Bos, Thomas Van Eenenaam, and Bruce Van Buskirk for their assistance in preparing several compounds and in preliminary product analyses, and Robert C. Rickard for obtaining the esr spectrum of radical **28**. We also wish to thank Dr. James W. Wilt for helpful discussions concerning this research.

Radical Addition of Trimethyltin Hydride to Conjugated Enynes

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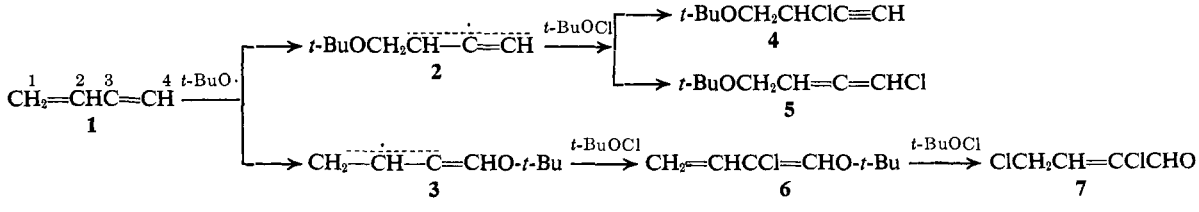
Abstract: The addition of trimethyltin hydride (**8**) to 1-penten-3-yne (**9a**) at 60–85° with AIBN catalysis gives a mixture of 1,2 adduct **10**, 4,3 adducts **11** and **12**, 4,1 adduct **13**, and probably 1,4 adduct **14**, as well as telomeric adducts. Monoadduct composition and total yield are dependent both on the ratio **9a**/**8** and on the concentration of **8**. The addition of stannane **8** to 2-methyl-1-buten-3-yne (**9b**) gives 1,2 adduct **16**, 1,4 adduct **17**, and 4,3 adducts **18** and **19**. Similar treatment of *cis*- and *trans*-3-penten-1-yne (**9c**) gives largely mixed 4,3 adducts **21** while the 2-hexen-4-ynes (**9d**) gave largely the corresponding adducts **23**; in the latter case, addition is accompanied by geometrical isomerization of **9d**. These results are discussed (Scheme I) in terms of a free-radical chain mechanism in which the intermediate propargylic (**24**) and methyleneallylic radicals (**25**) formed by attack of trimethylstannyl radicals on enyne **9** undergo not only product formation but also competitive telomerization and reversal of addition. This situation is to be contrasted with addition of *tert*-butyl hypochlorite wherein neither telomerization nor reversibility is a serious complication.

We have described[1] the photoinitiated addition of *tert*-butyl hypochlorite to vinylacetylene (**1**) and its monomethylated homologs in terms of a free-radical chain mechanism involving both propargylic[2] and methyleneallylic[2b–d] radical intermediates. Attack of *tert*-butoxy radical at the olefinic terminus of parent enyne **1** to form propargylic radical **2** was favored over attack at the acetylenic terminus to form methyleneallylic radical **3** by a factor of ~4 at ambient temperatures. This ratio was moderately sensitive to the position of methyl substitution in the enyne, being >10 for 1-penten-3-yne and 1–1.5 for the 3-penten-1-ynes, but did not fall below unity in the C_5H_6 series.



The propargylic radical intermediates underwent atom transfer to give mixtures of 1,2 and 1,4 adducts, the ratio being 10:1 for adducts **4** and **5** derived from radical **2** but again depending on the substitution pattern[2a] for the other enynes. The methyleneallylic radicals gave in all cases largely 4,3 adducts[2b,d] such as **6**, isolated as aldehyde **7**; no conclusive evidence was obtained for 4,1 adducts.

In a less detailed study of the addition of *N*-chloropiperidinium ion to enynes,[3] we also observed a preference for initial radical attack at the olefinic terminus.

Concurrent with these studies, several reports from Mal'tseva and coworkers[4] appeared which described the addition of triethyltin hydride to alkylated conjugated enynes at 80–120°. Moderate yields of monoadducts were obtained along with unidentified higher boiling products. The distilled monoadduct fractions were never separated into individual components but adduct structures were assigned on the basis of glpc, spectral, and chemical properties. In all cases, regardless of the substitution pattern of the enyne, the major product was a 4,3 adduct, although lesser amounts of 1,2, 1,4 and/or 4,1, and 3,4 adducts were reported as well as minor amounts of substitution products in which a terminal acetylenic hydrogen atom was replaced by a triethylstannyl group. These hydrostannation reactions were reported to be only mildly accelerated by azobisisobutyronitrile (AIBN) and unaffected by hydroquinone. The yield and composition of monoadducts were rather insensitive to the initial ratio of enyne/stannane which was varied from 10:1 to 1:1.

In spite of the somewhat equivocal response of the

(1) M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **35**, 4038 (1970).
(2) (a) R. M. Fantazier and M. L. Poutsma, *J. Amer. Chem. Soc.*, **90**, 5490 (1968); (b) M. L. Poutsma, *Tetrahedron Lett.*, 2925 (1969); (c) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **92**, 4110 (1970); (d) L. R. Byrd and M. C. Caserio, *ibid.*, **92**, 5422 (1970); (e) P. S. Engel and D. J. Bishop, *ibid.*, **94**, 2148 (1972); (f) P. H. Kasai, *ibid.*, **94**, 5950 (1972).
(3) M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **36**, 2572 (1971).
(4) E. N. Mal'tseva, V. S. Zavgorodnii, I. A. Maretina, and A. A. Petrov, *J. Gen. Chem. USSR*, **38**, 209 (1968); E. N. Mal'tseva, V. S. Zavgorodnii, and A. A. Petrov, *ibid.*, **39**, 138 (1969); E. N. Mal'tseva and V. S. Zavgorodnii, *ibid.*, **40**, 2046 (1970).

reaction to radical initiators and inhibitors and in spite of the claim of certain minor products (3,4 adducts and substitution products) which would not be predicted, the Russian workers[4] preferred a radical chain mechanism for the hydrostannation of enynes. Indeed this seems a rational choice in view of the structure of the major products and of the demonstrated radical nature of the hydrostannation of conjugated dienes.[5] However, the authors[4] suggested a possible component of the reaction to be "molecular" to rationalize largely cis orientation of the Et_3Sn and H groups in the 4,3 adduct. Also, we would note that formation of 3,4 adduct could be suggestive of nucleophilic addition *via* attack of the stannane on the triple bond as a hydride donor, a process observed for hydrostannation of acetylenes containing electron-withdrawing groups.[6]

Hydrostannation of diacetylene with triphenyltin hydride gives a 1,4-distannyl-1,3-diene product,[7] and the second stage of this reaction may also represent a 4,3 addition to a substituted enyne.

If these hydrostannations of enynes are radical in nature, then the predominance of 4,3 adducts implies a difference between *tert*-butoxy and protonated piperidino radicals on the one hand and triethylstannyl radical on the other with respect to the preferred position of attack on enynes. However, several factors suggested to us that the observed final product distributions after isolation might not represent the initial position of radical attack. First, the unidentified higher boiling products could be either diadducts or telomers, formation of either of which could distort the final product composition. Secondly, since some reversibility has been detected in the radical addition step of stannyl radicals to styrene[8a] and piperylene,[8b] reversibility might be expected for enynes as well and could also destroy any 1:1 correspondence between observed final products and the position of initial radical attack.

In our initial study,[1] *tert*-butyl hypochlorite was chosen as a reagent which should minimize both reversibility of radical addition and telomerization as a competitor for atom transfer. Indeed no evidence for either mechanistic complication could be found as judged by failure of recovered 3-penten-1-ynes to be geometrically isomerized[9] even though products from olefinic attack were formed and by failure to isolate telomeric products. We have now investigated the addition of trimethyltin hydride (**8**) to conjugated enynes and wish to report that, while the reaction does follow a radical pathway, both these complications are serious as judged by dependence of product composition on the enyne/stannane ratio (in contrast to the Russian reports[4]), by isomerization of recovered enynes, and by identification of telomeric products. Therefore, evaluation of the preferred position of attack of stannyl radicals on various enynes requires detailed consideration of the course of the reactions rather than simply of final product compositions.

Results

1-Penten-3-yne. Reaction of a twofold excess of neat 1-penten-3-yne (**9a**) with stannane **8** proceeded smoothly at 80–85° in the presence of ~5 mol % AIBN to produce a distilled monoadduct fraction in 45–50% isolated yield as well as a higher boiling fraction. Reaction in the absence of AIBN was much slower but eventually gave a similar monoadduct yield and composition. The uncatalyzed reaction could be further decelerated by addition of small amounts of the stable radical galvinoxyl[10] as a radical inhibitor[5a] (see Experimental Section).

Glpc analysis both before and after distillation revealed five components with retention times appropriate for monoadducts ($Me_3SnC_5H_7$). The major component, collected by preparative glpc, was assigned as the 1,2 adduct, 3-pentyn-1-yltrimethyltin (**10**), based on spectral evidence and authentic synthesis from 3-pentyn-1-ol (Scheme I). The next two most prevalent, only partially resolved products, which were collected together, were rapidly cleaved by trifluoroacetic acid (TFA) in *n*-heptane solution at 25° to form *cis*- and *trans*-piperylene. This conversion along with their spectral properties allowed their assignment as the 4,3 adducts, 2,4-pentadien-2-yltrimethyltin. There was enough difference in rates of protolysis to associate the major component with *trans*-piperylene and the minor with *cis*-piperylene. On the basis of the established retention of configuration of electrophilic cleavages of vinylic carbon–metal bonds,[11] we assigned the *Z* configuration **11** to the major 4,3 adduct and the *E* configuraion **12** to its partner. A fourth minor component, clearly an allene from ir evidence, was assigned as the 4,1 adduct, 2,3-pentadien-2-yltrimethyltin (**13**), rather than a 1,4 adduct based on nmr evidence. Cleavage of allene **13** with TFA gave not only 2,3-pentadiene as expected but also a comparable amount of 2-pentyne presumably *via* an S_E2' protolysis as observed[12] for allylic tin compounds.[13] The final minor product **14** appeared to be altered when passed through a thermal conductivity glpc detector and has resisted positive identification. However, similar behavior of an identified 1,4 adduct from enyne **9b** (see below) suggests a 1,4 adduct structure, 2,3-pentadien-1-yltrimethyltin, for **14** as well. Preparation of the authentic 3,4 adduct, 1,3-pentadien-3-yltrimethyltin (**15**), as a mixture of geometrical isomers, from 3-bromo-1,3-pentadiene revealed that product **14** was definitely not structure **15**; neither was any significant amount of diene **15** present in the original hydrostannation product from enyne **9a**. Mass spectra of

(5) (a) W. P. Neumann and R. Sommer, *Justus Liebigs Ann. Chem.*, **701**, 28 (1967); (b) R. H. Fish, H. G. Kuivila, and I. J. Tyminski, *J. Amer. Chem. Soc.*, **89**, 5861 (1967).

(6) A. J. Leusink, H. A. Budding, and W. Drenth, *J. Organometal. Chem.*, **9**, 295 (1967); A. J. Leusink and H. A. Budding, *ibid.*, **11**, 533 (1968).

(7) F. C. Leavitt and L. U. Matternas, *J. Polym. Sci.*, **62**, S68 (1962).

(8) (a) H. G. Kuivila and R. Sommer, *J. Amer. Chem. Soc.*, **89**, 5616 (1967); (b) H. J. Albert, W. P. Neumann, W. Kaiser, and H. P. Ritter, *Chem. Ber.*, **103**, 1372 (1970).

(9) See M. L. Poutsma and P. A. Ibarbia, *J. Org. Chem.*, **36**, 3657 (1971) for correction of a typographical error in ref 1.

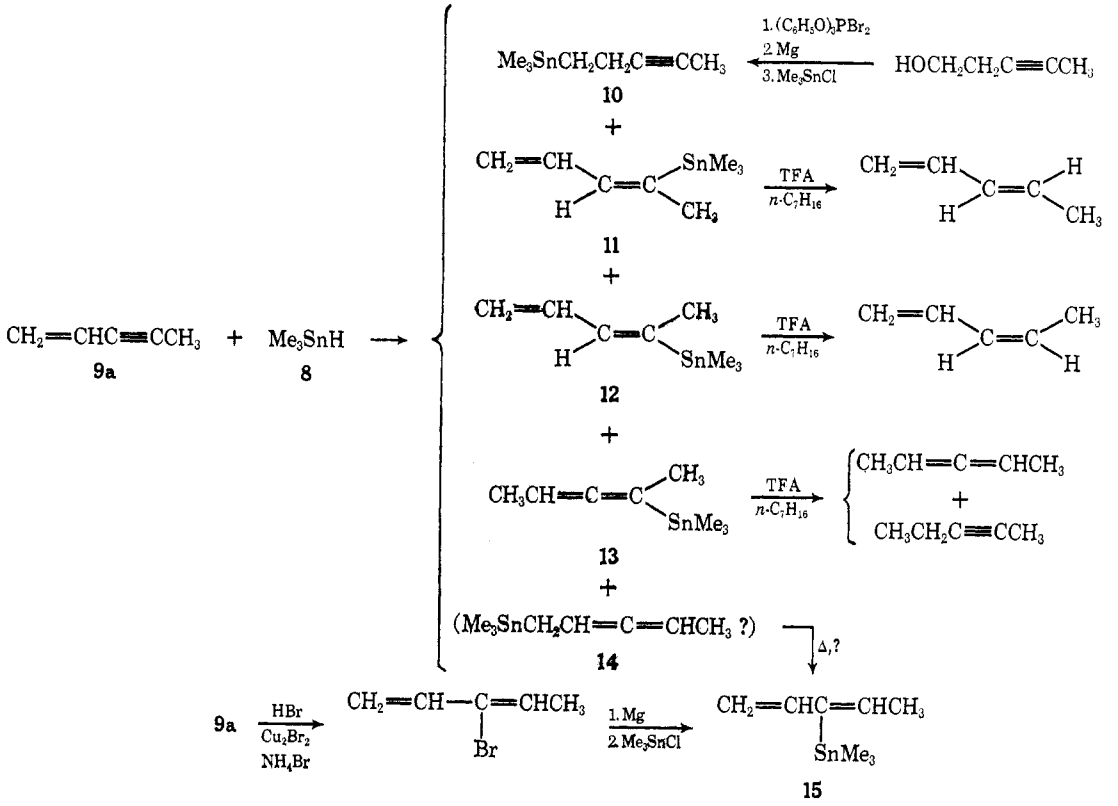
(10) G. M. Coppinger, *J. Amer. Chem. Soc.*, **79**, 501 (1957).

(11) H. G. Kuivila, W. Rahman, and R. H. Fish, *ibid.*, **87**, 2835 (1965); P. Baekelmans, M. Grelen, P. Malfroid, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **77**, 85 (1968).

(12) H. G. Kuivila and J. A. Verdone, *Tetrahedron Lett.*, 119 (1964).

(13) The analogous possibility of S_E2' rearrangement in electrophilic cleavage of allenylcarbinyltin derivatives casts doubt on the use[4] of an observed trace of $CH_2{=}C(CH_3)C(Br){=}CH_2$ in the bromination product of the hydrostannation product from enyne **9b** as evidence for a 3,4 adduct $CH_2{=}C(CH_3)C(SnEt_3){=}CH_2$ because this bromide could have been derived from a 1,4 adduct $Et_3SnCH_2C(CH_3){=}C{=}CH_2$.

Scheme I



adducts **10–13** were consistent with the formulation $Me_3SnC_5H_7$.

The higher boiling fraction from reaction of enyne **9a** with stannane **8** was examined by glpc–mass spectral interfacing and evidence for both 2:1 telomers ($Me_3SnC_{10}H_{18}$) and diadducts ($Me_3SnC_5H_8SnMe_3$) was obtained. In experiments carried out with even greater initial **9a**:**8** ratios and run to only partial conversion so as to deemphasize diadduct formation, evidence for 3:1 as well as 2:1 telomers was obtained.[14]

This hydrostannation was followed quantitatively in benzene solution at 60° by periodic sampling of solutions containing enyne **9a**, stannane **8**, AIBN, and toluene internal standard. Glpc analysis for formation of products **10–14** and disappearance of reactants **8** and **9a** allowed evaluation of the course of the reaction. A typical run is detailed in Table I.

Table I. Reaction of 1-Penten-3-yne (**9a**) with Trimethyltin Hydride (**8**) in Benzene Solution at 60° [a]

Time, hr	$[9a]_0 - [9a]$	$[8]_0 - [8]$	$\Sigma[10] - [14]$	$([11] + [12])/[10]$	[13]/[10]	[14]/[10]	[11]/[12]
1	0.22	0.19	0.072	0.36	*b*	*b*	9.0
2.5	0.56	0.43	0.18	0.46	0.05	0.06	7.9
4	1.17	0.64	0.29	0.51	0.04	0.06	3.0
23	1.90	1.17	0.40	0.50	0.05	0.05	2.2

[a] Initial concentrations: $[9a]_0 = 3.93$ *M*; $[8]_0 = 1.17$ *M*; $[AIBN]_0 = 0.042$ *M*; $[C_6H_5CH_3]_0 = 0.64$ *M*. All entries in columns 2–4 are in *M* units. For product designations, see text. [b] Amounts of **13** and **14** too small for accurate determination.

A summary of this and three other analogous runs is given in Table II where "initial" values are defined as those at the first sampling point, generally at 10–15% consumption of the limiting reagent, and "final" values are those at the last sampling point, always >80% consumption of the limiting reagent. A complex dependence of product yield and composition on initial reactant concentrations and on extent of reaction is obvious.

Hydrostannation could also be carried out in benzene solution at 25° by photolysis through a Pyrex filter in the presence of AIBN and produced the same set of products **10–14**. Under these conditions, the dominant product was 1,2 adduct **10** regardless of $[9a]_0/[8]_0$ as shown in Table III. Attempts to carry out the reaction in sealed tubes at ≥100° generally led to violent exotherms and explosions.

2-Methyl-1-buten-3-yne. The reaction of neat 2-methyl-1-buten-3-yne (**9b**) with stannane **8** could also be carried out at 60–80° with AIBN (on a small scale) or at 25° with photolysis and AIBN. In both cases, glpc analysis revealed four products in the monoadduct region. Nmr spectral positions and relative intensities compared with relative glpc intensities allowed these to be assigned as the 1,2 adduct, 2-methyl-3-butyn-1-yltrimethyltin (**16**), the 1,4 adduct, 2-methyl-2,3-butadien-1-yltrimethyltin (**17**), and the isomeric 4,3 adducts, (*Z*)- (**18**) and (*E*)-3-methyl-1,3-butadien-1-yltrimethyltin (**19**). Adduct **16** and a mixture of adducts **18** and **19** could be isolated by preparative glpc. However, similar collection of adduct **17** gave a material with spectral properties absent from both the original crude product and the distilled monoadduct fraction and different from those assigned to allene **17**. Spectral properties of this new product, presumably formed by rearrangement of **17** in the glpc thermal conductivity detector, point strongly to 3-methyl-1,3-butadien-2-yltrimethyltin (**20**), formally the result of a 1,3-stannyl

(14) See Y. G. Kryazhev and R. G. Sultangareev, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1364 (1967) for a brief account of telomerization of $CH_2{=}CHC{\equiv}CC(CH_3)_2OCH_3$ in the presence of CBr_4.

Table II. Reaction of 1-Penten-3-yne (**9a**) with Trimethyltin Hydride (**8**) in Benzene Solution at 60° [a]

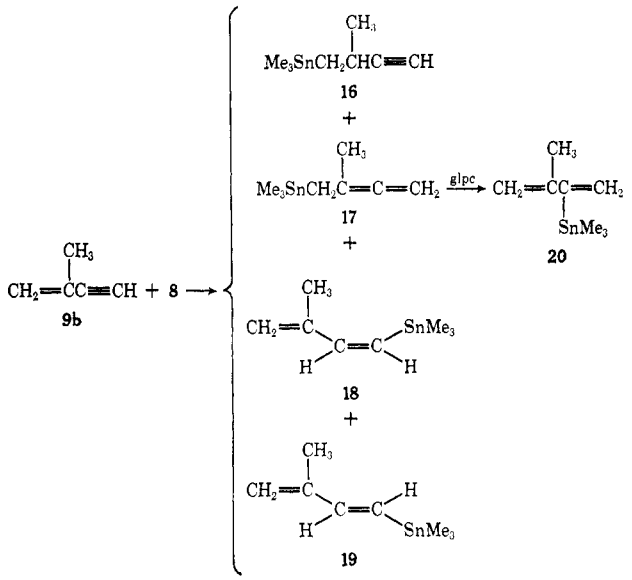
Entry	$[9a]_0$	$[8]_0$	$[9a]_0/[8]_0$	$(\Sigma[10]-[14])/([9a]_0-[9a])$ Initial	Final	$(\Sigma[10]-[14])/([8]_0-[8])$ Initial	Final	$([11]+[12]+[13])/[10]$ Initial	Final	[11]/[12] Initial	Final
1	3.93	1.17	3.4	0.31	0.21	0.36	0.35	0.41[b]	0.54	9.0	2.2
2	1.43	1.50	0.95	0.79	0.68	0.78	0.51	0.31	0.35	*c*	1.4
3	0.60	0.93	0.65	1.1	0.64	0.85	0.38	0.50	0.31	3.3	1.4
4	1.55	4.00	0.39	1.1	0.34	*c*	0.13	0.13	0	3.5	*d*

[a] Each run contained $[AIBN]_0 = 0.04$–0.05 *M* and $[C_6H_5CH_3]_0 = 0.6$–0.7 *M*. All entries in columns 2 and 3 are in *M* units. For definition of "initial" and "final," see text. [b] Includes a calculated contribution from **13**, assuming [13]/[10] = 0.05. [c] Not determined. [d] Neither **11** nor **12** survived.

Table III. Reaction of 1-Penten-3-yne (**9a**) with Trimethyltin Hydride (**8**) in Benzene Solution at 25°; Initial Samples[a,b]

Entry	$[9a]_0$	$[8]_0$	$[9a]_0/[8]_0$	$(\Sigma[10]-[14])/([9a]_0-[9])$	$(\Sigma[10]-[14])/([8]_0-[8])$	$([11]+[12]+[13]^c)/[10]$
1	3.15	0.42	7.5	0.12	0.42	0.11
2	3.29	3.44	0.96	0.67	0.51	0.03
3	0.61	1.59	0.38	1.1	0.51	0.04

[a] Photolyzed through Pyrex with $[AIBN]_0 = 0.05$–0.07 *M* and $[C_6H_5CH_3]_0 \sim 0.7$ *M*. [b] Entry 1 at 29% consumption of **8**; entry 2 at 27% consumption of **9a**; entry 3 at 34% consumption of **9a**. [c] The amount of **13** (and of **14**) was too small to measure accurately.



shift.[15] Telomer formation was again indicated by higher boiling materials.

Although hydrostannation of enyne **9b** was not studied in as much detail as that of **9a**, some selected experiments are described in Table IV with data determined by glpc analysis.

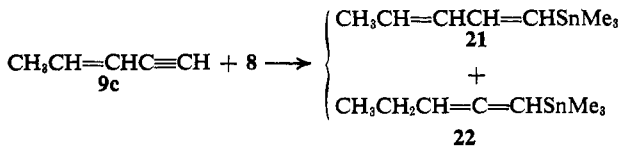
3-Penten-1-yne. Hydrostannation of 3-penten-1-yne (**9c**) proceeded in parallel fashion, and glpc examination of the distilled monoadduct fraction (45% yield with $[9c]_0/[8]_0 = 1.7$) revealed at least four partially resolved peaks. However, the absence of doublets near δ 1 ppm in the nmr spectrum ruled out any significant quantity of 1,2 or 1,4 adducts, each of which would contain the $CH_3CH(SnMe_3)$ structural unit. The spectrum was consistent with the monoadduct fraction's being ~90% the mixed geometrical isomers of the 4,3 adduct, 1,3-pentadien-1-yltrimethyltin (**21**).

(15) A radical-catalyzed rearrangement of allylic tin compounds is described in H. J. Albert, W. P. Neumann, and H. O. Ritter, *Justus Liebigs Ann. Chem.*, 737, 152 (1970).

Table IV. Reaction of 2-Methyl-1-buten-3-yne (**9b**) with Trimethyltin Hydride (**8**)

Reaction conditions	16–19, % yield	16:17:18:19
1. $[9b]_0 = 1.54$ *M*; $[8]_0 = 0.82$ *M*; $[AIBN]_0 = 0.04$ *M*; $[C_6H_5CH_3]_0 = 0.4$ *M*; benzene solution. Heated at 62° to 64% consumption of **8**.	22 (glpc)	20:5:52:23
2. Reaction 1 at 92% consumption of **8**.	25 (glpc)	17:6:35:42
3. $[9b]_0/[8]_0 = 1.6$; $[AIBN]_0/[8]_0 = 0.05$; no solvent. Irradiated at 25° to >90% consumption of **8**.	36 (isolated)	53:27:14:6[a] 54:26:14:6[b]

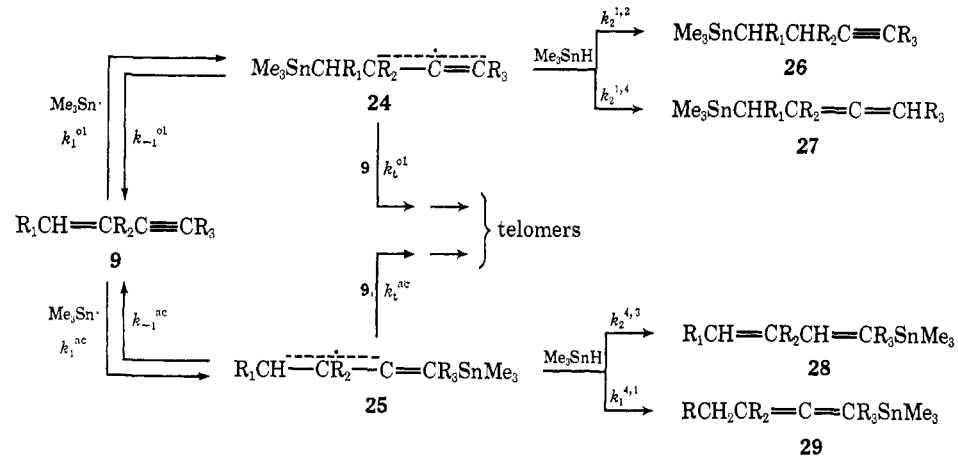
[a] Before distillation. [b] After distillation; nmr analysis gave **16**:**17**:(**18** + **19**) = 52:26:22.



A minor amount of the 4,1 adduct, 1,2-pentadien-1-yltrimethyltin (**22**), was suggested by an ir band at 1925 cm^{-1} and an nmr *triplet* at δ 1.03 ppm (CH_2CH_3 structural unit). A run starting with *cis*-**9c** (0.69 *M*) and enyne **8** (0.54 *M*) in benzene solution proceeded at 60° to 90% consumption of **8** without detectable formation of *trans*-**9c**. A parallel run with *trans*-**9c** (2.34 *M*) and **8** (1.06 *M*) failed to produce *cis*-**9c** up to 83% consumption of **8**. In these runs, the monoadduct yields were 75–100% (glpc). Different distributions among the isomers of diene **21** were produced from *cis*- and *trans*-**9c**, and the diene composition within each run changed with time. However, structural assignments for the individual isomers of **21** were not achieved.

2-Hexen-4-yne. Reaction of neat 2-hexen-4-yne (**9d**) (>90% cis) with stannane **8** in the presence of AIBN at 85° ($[9d]_0/[8]_0 = 1.23$) gave a distilled monoadduct fraction in 40% yield whose nmr spectrum indicated it to be almost exclusively mixed isomers of the 4,3 adduct, 2,4-hexadien-2-yltrimethyltin (**23**), although ir spectroscopy indicated a minor allenic component. Glpc analysis again showed several bands presumably owing to the geometrical isomers of diene **23**. Irradiation of a similar neat reaction mixture at 25° gave a distilled monoadduct fraction of similar composition in 65% yield. To probe for isomerization of unreacted enyne **9d**, two parallel reactions were run at 60° in *p*-xylene solvent (chosen only because benzene interfered with glpc analysis of enyne **9d**)

Scheme II



a, $R_1 = R_2 = H; R_3 = CH_3$ c, $R_2 = R_3 = H; R_1 = CH_3$
b, $R_1 = R_3 = H; R_2 = CH_3$ d, $R_1 = R_3 = CH_3; R_2 = H$

and sampled periodically as shown in Table V. The yield (glpc) of product **23** was $\geq 80\%$ in each case.

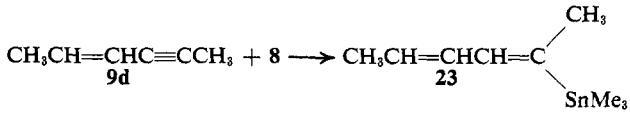


Table V. Reaction of *cis*- and *trans*-2-Hexen-4-yne (**9d**) with Trimethyltin Hydride (**8**) in *p*-Xylene Solution at 60°

Consumption of 8 (%)	Cis/trans ratio of residual 9d From *cis*-9d[a]	From *trans*-9d[b]
12	>100	
26		0.095
29	67	
62	7.2	
75		0.35
78	6.4	
83	4.7	
90		0.48
>98	2.8	0.81

[a] $[cis\text{-}9d]_0 = 2.43\ M$; $[8]_0 = 1.20\ M$; $[AIBN]_0 = 0.05\ M$; $[C_6H_5CH_3]_0 = 0.51\ M$. [b] $[trans\text{-}9d]_0 = 2.14\ M$; $[8]_0 = 1.04\ M$; $[AIBN]_0 = 0.05\ M$; $[C_6H_5CH_3]_0 = 0.54\ M$.

Discussion

The response of the reaction of enynes **9a–d** with stannane **8** to radical initiators and inhibitors,[5a] the formation of examples of all four possible types of monoadducts (1,2 adduct **26**, 1,4 adduct **27**, 4,3 adduct **28**, and 4,1 adduct **29**), and the isolation of telomeric products are all in accord with a free-radical pathway involving stannyl-substituted propargylic (**24**) and methyleneallylic (**25**) radicals as intermediates (Scheme II). Under our conditions, we found no initial products other than types **26–29**. In particular, the 3,4 adducts **20** (and probably **15**) encountered were not initial products but appeared to be rearrangement products of initial 1,4 adducts **17** (and probably **14**) formed during glpc analysis; hence there is no need to postulate a competitive nucleophilic pathway.[6] Also, as will be shown below, the stereochemistry of the 4,3 adducts is consistent with a radical mechanism and does not demand a "molecular" cis addition pathway.[4]

Several observations show, however, that translation of observed final adduct compositions into the ratio of rate constants for initial attack of the trimethylstannyl radical on the enyne (k_1^{o1}/k_1^{ac}) is less than direct because of contributions from reversal of the radical addition step and of telomerization. Reversal of addition[8] is indicated explicitly by observed cis–trans isomerization of enyne **9d** and implicitly by the variations in product composition for enyne **9a** as a function of initial reactant concentrations (see below). Telomerization is indicated explicitly by product isolation and implicitly by only moderate yields of monoadducts under certain reaction conditions even at early stages of the reaction where diadduct formation is still minimal.

From the minimum reaction network thus indicated in Scheme II and the usual steady-state approximations for intermediates **24** and **25**, one can derive eq 1 which reduces to the more familiar eq 2 only if the

$$\frac{d(26 + 27)}{d(28 + 29)} = \left[\frac{k_1^{o1}}{k_1^{ac}}\right]\left[\frac{(k_2^{1,2} + k_2^{1,4})}{(k_2^{4,3} + k_2^{4,1})}\right] \times \left[\frac{(k_2^{4,3} + k_2^{4,1}) + k_t^{ac}(9/8) + k_{-1}^{ac}(1/8)}{(k_2^{1,2} + k_2^{1,4}) + k_t^{o1}(9/8) + k_{-1}^{o1}(1/8)}\right] \quad (1)$$

$$d(26 + 27)/d(28 + 29) = k_1^{o1}/k_1^{ac} \quad (2)$$

terms involving k_{-1} and k_t are negligible compared with those involving k_2. Thus, we note that to minimize complications from reversibility one should keep [**8**] as numerically large as possible and that to minimize complications from telomerization one should keep [**9**]/[**8**] $\ll 1$. Although each of these conditions could be approached by running the reaction neat with a large excess of stannane, they are not compatible with the further requirement to avoid secondary hydrostannation of unsaturated adducts **26–29** which demands [**9**]/[**8**] $\gg 1$. The appropriate conditions for deriving best estimates of k_1^{o1}/k_1^{ac} from product ratios is then to equate it to the (**26** + **27**)/(**28** + **29**) ratio extrapolated to zero conversion of runs with $[9]_0/[8]_0$ as small as possible.

Our most extensive data collected to test the model of Scheme II and eq 1 were obtained with enyne **9a** at 60° (Table II). It was not possible to gather accurate enough product composition data at very low conversions to claim a true extrapolation to zero conversion, but the "initial" and "final" values as defined

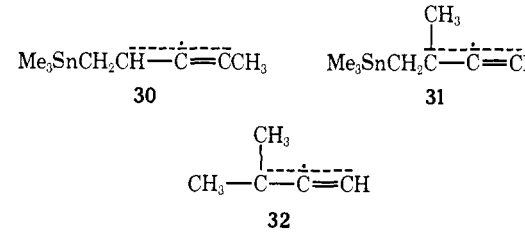
in Table II clearly reveal the predicted trends. First, note that the initial yield of monoadducts based on the limiting reagent smoothly increased from ~35% to near quantitative as $[9]_0/[8]_0$ decreased from 3.4 to 0.39 as predicted if telomerization were the major cause of less than quantitative initial yields. Secondly, however, the final yields were maximal for $[9]_0/[8]_0 \sim 1$. This behavior is also consistent because for $[9]_0/[8]_0 > 1$, telomerization reduces the final yield even more than the initial yield since [9]/[8] steadily increases during reaction, whereas for $[9]_0/[8]_0 < 1$, polyadduct formation related to the steadily increasing excess of stannane **8** during the reaction reduces the final yield. Thirdly, the initial ratio of product **10** derived from olefinic attack[16] to products **11–13** derived from acetylenic attack is not a smooth function of $[9]_0/[8]_0$ but rather of the absolute value of $[8]_0$ as predicted for distortions related to competition between atom transfer (k_2) and reversibility (k_{-1}). Since this product ratio increases as $[8]_0$ increases and hence as reversibility becomes relatively less important (while initial yields remain high; entries 3 and 4 of Table II), the implication is that reversibility is a more serious complication for olefinic attack; *i.e.*, $k_{-1}^{ol}/k_1^{ol} > k_{-1}^{ac}/k_1^{ac}$. The same trend of increasing *apparent* acetylenic attack as [8] decreases is seen in entry 1 of Table II where the final ratio ([11] + [12] + [13])/[10] is greater than the initial ratio. The reverse trend in entry 4 on the other hand suggests that polyaddition selectively consumes **11–13** compared to **10**, a conclusion fully in accord with known rates of radical additions to dienes, allenes, and acetylenes. The final conclusion then is that k_1^{ol}/k_1^{ac} for enyne **9a** is >7.7 (entry 4). Thus trimethylstannyl radical shows considerable selectivity for attack at the olefinic carbon of this enyne, having a free olefinic terminus and a methyl-substituted acetylenic terminus, just as *tert*-butoxy radical does;[1] this conclusion would not have been reached from consideration of final product ratios.[4]

For reaction at 25°, similar trends in initial product ratios and yield are seen in Table III. The apparent k_1^{ol}/k_1^{ac} ratio is greater than at 60°, but the data are not detailed enough to be sure that this reveals a true temperature effect on k_1^{ol}/k_1^{ac} or whether reversibility is simply less of a complication at lower temperature. Since chain transfer constants generally decrease with decreasing temperature, telomerization might be relatively more serious at 25°.[17]

The data for enyne **9b** (Table IV) suggest a trend toward a smaller k_1^{ol}/k_1^{ac} value as expected for steric reasons[1] when shifting the methyl group from the acetylenic terminus to the internal carbon. Moving it to the olefinic terminus in enyne **9c** led to observation only of products of acetylenic attack regardless of $[9c]_0/[8]_0$. Although k_1^{ol}/k_1^{ac} may be larger than the very small value implied by the product data for the reasons detailed above, it must still be $\ll 1$ based on the failure to observe isomerization of recovered **9c**. If reversibility occurred for **9a** and for **9d** (see below), its failure to be observed for **9c** by isomerization of recovered starting enyne must imply $k_1^{ol}/k_1^{ac} \ll 1$. Finally, the products from enyne **9d** reveal predominant acetylenic attack while the observed isomerization (Table V) implies that $(k_1^{ol}/k_1^{ac})^{9d} > (k_1^{ol}/k_1^{ac})^{9c}$. In fact, this substrate was chosen to reveal isomerization from reversibility after **9c** had failed to do so, because the added methyl group at the acetylenic terminus should have enhanced olefinic attack compared to **9c** for both steric and electronic reasons.[1]

In summary then, the dependence on enyne structure is that k_1^{ol}/k_1^{ac} decreases in the order **9a** > **9b** > **9d** > **9c**, the same order as observed for *tert*-butoxy radical[1] but with a more sensitive dependence on structure.[18] Unfortunately, our inability to perform controlled experiments of the type outlined in Table II with the parent vinylacetylene did not allow us to evaluate k_1^{ol}/k_1^{ac} for the unsubstituted system.[19]

Evaluation of the ratios $k_2^{1,2}/k_2^{1,4}$ and $k_2^{4,3}/k_2^{4,1}$ which define the ambident properties of radicals **24** and **25** toward enyne **8** is not subject to distortion by reversibility and telomerization and can be determined directly from observed initial product ratios so long as the adducts do not interconvert and they are not consumed by further hydrostannation. We have not observed interconversions and the second criterion is met by keeping $[9]_0/[8]_0$ high. Values of $k_2^{1,2}/k_2^{1,4}$ at 60° for radicals **30** and **31** are ≥10 (Table I subject to uncertainties in the structure of **14**) and ~4 (entry 1, Table IV), a trend in accord with previous results[2a,b,d] concerning the effects of alkyl substitution on the ambident behavior of propargylic radicals. The latter value for **31** can be compared with a value of 1.7 for



30 **31**

32

the corresponding reaction of radical **32**, having the same carbon skeleton but lacking the β-trimethylstannyl group, with tri-*n*-butyltin hydride at 65°;[2a] any neighboring group effect[20] of the β-stannyl group is minimal.

In all cases, the ratio $k_2^{4,3}/k_2^{4,1} \gg 1$ but 4,1 adducts were clearly observed for enynes **9a** (ratio ~10; Table I), **9c** (ratio ~10), and **9d** (ratio >10). The behavior of the ratio of dienes **11** and **12** from enyne **9a** as a function of extent of conversion (Table I) suggests that 4,3 addition occurs ≥90% trans but that the dienes equilibrate during reaction.[21] Dienes **18** and **19** from

(16) Product **14** probably should also be included but the correction would be minor; see Table I.

(17) C. Walling and E. S. Huyser, *Org. React.*, **13**, 99 (1963).

(18) Since addition of *tert*-butoxy radical is more exothermic than that of trimethylstannyl radical based on relative C–O and C–Sn bond strengths, the greater selectivity of the latter radical is anticipated.

(19) If the effects of adding methyl groups at both termini in enyne **9d** cancel, it would then appear that the relatively nucleophilic trialkylstannyl radical does prefer the acetylenic terminus relative to the olefinic terminus in contrast to the electrophilic *tert*-butoxy radical. However, this tempting conclusion is experimentally tenuous at best.

(20) P. J. Krusic and J. K. Kochi, *J. Amer. Chem. Soc.*, **93**, 846 (1971).

(21) A possible isomerization mechanism is reversible attack of $Me_3Sn\cdot$ at the tin-bearing terminus of the diene.[8b] Attack at the other terminus gives isomerization only if the intermediate allylic radical has time for internal rotation.[8b] A model reaction for the former possibility is the observed bishydrostannation of phenylacetylene to form $C_6H_5CH_2CH(SnR_3)_2$,[22] the second stage of which must involve attack of $R_3Sn\cdot$ on $C_6H_5CH{=}CHSnR_3$.

(22) M. Delmas, J. C. Maire, and R. Pinzelli, *J. Organometal. Chem.*, **16**, 83 (1969); A. J. Leusink and J. G. Noltes, *ibid.*, **16**, 91 (1969).

enyne **9b** behave similarly. Some stereoselectivity in the additions to enynes **9c** and **9d** is also evident but could not be quantified owing to difficulties in product separation.

Finally, the observation that telomerization is a serious complication for addition of stannane **8** to enynes but not for addition of *tert*-butyl hypochlorite[1] is in accord with the known more favorable atom transfer properties of hypochlorites compared with stannanes.[2,3]

Experimental Section

Infrared spectra were routinely recorded as liquid films on a Beckman IR 10 spectrometer. Ultraviolet spectra were recorded in *n*-heptane solution on a Cary 14 spectrometer. Nmr spectra were obtained in carbon tetrachloride solution on a Varian A60 spectrometer, and results are expressed in parts per million downfield from internal tetramethylsilane (δ). Mass spectra were recorded at 70 eV with an AEI MS 12 spectrometer. Boiling points are uncorrected. Glpc analyses were performed on either Apiezon L or poly(propylene glycol) columns at 60–120° with the injector and thermal conductivity detector held at 150°.

Starting Materials. The preparation of enynes **9a**, **9b**, and *cis*- and *trans*-**9c** has been reported.[1] 2-Hexen-4-yne (**9d**) was prepared by treatment of the tosylate of 4-hexyn-2-ol (Farchan Research Laboratories) with aqueous base.[24] Distillation through a Teflon spinning band column gave samples of *cis*-**9d**, bp 91.5°, ir 718 cm^{-1}, nmr $J^{CH=CH}$ = 11 Hz; and *trans*-**9d**, bp 99.5°, ir 955 cm^{-1}, nmr $J^{CH=CH}$ = 15.5 Hz; each in >99% purity.[25] Trimethyltin hydride (**8**) was prepared as described by Fish, *et al.*[5b] AIBN was crystallized from ether and stored at low temperature.

Reaction of 1-Penten-3-yne (9a) with Trimethyltin Hydride (8). In a typical reaction, a mixture of 3.80 g (57.5 mmol) of enyne **9a**, 5.11 g (31.0 mmol) of stannane **8**, and 0.25 g (1.5 mmol) of AIBN was heated in a sealed tube for 20 hr at 80–85°. Glpc analysis revealed complete consumption of **8** but some residual **9a**. Distillation through a short column gave: (1) 3.37 g (47% calculated as $Me_3SnC_5H_7$), bp 50–60° (7 Torr), and (2) 1.32 g, bp 70–80° (0.02 Torr). Glpc analysis (poly(propylene glycol)) of fraction 1 showed a set of five closely spaced peaks (A–E in order of increasing retention time) in relative ratios very similar to those observed in the crude reaction product before distillation (E > B ~C > A~ D). The nmr spectrum was the expected composite of the individual spectra of the major, ultimately isolated adducts **10–12** (see below) and no unexplained resonances were present except for a small singlet at 1.5 ppm which was absent from parallel runs conducted (for a longer period) without AIBN; resonances from small amounts of products **13** and **14** (see below) would have been obscured in the spectrum of fraction 1.

Reaction between **9a** and **8** also occurred very slowly over several hours at 20–25° by irradiation with a high-pressure mercury lamp through a Pyrex filter. The photoinitiated reaction was further accelerated by the presence of catalytic amounts of AIBN.

Response of Reaction of Enyne 9a with Stannane 8 to Initiators and Inhibitors. A stock solution of 750 mg (11.3 mmol) of enyne **9a**, 801 mg (4.86 mmol) of stannane **8**, and 152 mg of toluene was made up in 5.00 ml of benzene. To one 0.5-ml aliquot, designated I, was added 4.1 mg (0.0097 mmol, 2 mol % of **8**) of galvinoxyl.[10] Aliquot II was unaltered. To a final 0.5-ml aliquot, designated III, was added 3.3 mg (0.020 mmol, 4 mol% of **8**) of AIBN. Each aliquot was then heated in a sealed vial for 19 hr at 60°. Glpc analysis, compared with the toluene internal standard, showed the per cent consumption of stannane **8** to be 13, 25, and 88% in samples I, II, and III, respectively, while the accumulated monoadduct yields were 0.6, 12, and 56%, respectively.

Product Separation and Identification from Reaction of Enyne 9a with Stannane 8. Isolation of the major component E of the distilled fraction by preparative glpc gave a material with nmr bands at 2.33 (m), 1.72 (t, J = 2.5 Hz), 1.00 (t, J = 6.5 Hz), and 0.10 (s) ppm in a ratio of 2:3:2:9;[26a] mass spectral peaks[26b] at *m/e* (rel intensity) 232 (5) (P), 217 (100) (P − CH_3), 189 (62), 165 (45) ($(CH_3)_3Sn$), and 135 (25) (CH_3Sn); and no ir bands indicative of allenic or olefinic functionality. Its assignment as 3-pentyn-1-yltrimethyltin (**10**) was confirmed by authentic synthesis (see below).

Anal. Calcd for $C_8H_{16}Sn$: C, 41.61; H, 6.99. Found: C, 41.90; H, 6.96.

Isolation by preparative glpc of B and C together gave a material (B:C ~ 2) with the following spectral properties: ir bands at 1620 (conj. C=C) and 980 and 890 cm^{-1} ($CH=CH_2$); uv λ_{max} 237 nm (ϵ 21,000); nmr bands at 6.9–5.8 (m), 5.2–4.8 (m), 1.98 (narrow m), and 0.20 (s) and 0.13 (s) ppm in a ratio of 2:2:3:9 (9 for the sum of the two $(CH_3)_3Sn$ singlets; the δ 0.20-ppm band is associated with the more abundant B). These were therefore assigned as the geometrical isomers of 2,4-pentadien-2-yltrimethyltin (**11** and **12**). Glpc–mass spectral interfacing allowed determination of mass spectral peaks for B at *m/e* (rel intensity) 232 (<2), 217 (<40), 165 (<23), 135 (<40), and 67 (100) (C_5H_7) and for C at 232 (11), 217 (100), 165 (65), 157 (55) ($(CH_3)_2SnH$), 135 (40), and 67 (50).

Anal. Calcd for $C_8H_{16}Sn$: C, 41.61; H, 6.99. Found: C, 41.83; H, 6.98.

A solution of 38.5 mg (0.167 mmol) of a collected mixture of dienes B and C (B:C ~ 2) and 6 mg of *n*-pentane in 0.5 ml of *n*-heptane was treated with successive aliquots of trifluoroacetic acid (TFA) at ambient temperature. Addition of ~3 μl (~0.04 mmol) led to immediate precipitation of trimethyltin trifluoroacetate. Glpc analysis, compared with the *n*-pentane internal standard, showed the presence of *cis*- and *trans*-piperylene (2.1:1 ratio; ~0.045 mmol) and a relatively greater disappearance of C than of B. On addition of further aliquots of TFA, the *cis*/*trans*-piperylene ratio smoothly decreased to 0.7 as ultimately both C and, more slowly, B disappeared and 0.17 mmol of total piperylenes formed. In control experiments, the individual piperylene isomers were neither extensively isomerized nor consumed by TFA under conditions which cleaved B and C. Hence B is assigned the *Z* configuration **11** and C the *E* configuration **12**. Treatment of acetylenic adduct **10** with TFA under these conditions gave little reaction even after 16 hr.

One of the minor components, A, was isolated by preparative glpc in >80% purity. The ir band at 1945 cm^{-1} (C=C=C), visible in all crude reaction mixtures of **9a** and **8**, was associated with this product which was assigned as 2,3-pentadien-2-yltrimethyltin (**13**), rather than 2,3-pentadien-1-yltrimethyltin, on the basis of two nmr doublets at 1.93 (J = 2.5 Hz, $CH=C=C(CH_3)$) and 1.58 ppm (J = 6.5 Hz, $CH_3CH=$) of equal area; the olefinic proton occurred as a broad band at 4.5 ppm and the $(CH_3)_3Sn$ group at 0.13 ppm. Mass spectral peaks (glpc interface) occurred at *m/e* (rel intensity) 232 (11), 165 (100), 135 (28), 67 (67), and 41 (25). Cleavage of **13** with TFA in *n*-heptane as described above was even more rapid than that of dienes **11** and **12** (as determined from treatments of monoadduct mixtures with TFA) and produced an approximately equal mixture of 2,3-pentadiene and 2-pentyne.

All attempts to collect the final product D = **14** led to materials which showed little D on reinjection but rather a mixture with its major peak having a retention time between that of **11** and **12**. The nmr spectrum clearly eliminated **11** and **12** as *major* components and could be rationalized better with that of 1,3-pentadien-3-yltrimethyltin (**15**) (see below) as could the glpc retention time; however, this evidence can be considered strongly circumstantial but not conclusive.

3-Pentyn-1-yltrimethyltin (10). 3-Pentyn-1-ol (Farchan) was converted in *ca.* 25% yield to the corresponding bromide, bp 60° (40 Torr) (lit.[27] bp 94–96° (160 Torr)), by the procedure of Landor[28] which employs triphenyl phosphite dibromide. The bromide (2.5 g, 17 mmol) was converted to the Grignard reagent in dry THF which was then refluxed for 4 hr with 1.8 g (9 mmol) of trimethyltin chloride.[29] The cooled reaction mixture was treated

(23) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 981 (1972); F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875, 882 (1967); M. L. Poutsma and P. A. Ibarbia, *Tetrahedron Lett.*, 3309 (1972).

(24) G. Eglinton and M. C. Whiting, *J. Chem. Soc.*, 3650 (1960).

(25) The reported boiling point, presumably of a cis-rich mixture, is 91–92°: I. A. Favorskaia, E. M. Auvinen, and I. P. Artsybashev, *J. Gen. Chem. USSR*, **28**, 1832 (1958).

(26) (a) In nmr spectra of all adducts described herein, the nmr intensities have been corrected for the ^{117}Sn and ^{119}Sn satellites for protons coupled to Sn. (b) In mass spectra, the appropriate Sn isotope distribution was seen for all peaks containing Sn; masses reported are for the most abundant ^{120}Sn isotope.

(27) K. E. Schulte and M. Goes, *Arch. Pharm.*, **290**, 118 (1967); *Chem. Abstr.*, **51**, 12817 (1957).

(28) D. K. Black, S. R. Landor, A. N. Patel, and P. F. White, *J. Chem. Soc. C*, 2260 (1967).

(29) D. Seyferth and F. G. A. Stone, *J. Amer. Chem. Soc.*, **79**, 515 (1957).

with concentrated ammonium chloride solution and the products were extracted into ether. Evaporation of the dried extracts and distillation gave 0.86 g (41%) of coupling product **10**, bp 55–58° (7 Torr), in which glpc analysis revealed ~10% each of a much more and a much less volatile impurity. Spectral and glpc properties were fully in accord with those of major adduct E from reaction of **9a** and **8**.

1,3-Pentadien-3-yltrimethyltin (15). 3-Bromo-1,3-pentadiene (~75% pure) was prepared by hydrobromination of 1-penten-3-yne by the method of Petrov.[30] Conversion of 3.42 g (29 mmol) of crude bromide to the Grignard reagent and coupling with 3.3 g (16.5 mmol) of trimethyltin chloride in THF as described above followed by the usual work-up and bulb-to-bulb distillation gave 0.77 g of crude product, bp 50–60° (8 Torr). Glpc collection of the major peak (>80% of the crude product) gave diene **15**: ir bands at 1615, 985, and 890 cm^{-1}; uv λ_{max} 227 nm (ϵ 14,500); nmr bands at 7.1–4.9 (m), 1.85 (d, J = 6.5 Hz), and 0.28 (s) and 0.19 (s) ppm, the latter two in a 2:1 ratio. Treatment with TFA in carbon tetrachloride solution gave *cis*- and *trans*-piperylene in a 1:2 ratio; hence the coupling product contained a predominance of (*Z*)-**15** over (*E*)-**15**. The glpc retention time of (mixed) **15** was between that of dienes **11** and **12** and hence unknown **14** = D clearly does not have structure **15**, although its glpc-induced rearrangement product may. Also, comparison of the nmr spectra of synthetic **15** with those of crude reactions mixtures of **9a** and **8** and of the glpc-collected sample of (**11** + **12**) indicates that no significant amount of **15** was in the initial products from **9a** and **8**.

Evidence for Telomer Formation During Reaction of Enyne 9a with Stannane 8. Glpc–mass spectral interfacing examination of the high-boiling fractions from reaction of **9a** and **8** revealed several peaks. However, the associated mass spectra could be divided into two classes, one having a set of peaks characterized by the isotopic distribution from one Sn atom centered at *m/e* 283 corresponding to P − CH_3 for a 2:1 telomer, and the other having a set of even more complex peaks centered at *m/e* 380–390 corresponding to P − CH_3 for a diadduct. To maximize telomer formation at the expense of diadduct formation, a solution of 1.96 g (24.5 mmol) of enyne **9a**, 1.56 g (9.45 mmol) of stannane **8**, and 85 mg (0.52 mmol) of AIBN in benzene solution (10 ml total) was heated in a sealed tube at 60–65° for only 1.2 hr. Glpc–mass spectral investigation revealed, at retention times much longer than those of the usual monoadducts, a broad peak dominating several other minor ones although mass spectra of several cuts within this peak suggest inhomogeneity. Significant peaks occurred at *m/e* 283, 165, and 133; the latter had no Sn isotope pattern and hence is most probably $C_{10}H_{13}$ as anticipated for a 2:1 telomer. At still longer retention time were seen lesser amounts of 3:1 telomers as judged by peaks at *m/e* 364 (P), 349 (P − CH_3), and 199 ($C_{15}H_{19}$), the former two containing one Sn atom and the latter one no Sn atoms.

Quantitative Study of Reaction of Enyne 9a with Stannane 8. Solutions of exactly weighed amounts of AIBN and toluene and approximate amounts of **9a** and **8** were made up in benzene in a 5.00-ml volumetric flask. The flask was closed with a tight-fitting rubber septum and placed in a constant-temperature bath. Aliquots were withdrawn with a microsyringe and analyzed for concentrations of reactants **9a** and **8** and products **10–14** by comparing glpc areas with that of the toluene standard. The analyses were performed with a poly(propylene glycol) column run isothermally at 60° for elution of **9a** and **8**, linearly programmed to 120°, and finally held at 120° for elution of **10–14**. Calibration factors were determined for **9a**, **8**, **10**, and (**11** + **12**); factors for **13** and **14** were assumed to be the same as for **10** and (**11** + **12**) which were themselves identical. (The same factor was also used for semiquantitative estimates of yields in reactions of the other enynes.) Control experiments showed negligible loss of the volatile reactants in the absence of reaction and no reaction in the glpc inlet. Results are shown in Tables I–III.

Reaction of 2-Methyl-1-buten-3-yne (9b) with Trimethyltin Hydride (8). Attempts to carry out reactions of the more volatile enyne **9b** with stannane **8** in sealed tubes in the range 60–100° in the absence of solvent, as had been successful for enyne **9a**, led to frequent ruptures of the tubes; hence preparative reactions were done at lower temperature with photoinitiation. A mixture of 3.78 g (57.3 mmol) of enyne **9b**, 5.90 g (35.7 mmol) of stannane **8**, and 0.30 g (1.8 mmol) of AIBN was irradiated for 22 hr at 25° with a 400-W high-pressure mercury lamp through a Pyrex filter. Glpc analysis (Apiezon L) revealed that **8** was largely consumed, and four peaks (F–I in order of increasing retention time) were observed in the region expected for monoadducts (F:G:H:I = 53:27:14:6). Distillation gave 2.88 g (36%) of a monoadduct fraction, bp 55–60° (10–8 Torr), as well as 1.40 g, bp 70–85° (0.1 Torr). The distilled monoadduct fraction showed F:G:H:I = 54:26:14:6. Nmr analysis allowed tentative structural assignments to the products as 2-methyl-3-butyn-1-yltrimethyltin (**16** = F) (52% based on doublets at 1.13 and 1.28 ppm), 2-methyl-2,3-butadien-1-yltrimethyltin (**17** = G) (26% based on a narrowly spaced multiplet at 4.67 ppm for the >C=C=CH_2 protons weakly coupled to five nearly equivalent protons), and mixed isomers of 3-methyl-1,3-butadien-1-yltrimethyltin (**18** and **19** = H and/or I) (22% based on a broad multiplet at 5.02 ppm for the CH_2=C< group).

Preparative glpc allowed isolation of a pure sample of **16**: ir bands at 3300 and 2105 cm^{-1} (C≡CH); nmr bands at 3.0–2.5 (m), 1.97 (d, J = 2.5 Hz), 1.28 (d, J = 6.5 Hz), 1.13 (d, J = 7 Hz), and 0.20 (s) ppm in a ratio of 1:1:3:2:9. Also isolated was a pure mixture of **18** and **19** in a ratio of ~2:1, and nmr parameters could be assigned to each: the more abundant H had an olefinic AB pattern (δ_A 7.03, δ_B 5.93 ppm, J_{AB} = 13.5 Hz) and bands at 5.02 (m), 1.98 (m), and 0.33 (s) ppm; the analogous parameters for I were δ_A 6.66, δ_B 6.28 ppm, J_{AB} = 19 Hz, 5.02 (m), 2.05 (m), and 0.33 (s) ppm. Hence H is the *Z* isomer **18** and I is the *E* isomer **19**. However, attempts to collect G, tentatively assigned as **17**, gave a material with very similar retention time but lacking the 4.67-ppm nmr multiplet and the 1950-cm^{-1} ir band which had been present in both the crude and distilled products. Instead, it had new nmr bands *not* present at any stage before glpc collection. Spectral properties point strongly to the structure 3-methyl-1,3-butadien-2-yltrimethyltin (**20**) for this material: ir 913 and 881 cm^{-1} (>C=CH_2); uv λ_{max} 226 nm (ϵ 10,800); nmr bands at 5.85 (d, J ~ 2 Hz), 5.30 (narrow m), 5.00 (narrow m), 4.83 (narrow m), 1.95 (narrow m), and 0.27 (s) ppm in the ratio 1:1:1:1:3:9; an nmr spectrum at 220 MHz showed that each of the single-proton bands was associated with a distinct chemical shift rather than with coupling.

Small-scale reactions could be safely carried out at 60–85° in benzene solution. The same products **16–19** were seen, but dienes **18** and **19** increased at the expense of acetylene **16** and allene **17** (Table IV).

Reaction of 3-Penten-1-yne (9c) with Trimethyltin Hydride (8). A mixture of 3.80 g (57.6 mmol) of 3-penten-1-yne (**9c**) (trans/cis = 1.16), 5.49 g (33.3 mmol) of stannane **8**, and 0.25 g (1.5 mmol) of AIBN was heated in a sealed tube at 80–85° for 20 hr. After evaporation of excess enyne **9c**, the nmr spectrum of the residue was characterized by strong absorption in the olefinic and allylic proton regions, negligible absorption in the region 1.5–0.5 ppm, and the presence of at least three resolved high-field singlets characteristic of Me_3Sn groups. Glpc analysis (Apiezon L) revealed at least four peaks in the monoadduct region (J–M) in a ratio of ~1:2.5:1.5:5. Distillation gave 3.47 g (45%) of mixed monoadducts, bp 55–60° (8 Torr), with a glpc pattern in the monoadduct region similar to that of the crude product. Attempted separation by preparative glpc was only partially successful in that a mixture of J, K, and L (26:59:15) and a second mixture of L and M (36:64) could be collected. The former mixture retained the ir band at 1925 cm^{-1} which had been present in the crude product and had nmr bands at 7.1–5.4 (m), 1.95–1.8 (m), 1.03 (t, J = 7 Hz, area ~one-fourth of the 1.95–1.8 multiplet), 0.22 (s), and 0.13 ppm (s, area ~one-fifth of the 0.22 singlet). These spectra are consistent with the presence of largely 1,3-pentadien-1-yltrimethyltin (**21**) and a lesser amount (20–25% and hence most probably J) of 1,2-pentadien-1-yltrimethyltin (**22**). The second mixture had no allenic ir band but had nmr multiplets at 7.2–5.2 and 1.78 ppm and three singlets of comparable intensity at 0.23, 0.18, and 0.16 ppm, again consistent with the gross structure **21**; the three Me_3Sn singlets suggest that glpc peak M must be a composite. No success was achieved in attempting to correlate uniquely the four possible geometrical isomers of diene **21** with particular glpc peaks or nmr bands although the combined evidence suggests that all four are present. The failure to observe nmr doublets in the 1.5–0.5-ppm range in either the crude or distilled products rules out any significant amounts of 1,2 or 1,4 adducts which would contain the $CH_3CH(SnMe_3)$ group.

A benzene solution made up to contain 2.34 *M trans*-**9c** (2% cis contaminant), 1.06 *M* **8**, 0.54 *M* toluene, and 0.055 *M* AIBN was held at 60° and periodically sampled by glpc analysis. Up to 83% consumption of **8** based on the toluene internal standard,

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no formation of *cis*-**9c** was observed. In a parallel run with 0.69 *M cis*-**9c**, 0.66 *M* **8**, 0.44 *M* toluene, and 0.048 *M* AIBN, no formation of *trans*-**9c** was observed up to 90% consumption of **8**. The initial distribution among products J–M was quite different in the two runs, and each also changed noticeably with extent of conversion.

Reaction of 2-Hexen-4-yne (9d) with Trimethyltin Hydride (8). A mixture of 1.85 g (23.1 mmol) of enyne **9d** (largely cis), 2.79 g (16.9 mmol) of stannane **8**, and 0.16 g (0.98 mmol) of AIBN was heated in a sealed tube at 85° for 21 hr; glpc analysis revealed only a trace of residual **8**. Evaporation and distillation gave 1.65 g (40%), bp 55° (2.3 Torr), of product whose glpc spectrum (Apiezon L) was very similar to that before distillation and showed three resolved peaks in a ratio of 46:17:37. The nmr spectrum had a broad multiplet at 7.1–5.3, three broadened lines at 2.03, 1.90, and 1.80, and two singlets at 0.30 and 0.22 ppm with areas consistent for this product's being mixed geometrical isomers of 2,4-hexadien-2-yltrimethyltin (**23**). However, a weak ir band at 1925 cm^{-1} both in the crude and distilled products again indicates a minor adduct with allenic structure.

A mixture of 1.69 g (21.1 mmol) of enyne **9d** (cis/trans = 1.5), 2.42 g (14.7 mmol) of stannane **8**, and 0.15 g (0.93 mmol) of AIBN was irradiated with a high-pressure mercury lamp through Pyrex for 24 hr at 25°. Glpc analysis revealed no residual **8** and a monoadduct pattern very similar to that from the thermal reaction described above. Distillation gave 2.33 g (65%), bp 47–52° (2 Torr), of mixed adducts with an nmr spectrum very similar to that described above.

A pair of parallel experiments to probe for isomerization of unreacted enyne **9d** as a function of extent of consumption of stannane **8** was carried out at 60° in xylene solvent, and results are described in Table V.

Apolar Influences in the Poly[4(5)-vinylimidazole] Catalyzed Hydrolyses of 3-Nitro-4-acyloxybenzoic Acid Substrates

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Abstract: The effects of the acyl chain length in the substrate and volume per cent of water in the aqueous–alcohol solvent systems on the rate of hydrolysis of 3-nitro-4-acyloxybenzoic acid substrates (S_n^-) catalyzed by imidazole (Im) and poly[4(5)-vinylimidazole] (PVIm) were determined. They demonstrate the importance of apolar bonding in the rate enhancements observed for PVIm catalyzed reactions as compared to Im catalyzed reactions. The critical micelle concentrations (cmc) of the substrates in aqueous–alcohol solutions were determined spectroscopically. Knowledge of cmc values permitted a more meaningful interpretation of the kinetic data. In certain esterolysis reactions, deviations from pseudo-first-order kinetics were observed. With $[S_7^-] > [PVIm]$ in 15 and 20% 1-propanol–water systems, the kinetic behavior exhibited was indicative of "saturation" of the polymer with substrate. When $[PVIm] > [S_2^-, S_7^-, \text{or } S_{12}^-]$ cases were studied in 20% 1-propanol in water systems, an analogous saturation of the substrate with polymer was indicated by the kinetic behavior. The effect of varying the pH and temperature on these esterolysis reactions was also studied. An increase in r ($r = k_{PVIm}/k_{Im}$) was observed with decreasing pH.

Recently there has been considerable success in utilizing apolar (or hydrophobic) forces to enhance the esterolytic action of synthetic macromolecular catalysts,[1-5] as well as monomeric catalysts.[6,7] In some cases it has been possible to observe saturation kinetics, formally characteristic of a catalyst–substrate complex, as is observed in enzyme-catalyzed reactions.[1,3-5] Although the kinetic formalism is similar, the process is obviously different than that exhibited by an enzyme. Apolar interactions were also responsible for the dramatic rate enhancements observed for the poly[4(5)-vinylimidazole] (PVIm) catalyzed hydrolysis of the long-chain, anionic substrate 3-nitro-4-dodecanoyloxybenzoic acid (S_{12}^-), relative to monomeric imidazole (Im).[2]

We would now like to report the results of the PVIm catalyzed esterolyses of a series of anionic esters in varying alcohol–water solvent systems. The ester substrates differ only in the chain length of the acid portion of the ester.

Results and Discussion

The rates of hydrolysis of a series of 3-nitro-4-acetyloxybenzoic acid substrates (S_n^-) catalyzed by PVIm were observed in varying volume per cent alcohol–water solvent systems. This series of substrates was selected to allow a controlled qualitative variation of the apolar forces operating during the hydrolysis. Previous results on the PVIm catalyzed hydrolysis of S_{12}^- in ethanol–water solvent systems indicated that these apolar forces would be substantial[1] with long-chain substrates.

Critical Micelle Concentration of S_n^-. A prereq-

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