8 | 10.6 | 1.7 | 0.5 | 0.8 | 7.4 | 3-4 | | 0.13 | | 0.28 |
| 6 | 6.38 | 5.94 | 6.00 | 5.63 | 9.5 | 18.5 | 1.0 | 0.5 | 0.8 | 15.0 | 1.5 | 0.5 | 0.0 | 6.5 | 6-5 | | 0.09 | | 0.32 |
| 7[a] | 4.94 | 4.55 | | | 7.0 | | | 3.5 | | | 7.0 | | | | | | | | |

[a] $H_a$ is geminal proton to $C_3H_7$; $H_b$ is geminal proton to trimethyltin.

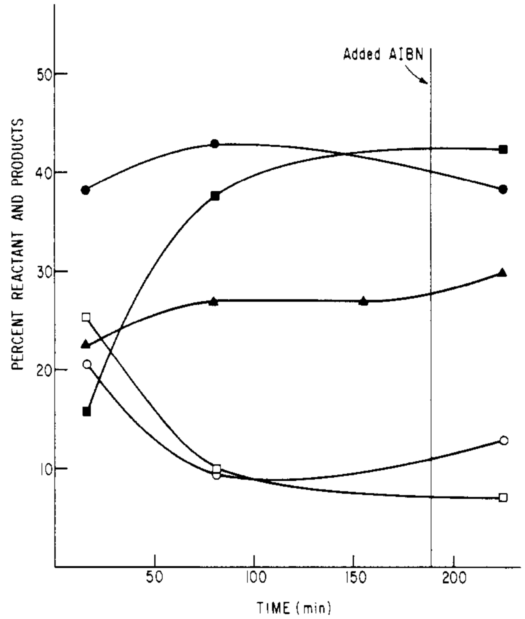
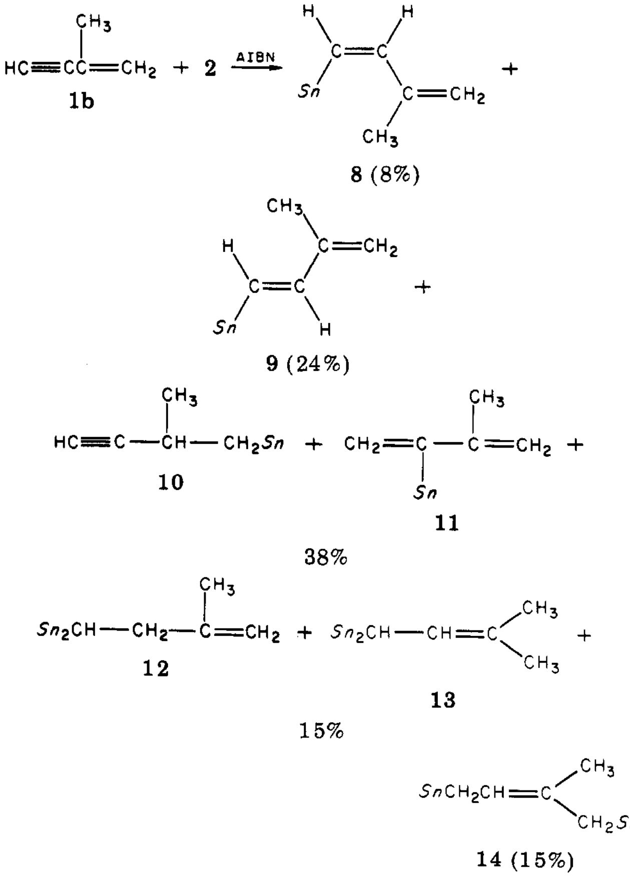


**Figure 4.** AIBN-catalyzed reaction of *trans*-**1a** with **2**: ●, *cis,trans*-**3** and allene **7**; □, *cis,cis*-**4**; ○, *trans,cis*-**5**; ■, *trans,trans*-**6**; ▲, *cis*-**1a**.

Scheme II



*Sn* ≡ Me$_3$Sn

AIBN, a much more complex product mixture was obtained. Since this enyne has a terminal double bond as well as a terminal triple bond, addition to both was observed. Also a larger amount of diadducts were obtained compared to the reaction of **1a**. Scheme II shows the structures of the products obtained, and in Figure 5 the production of these compounds is shown as a function of time. Again, these structures were assigned from $^1$H NMR

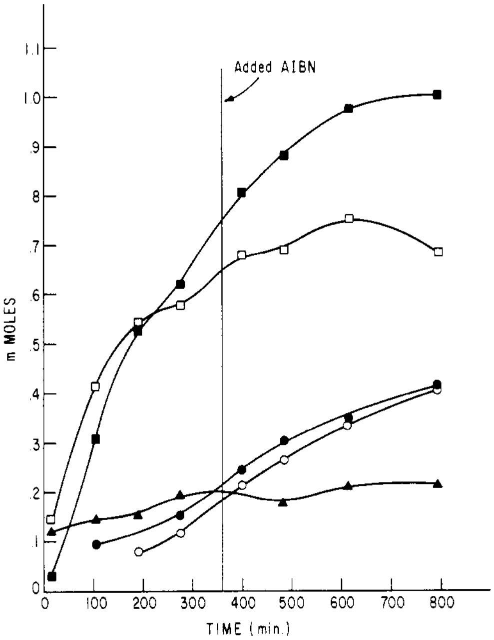
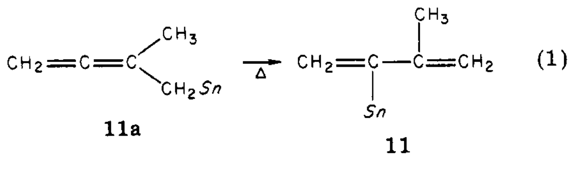


**Figure 5.** Reaction of **1b** with **2** at 60–65 °C, catalyzed by AIBN: ▲, *cis*-**8**; □, *trans*-**9**; ■, **10** and **11**; ●, **12** and **13**; ○, **14**.

spectra of samples collected by gas chromatography. The structures were confirmed by computer simulation of the spectra. These data are summarized in Table II.

The assignment of cis and trans geometry to compounds **8** and **9** is based on the values of $J_{ab}$ = 13.6 Hz for the cis isomer and 19.3 Hz for the trans. These values compare favorably with 13 and 18.5 Hz in comparable products from the hydrostannation of **1a**. Also the $\Delta\delta_{ct}$ for $H_a$ of **8** and **9** is 0.37 ppm compared with an average of 0.46 ppm from compounds **3–6**. The structure of compound **10** was assigned from the difference in chemical shift (about 0.05 ppm) for the magnetically nonequivalent geminal protons $H_d$ and $H_e$ and their large (13 Hz) coupling constant. Also, a mixture obtained by preparative gas chromatography, of this compound and the compound assigned structure **11**, showed an absorption at 2140 cm$^{-1}$ in the infrared spectrum.

The structure of compound **11** was assigned from very small coupling constants, $J_{ab}$ and $J_{de}$, for the two sets of olefinic protons. This indicates two terminal methylene groups. Poutsma and Ibarbia[3] also reported this compound as a product of the reaction **1b** with trimethyltin hydride. However they proposed that it was produced by a rearrangement of 2-methyl-1-(trimethylstannyl)-2,3-butadiene (**11a**) in the injection port of the gas chromato-

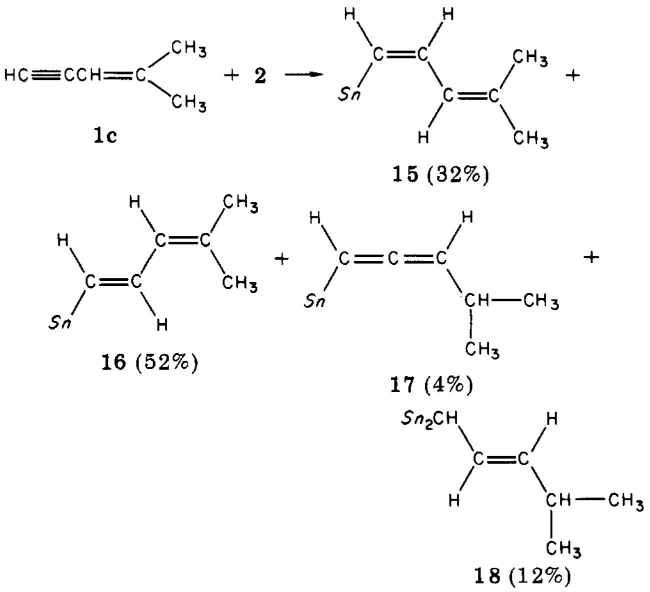


graph. In our reaction, also at 60–65 °C and catalyzed by AIBN, the infrared spectrum of the product mixture before separation showed only a faint trace of an absorption in the allene region while compound **11** is a major component of the separated product mixture. When the reaction was followed by $^1$H NMR, a multiplet appeared early at 4.67 ppm relative to $Me_4Si$. This resonance was assigned to the allenic protons of **11a**. There were no peaks in the spectrum at 4.77 and 5.80 ppm which are attributed to compound **11**. On continued heating at 60–65 °C, in the presence of trimethyltin hydride and AIBN, the 4.67 ppm peak disappeared and two peaks at 4.77 and 5.80 ppm appeared. The facility of this rearrangement is consistent with the observation by Kuivila, Rahman, and Fish[8] that in the hydrostannation of 3-methyl-1,2-butadiene, attack of the trimethyltin radical takes place exclusively at the middle carbon of the allene triad.

The diadducts **12**, **13**, and **14** were assigned structures consistent with their $^1$H NMR spectra. Compounds **12** and **13** must arise from 1,2 and 1,4 addition to either **8** or **9** at the double bond proximate to tin. In the absence of a 1,2 hydrogen atom shift, compound **14** must also arise from 4,1 addition to either **8** or **9**. The geometry at the double bond of **14** was not determined. The relative amounts of **12** plus **13** compared to **14** indicate that the double bond substituted by a trimethyltin group is about as reactive to a second addition as a terminal double bond. This may be contrasted with the work of Mal'tseva and Zavgordnii,[4c] who report that at 100 °C in the absence of AIBN, hydrostannation was preferred at a terminal carbon–carbon double bond to a conjugated triple bond substituted with a trialkyltin group. Finally, with respect to the diadducts, 3-methyl-2,4-bis(trimethylstannyl)-1-butene was not observed although it may have been present in small amounts. This product could arise from either 4,3 addition to **8** or **9** or 1,2 addition to **10**.

**2-Methyl-2-penten-4-yne.** The reaction of 2-methyl-2-penten-4-yne (**1c**) with **2** was also carried out neat at 60–65 °C under an atmosphere of nitrogen and catalyzed by AIBN. The product mixture as shown in Scheme III was considerably less complex.

Scheme III



*Sn* ≡ $Me_3Sn$

The chemical shift and coupling constant data for compounds **15**, **16**, and **18** are found in Table III. The structures were assigned from spectra of samples collected by preparative gas chromatography and the structures confirmed by computer simulation. Compound **15** is assigned the cis and **16** the trans configuration on the basis of the values of $J_{ac}$, 12.5 and 18.0 Hz, respectively. Also the $\Delta\delta_{ct}$ is 0.46 ppm consistent with comparable products from the hydrostannation of **1a** and **1b**. The presence of the allene **17** is based on the gas chromatogram in which a small peak (4% of total peak area) preceded the peaks assigned to **15**, **16**, and **18**. In the reaction of **1a**, the allene **7** was a component of the first peak eluted from the GC column. Also this crude reaction structure contained an

Table II. ¹H NMR Assignments for Products of Reaction between 1b and 2 (Scheme II)

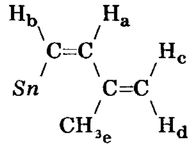
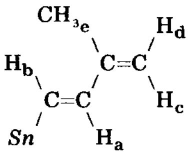
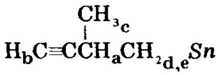
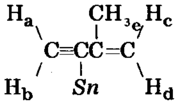
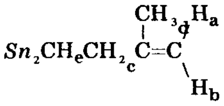
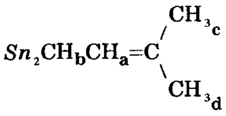
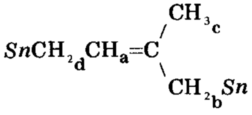
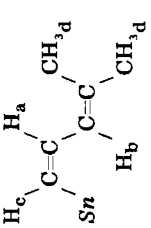
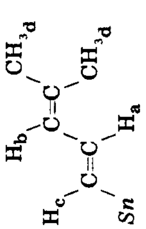
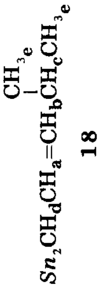
| | chem shifts, ppm, from $Me_4Si$ | | | | | coupling constants, Hz | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $J_{ab}$ | $J_{ac}$ | $J_{ad}$ | $J_{ae}$ | $J_{bc}$ | $J_{bd}$ | $J_{be}$ | $J_{cd}$ | $J_{ce}$ | $J_{de}$ |
|  **8** | 6.90 | 5.79 | 4.86 | 4.86 | 1.82 | 13.6 | 0.8 | 0.5 | 1.0 | 1.1 | 0.4 | 0.6 | 1.5 | 1.8 | 1.2 |
|  **9** | 6.53 | 6.14 | 4.96 | 4.91 | 1.82 | 19.3 | 0.4 | 0.3 | 0.4 | 0.4 | 0.4 | 0.2 | 1.5 | 1.7 | 1.2 |
|  $H_bC{\equiv}\overset{CH_{3c}}{C}CH_aCH_{2d,e}Sn$ **10** | 2.68 | 1.89 | 1.22 | 1.10 | 1.04 | 2.5 | 6.8 | 7.5 | 6.5 | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 13.0 |
|  **11** | 5.80 | 5.25 | 4.93 | 4.77 | 1.87 | 2.2 | 0.2 | 0.1 | 0.1 | 1.3 | 0.2 | 0.1 | 1.9 | 1.8 | 1.2 |
|  **12** | 5.24 | 4.97 | 1.56 | 2.12 | 0.16 | 1.5 | 1.2 | 1.7 | 0.1 | 1.7 | 1.2 | 0.1 | 0.2 | 10.0 | 0.1 |
|  **13** | 5.16 | 1.90 | 1.71 | 1.37 | | 13.5 | 1.7 | 1.2 | | 0.1 | 0.1 | | 0.1 | | |
|  **14** | 4.99 | 1.62 | 1.61 | 1.52 | | 1.5 | 1.2 | 8.5 | | 0.3 | 0.2 | | 0.2 | | |

Table III. $^1$H NMR Assignments for Products of Reaction between 1c and 2 (Scheme III)

| compd | chem shifts, ppm from $Me_4Si$ | | | | | coupling constants, Hz | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $J_{ab}$ | $J_{ac}$ | $J_{ac}$ | $J_{ae}$ | $J_{bc}$ | $J_{bd}$ | $J_{be}$ | $J_{cd}$ | $J_{ce}$ | $J_{de}$ |
|  **15** | 7.08 | 5.69 | 5.80 | 1.71 | | 10.5 | 12.5 | 0.2 | 0.2 | 0.9 | 1.2 | 1.7 | 0.2 | 0.2 | 0.2 |
|  **16** | 6.61 | 5.73 | 5.95 | 1.71 | | 10.0 | 18.0 | 0.2 | 0.2 | 0.8 | 1.2 | 1.7 | 0.2 | 0.2 | 0.2 |
|  $Sn_2CH_dCH_a{=}CH_b\overset{CH_{3e}}{\overset{\vert}{CH_c}}CH_{3e}$ **18** | 5.50 | 5.01 | 2.21 | 1.51 | 0.93 | 15.0 | 1.7 | 10.5 | 0.2 | 6.5 | 1.7 | 0.2 | 0.1 | 6.5 | 0.1 |

IR absorption at 1925 cm$^{-1}$. The structure of the allene is based on 1,4 addition of tin hydride to the enyne, which is reasonable on the basis of a tertiary radical at $C_4$. An $^1$H NMR spectrum was not obtained for this compound.

Compound **18** arises from 1,4 addition to either **15** or **16**. It is assigned the *trans* configuration from the magnitude of $J_{ab}$. This was the only diadduct obtained. It is not surprising that the product corresponding to 4,3 or 4,1 addition was absent since the presence of two methyl groups exerts serious steric hindrance to addition at the double bond.

The product isomerization reaction was further studied in this series by exchange of trialkyltin groups. A mixture of **15** and **16** was heated at 60 °C with triethyltin hydride and AIBN. Analysis by gas chromatography showed that a portion of the triethyltin hydride was consumed and trimethyltin hydride appeared with an appropriate retention time in the chromatogram of the product mixture.

## Discussion

The results described above are consistent with the mechanism for hydrostannation of conjugated enynes proposed by Poutsma and Ibarbia.[3] We have found catalysis by AIBN and inhibition by galvinoxyl. Attack at the terminal triple bond is favored over attack at the terminal double bond, and the reaction is subject to steric effects of alkyl substituents at the double bond. The initial addition of the trialkyltin group and hydrogen to the triple bond is anti leading to a cis configuration at the new double bond. Isomerization of this double bond as well as the original double bond takes place extensively on the presence of trimethyltin radicals leading eventually to a predominance of the thermodynamically more stable isomers. If a syn molecular addition were involved, galvinoxyl would not be expected to inhibit the path and thus the effect shown in Figure 3 would be reversed and the concentrations of **5** and **6** would continue to increase.

A major difference in our results from the work of Poutsma and Ibarbia[3] is that we do not find telomerization to be a significant factor in the overall process. All major projects were isolated by gas chromatography and all had $^1$H NMR spectra consistent with mono- or diadducts. Because of molecular weight considerations, the retention times of telomers, having a 2:1 enyne–tin hydride composition, would be intermediate between monoddacts and diadducts. This area of the chromatogram was devoid of signals. If telomerization was a significant factor, then we would expect to observe it since most of our reactions were run with a 100 mol % excess of enyne. Also telemers have not been observed in other free radical hydrostannation reactions.[6]

The isomerization mechanism of both the double bond in the starting enyne and the butadienyl system probably involves a reversible addition of a second trialkyltin radical. This was indicated by an experiment in which a mixture of compounds **15** and **16** was mixed with triethyltin hydride in the presence of AIBN. After being treated at 60 °C for 2 h, the mixture was analyzed by gas chromatography. Part of the triethyltin hydride had been consumed and trimethyltin hydride appeared in the product mixture. Kuivila and Sommer[6] have reported similar results with isolated carbon–carbon double bonds.

## Experimental Section

**General Data.** All gas chromatography was carried out on a Varian Autoprep with manual temperature programming. In most runs the temperature was programmed from 50–170 °C over about 45 min. The column used was 12 ft × $^3/_8$ in. stainless steel packed with 15% polyphenyl ether on Diatoport S, 60–80 mesh.

IR spectra were run on a Perkin-Elmer Model 137. $^1$H NMR spectra were recorded on a Varian Model T60 and a Varian Model HA100 with spin decoupling. Elemental analyses were performed by the Element-Analytical Department, Institute for Organic Chemistry, TNO, Utrecht, The Netherlands. All boiling points are uncorrected.

**Starting Materials.** Tributyltin hydride was prepared from tributyltin chloride and lithium aluminum hydride.[10] Trimethyltin hydride (2) was prepared by a hydride–chloride exchange between tributyltin hydride and trimethyltin chloride.[11] Triethyltin hydride was prepared by the same method. 3-Hexen-1-yne (**1a**) was prepared by the method of Brandsma;[12] 2-methyl-1-buten-3-yne (**1b**) and 2-methyl-2-penten-4-yne (**1c**) were obtained from L. Brandsma and purified by distillation under nitrogen before use. Xylene and toluene were dried over molecular sieves before use as internal standards for GC.

**Reaction of 3-Hexen-1-yne (1a) with Trimethyltin Hydride (2).** A typical reaction between this enyne and trimethyltin hydride was carried out as follows. In a small reaction flask, fitted with a rubber syringe cap, were placed 25 mmol of enyne, 12 mmol of trimethyltin hydride, 2.5 mmol of dry xylene, and 2 mol % (based on tin hydride) of AIBN. The atmosphere over the reaction mixture was flushed with dry nitrogen. The flask was placed in a water bath at 60–65 °C and samples were withdrawn periodically by syringe for analysis by GC. Usually after 3–4 h the reaction had slowed sufficiently that addition of a second portion of AIBN was necessary. Samples which were withdrawn for analysis were injected into the gas chromatograph immediately at a column temperature of 50 °C. The column temperature was increased to 170 °C over a period of about 45 min. The temperature was held at the maximum until all peaks attributed to diaddition products had exited the detector. The peak areas were determined by using a Disc Integrator with correction for base line drift. Samples for elemental analysis and $^1$H NMR were collected by preparative GC. Typical results are shown in Figure 1. Anal. Calcd for $C_9H_{18}Sn$: C, 44.13; H, 7.41; Sn, 48.46. Found: C, 43.64; H, 7.62; Sn, 49.14.

**Reaction of 3-Hexen-1-yne (1a) with Trimethyltin Hydride (2). Galvinoxyl Added.** The enyne **1**, trimethyltin hydride, AIBN, and xylene were mixed as in the above procedure. Samples were withdrawn for GC analysis, and when the reaction had reached 30–40% completion, as determined by decrease in tin hydride, 2–4 mol % of galvinoxyl (mp 140.5–150.5 °C (lit.[13] 153.5 °C)) was added. The reaction mixture was then sampled until no further change in concentrations of reactants or products was observed.

**Isomerization of 3-Hexen-1-yne by Trimethyltin Radicals.** *cis*- and *trans*-3-hexen-1-yne were separated by preparative GC on the column described above. When pure trans was mixed with trimethyltin hydride and AIBN at 60 °C, the cis isomer appeared in the chromatogram within the first few minutes. The isomeric ratio of trans/cis was 70/30 at that point and did not change appreciably during the course of the reaction.

**Isomerization of Trimethyl(1,3-hexadien-1-yl)tins.** A. Samples of trimethyl (*cis*,*cis*-1,3-hexadien-1-yl)tin (**4**) and trimethyl(*trans*,*trans*-1,3-hexadien-1-yl)tin (**6**) were purified by preparative GC. Each isomer (about 50 mg, 0.2 mmol) was mixed separately with 50 mg (0.3 mmol) of trimethyltin hydride and 8 mol % (based on tin hydride) of AIBN under nitrogen. The mixture was heated at 60–65 °C, and samples were withdrawn for GC analysis. Each isomer was converted to the equilibrium mixture of four isomers (**3**–**6**) in less than 50 min.

B. A sample of pure trimethyl(*trans*,*trans*-1,3-hexadien-1-yl)tin (**6**) (about 0.2 mmol) was mixed with 50 mg (~0.3 mmol) of trimethyltin hydride and 3 mg (about 2 mol % based on tin hydride) of galvinoxyl under nitrogen. This mixture was heated at 60–65 °C and sample withdrawn for GC analysis. No isomerization was observed over a period of 75 min.

**Reaction of 2-Methyl-1-buten-3-yne (1b) with Trimethyltin Hydride (2).** The procedure used for reaction of this enyne with trimethyltin hydride was similar to that described above except that toluene, with its lower boiling point, was used as the internal standard for quantitative gas chromatography. Samples were withdrawn from the reaction mixture and analyzed by gas chromatography. The components of the product mixture were mostly separated by preparative gas chromatography and their structures determined by $^1$H NMR. Anal. (monoadducts) Calcd for $C_8H_{16}Sn$: C, 41.61; H, 6.99; Sn, 51.41. Found: C, 41.86; H, 7.25; Sn, 50.80.

**Isomerization of 11a.** In an NMR tube were placed 0.47 g (7.1 mmol) of 2-methyl-1-buten-3-yne, **1b**, 0.63 g (3.8 mmol) of trimethyltin hydride, and 11 mg of AIBN. An $^1$H NMR spectrum was recorded immediately, and then the tube was heated to 60–65 °C. Spectra were again recorded at 210 and 390 min as the reaction was progressing. The absorptions at 5.80 and 4.77 ppm, assigned to the olefinic protons of **11**, were absent but a multiplet at 4.67 ppm, not observed in the spectra of the products collected by gas chromatography, was present. A second 10-mg portion of AIBN was added and the mixture heated for an additional 200 min. At this point all of the tin hydride had been consumed and the absorptions at 5.80 and 4.77 ppm had appeared. Continued heating at 65 °C caused these absorptions to increase at the expense of the absorption at 4.67 ppm.

**Reaction of 2-Methyl-2-penten-4-yne (1c) with Trimethyltin Hydride (2).** This reaction was carried out by the procedure described above; xylene was used as the internal standard for analysis by gas chromatography. Anal. (monoadducts) Calcd for $C_9H_{18}Sn$: C, 44.13; H, 7.41; Sn, 48.46. Found: C, 44.19; H, 7.56; Sn, 47.11.

**Exchange of Trimethyltin for Triethyltin.** A mixture of 61 mg (0.25 mmol) of trimethyl(4-methylpenta-1,3-dien-1-yl)tin obtained by preparative gas chromatography from the reaction of **1c** and **2**, 36 mg (0.17 mmol) of triethyltin hydride, and 5 mg of AIBN were placed in a reaction vessel sealed by a septum cap. The mixture was sampled immediately and analyzed by gas chromatography. Three peaks were observed for the cis and trans isomers **15** and **16** and triethyltin hydride. After the mixture was heated at 60 °C for 135 min, the triethyltin hydride peak had diminished and a new peak with retention time of trimethyltin hydride had appeared. After 240 min the triethyltin hydride had disappeared completely and the trimethyltin hydride peak further increased.

**Acknowledgment.** This work was supported by grants from the Colgate Research Council and from the Netherlands Organization for Pure Scientific Research (ZWO). The support is gratefully acknowledged. We also wish to thank Mr. Jan Marsman for assistance with the $^1$H NMR simulation, the Department of Organic Chemistry, University of Utrecht, for the use of their computer and Professor H. G. Kuivila for helpful discussions.

**Registry No.** *cis*-**1a**, 17669-38-4; *trans*-**1a**, 2807-09-2; **1b**, 78-80-8; **1c**, 1595-53-5; **2**, 1631-73-8; **3**, 86309-24-2; **4**, 86309-25-3; **5**, 86309-26-4; **6**, 86309-27-5; **7**, 85366-24-1; **8**, 85618-02-6; **9**, 86309-28-6; **10**, 86309-29-7; **11**, 86309-30-0; **11a**, 86309-38-8; **12**, 86309-31-1; **13**, 86309-32-2; **14**, 86309-33-3; **15**, 86309-34-4; **16**, 86309-35-5; **17**, 86309-36-6; **18**, 86309-37-7; triethyltin hydride, 997-50-2.

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[10] van der Kerk, G. J. M.; Noltes, J. G.; Luijten, J. G. A. *J. Appl. Chem.* **1957**, *7*, 366.

[11] Neumann, W. P.; Pedian, J. *Tetrahedron Let.* **1964**, 2461.

[12] Brandsma, L. "Preparative Acetylenic Chemistry"; Elsevier: Amsterdam, 1971; p 124.

[13] Bartlett, P. D.; Funahashi, T. *J. Am. Chem. Soc.* **1962**, *84*, 2596.