In experiments employing cis-2-butene the olefin was checked before and after the reaction for the presence of the trans isomer; none was found.

The hydrogenation of 1,1'-dimethylbisethanoallene was carried out in ether solvent at 0° in the vacuum line using a 500-mm. partial pressure of hydrogen and a 5% palladium-on-charcoal catalyst. The uptake of hydrogen could not be determined accurately in the system, but subsequent gas chromatographic separation of the products and mass spectral analysis on the individual components showed them to be 2,6-dimethylheptane and 2-methyloctane. The third component expected, n-nonane was identified by retention time only.

Free-Radical Addition of Trimethyltin Hydride to Allenes[1]

Henry G. Kuivila,[2] W. Rahman,[3] and Richard H. Fish

Contribution from the Department of Chemistry, University of New Hampshire, Durham, New Hampshire. Received February 18, 1965

The azobisisobutyronitrile-catalyzed addition of trimethyltin hydride to allene, 1,2-butadiene, 2,3-pentadiene, 2-methyl-2,3-pentadiene, and 3-methyl-1,2-butadiene has been studied. Structures and configurations of all of the adducts have been assigned on the basis of infrared and n.m.r. spectroscopy, degradation, or comparison with authentic samples prepared by other methods. Information regarding the direction of addition and stereochemistry thus obtained is discussed in terms of the probable mechanism and the roles of electronic and steric factors on the individual steps of the over-all reaction.

The addition of free radicals to allenes has been the subject of several investigations, results of which have not yet provided a clear understanding of the factors which determine the direction of addition. For example, Haszeldine and co-workers[4] have shown that the highly electrophilic trifluoromethyl radical attacks the terminal position of allene exclusively, indicating an intermediate vinylic radical. On the other hand, addition of hydrogen bromide gives products resulting from attack at the central carbon by the electrophilic bromine atom suggesting an intermediate allylic radical.[5,6] The addition of thiyl radicals occurs preferentially, but not exclusively, at the terminal carbon atom on allene.[7-9] Methyl substitution increases the tendency for central carbon attack which amounts to 12.8, 48.2, and 100% for attack by the ethylthiyl radical on allene, 1,2-butadiene, and 3-methyl-1,2-butadiene, respectively.[8] It has been argued, on the basis of relative reactivities of allenes and substituted allenes, that the relatively nucleophilic methyl radical attacks the central carbon of allenes.[10,11]

It has been shown that the addition of organotin hydrides to olefins is catalyzed by free-radical sources such as azobisisobutyronitrile (AIBN) and benzyl hyponitrite.[12] The organotin radical (Sn· = R_3Sn) presumably initiates the addition reaction chain (eq. 1 and 2).[13] We undertook to examine the prod-

$$Sn\cdot + RCH{=}CH_2 \longrightarrow RCHCH_2Sn \qquad (1)$$

$$R\dot{C}HCH_2Sn + SnH \longrightarrow RCH_2CH_2Sn + Sn\cdot \qquad (2)$$

ucts of addition of trimethyltin hydride to allene and four methyl-substituted allenes in order to ascertain the pattern of addition, with respect to both direction of addition and stereochemistry of products, as a function of allene structure.

Results

The addition reactions, catalyzed by AIBN, were carried under similar conditions. In each case an excess of allene was used and the reaction mixtures were heated at 100 ± 5° for 9 hr. to ensure complete reaction. The products were first analyzed by gas-liquid chromatography (g.l.c.) to determine relative amounts of isomeric adducts, and the total yield of adducts was subsequently determined by isolation. In no case was there any indication of higher boiling products which would result from the addition of 2 moles of hydride to 1 mole of allene. Individual adducts were

(1) (a) Supported in part by the U. S. Army Research Office (Durham) and by the National Science Foundation. Purchase of the nuclear magnetic spectrometer used in this work was also made possible by a grant from the Foundation. (b) Presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 9, 1965, Abstracts p. 48P. (c) Taken from the Ph.D. Dissertation of R. H. Fish, University of New Hampshire, Feb. 1965.

(2) Department of Chemistry, State University of New York at Albany, Albany, N. Y.

(3) Research Associate on leave from the Aligarh Muslim University, Aligarh, India.

(4) R. N. Haszeldine, K. Leedham, and B. R. Steele, *J. Chem. Soc.*, 2040 (1954).

(5) D. Kovachic and L. C. Leitch, *Can. J. Chem.*, 39, 363 (1961).

(6) K. Griesbaum, A. A. Oswald, and D. N. Hall, *J. Org. Chem.*, 29, 2404 (1964).

(7) H. J. van der Ploeg, J. Knotnerus, and A. F. Bickel, *Rec. trav. chim.*, 81, 775 (1962).

(8) T. L. Jacobs and G. E. Illingworth, Jr., *J. Org. Chem.*, 28, 2692 (1963).

(9) K. Griesbaum, A. A. Oswald, E. R. Quiram, and W. Naegele, *ibid.*, 28, 1952 (1963).

(10) A. Rajbenbach and M. Szwarc, *Proc. Roy. Soc.* (London), A251, 1266 (1959).

(11) A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, 83, 4732 (1961).

(12) W. P. Neumann, H. Niermann, and R. Sommer, *Angew. Chem.*, 73, 768 (1961); *Ann. Chem.*, 659, 27 (1962).

(13) H. G. Kuivila in "Advances in Organometallic Chemistry" Vol. I, F. G. A. Stone and R. West, Ed., Academic Press Inc., New York, N. Y., 1964.

separated by g.l.c. when possible, subjected to elemental analysis, and assigned structures on the basis of infrared and nuclear magnetic resonance (n.m.r.) spectra. In a few cases structures were assigned after comparison of properties with authentic samples prepared by alternate procedures. The structures of all of the products isolated are given in Chart I. Yields and product distributions, analytical data, and characteristic infrared bands are listed in Table I. N.m.r. data, including chemical shifts in τ units, coupling constants in cycles per second, and assignments are given in Table II.

Chart I. Trimethyltin Hydride–Allene Adducts
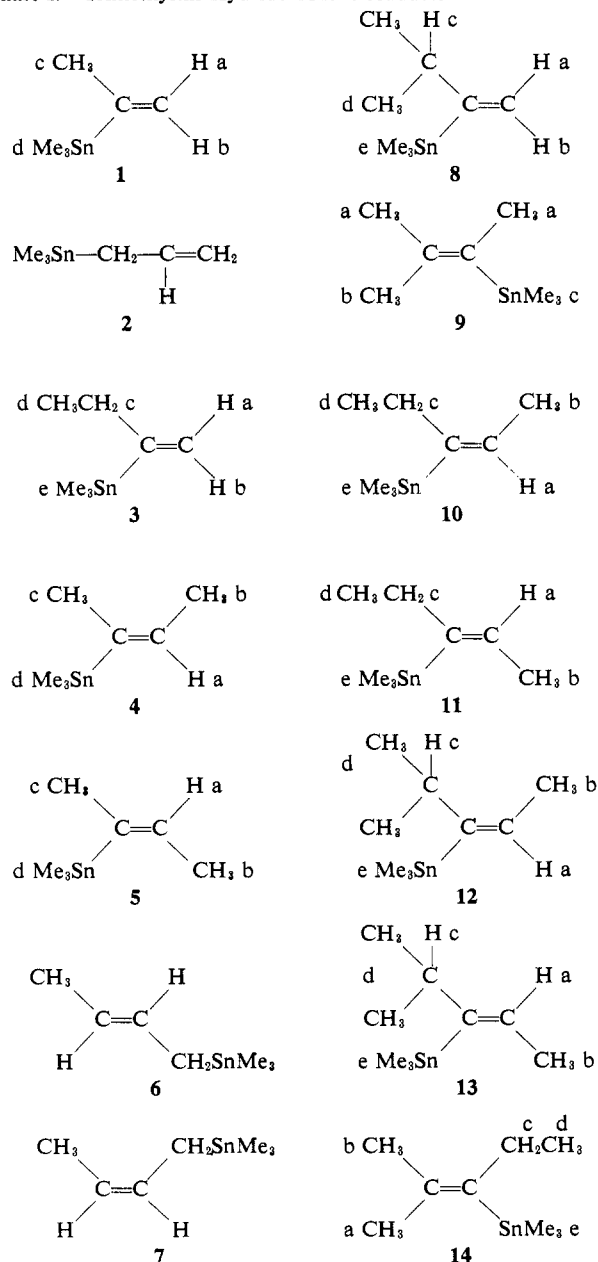
Allene. Allene provided, in 67% yield, a mixture containing 54.8% of trimethylallyltin[2] and 45.2% of prop-2-enyltrimethyltin. The former is well known, and the infrared and n.m.r. data obtained on the latter agreed with those reported by Seyferth and Vaughan.[14] Allene does not isomerize to propyne under the reaction

conditions. This was demonstrated by the observation that the excess unreacted hydrocarbon did not contain propyne. Furthermore, propyne reacted with trimethyltin hydride under our reaction conditions to yield 43% of a mixture containing 70.4% of *trans*-propen-1-yltrimethyltin, 29% of *cis*-propen-1-yltrimethyltin, and about 0.6% of propen-2-yltrimethyltin.

1,2-Butadiene. The product obtained in 72.6% yield contained components whose structures were assigned as follows. But-1-en-2-yltrimethyltin (**3**) showed the strong out-of-plane deformation band of a terminal methylene group at 915 cm.$^{-1}$. Its n.m.r. spectrum showed nine CH$_3$Sn protons at τ 9.82, a CH$_3$C triplet centered at 8.95, a methylene quartet centered at 7.65, and vinyl multiplets of unit area at 4.88 and 4.33. Each of the but-2-en-3-yltrimethyltins **4** and **5** showed signals with the expected areas from three methyl groups attached to tin, two other methyl groups, and one vinyl proton. Cleavage of a sample containing mostly **4** with trifluoroacetic acid gave a mixture of 2-butenes containing 94% *cis* and 6% *trans* isomer. Since electrophilic cleavage of vinylic carbon–metal bonds proceeds with retention of configuration the configurations of **4** and **5** are established. The structures and configurations of the but-2-en-1-yltrimethyltins **6** and **7** were made by comparison of the infrared and n.m.r. spectra with those of samples prepared from trimethyltinsodium and 1-chloro-2-butene by Verdone.[15]

3-Methyl-1,2-butadiene. Only products from central attack by the trimethyltin radical appeared. The yield was 72% of a mixture containing 27% of 3-methylbut-1-en-2-yltrimethyltin **8** and 73% of 2-methylbut-2-en-3-yltrimethyltin **9**. These could be distinguished unambiguously by the terminal vinyl band at 916 cm.$^{-1}$ in the infrared spectrum of **8** and appropriate numbers of protons with expected chemical shifts and multiplicities in the n.m.r. spectra.

2,3-Pentadiene. This allene provided a 65% yield of a mixture which we could not separate by g.l.c. The n.m.r. spectrum had CH$_3$Sn peaks at τ 9.86 and 9.93, with areas in the ratio 46 to 54. The two vinyl quartets were centered at τ 4.35 and 3.95. By analogy with **4** and **5** the isomer with the CH$_3$Sn signal at higher field is tentatively assigned configuration **10**, with the trimethyltin group and the vinyl proton *cis* to each other, and the other isomer is designated as **11**.

2-Methyl-2,3-pentadiene. The adduct mixture obtained from this allene in 82.5% yield could be separated into two fractions by g.l.c. One fraction, comprising 45.5% of the mixture, showed no bands above 3000 cm.$^{-1}$ in the infrared spectrum and no vinyl resonance in the n.m.r. spectrum. The latter spectrum exhibited two singlet methyl protons at τ 8.27 and 8.20 and a triplet at 9.12, along with the tin–methyl protons at 9.85, and the methylene quartet centered at 7.80 as would be expected for 2-methylpent-2-en-3-yltrimethyltin, **14**. The second fraction (54.5%) proved to be a mixture containing 77.6% of **13** and 22.4% of **12** as indicated by the areas of the peaks due to the trimethyltin protons. Configurational assignments were based on analogy with **4** and **5**, the trimethyltin resonance at the higher field being assigned to the isomer in which the trimethyltin group is *cis* to hydrogen.

(14) See Table I, footnote *c*.

(15) See Table I, footnote *d*.

Table I. Preparative, Physical, and Analytical Data on Trimethyltin Hydride–Allene Adducts

Allene	Yield, %	Product distribution[a] Compd.	%	B.p., °C. (mm.)	n^{25}D
$H_2C=C=CH_2$[b]	67	1[c]	45.2	123.5–124.5 (760)	1.4608
		2[d]	54.8		1.4740
CH_3\ C=C=CH_2[e] / H	72.6	3	31.5	55–57 (25)	1.4656
		4	38.6		1.4738
		5	16.3		1.4753
		6[d]	10.0		
		7[d]	3.5		
CH_3\ C=C=CH_2[f] / CH_3	72	8	26.8	37.5–39 (2.5)	1.4678
		9	73.2		1.4847
CH_3\ CH_3[g] /C=C=C\ H H	65	10 and 11[h]	100.0	39–41 (1.4)	1.4750
CH_3\ CH_3[i] /C=C=C\ CH_3 H	82.5	12 and 13[j]	54.5	39.5–40 (1.2)	1.4779
		14	45.5		1.4837

Compd.	Calcd. C	Calcd. H	Found C	Found H	Prominent infrared bands,[k] cm.$^{-1}$
1					3040 m, 1600 w, 1440 s, 1190 s, 910 s, 765 s
2					3080 m, 1630 s, 1190 s, 985 m, 880 s, 763 s
3	38.41	7.32	38.67	7.49	3055 m, 1600 w, 1460 s, 1190 s, 915 s, 765 s
4	38.41	7.32	38.31	7.49	3000 vw, 1615 m, 1440 m, 1190 s, 765 s
5	38.41	7.32	38.28	7.21	3000 vw, 1625 m, 1450 m, 1190 m, 820 m, 770 s
6					3010 m, 1650 m, 1430 s, 1185 m, 960 s, 765 s
7					3012 m, 1648 s, 1450 m, 1400 m, 1190 s, 770 s, 725 w
8	41.23	7.73	41.40	7.90	3030 m, 1590 w, 1450 m, 1360 m, 1375 m, 1190 s, 916 s, 770 s
9	41.23	7.73	41.41	7.95	1630 s, 1450 s, 1190 s, 770 s
10 and 11	41.23	7.73	41.42	7.81	3005 w, 1625 m, 1450 m, 1190 m, 835 m, 770 s
12 and 13	43.76	8.10	43.56	8.02	3005 vw, 1620 m, 1460 m, 1380 m, 1360 m, 1189 m, 835 m, 770 s
14	43.76	8.10	43.47	7.87	1620 m, 1440 m, 1188m, 760 s

[a] All products were separated on a 20-ft. 20% silicone nitrile (G.E. XF 1150) column on chromosorb P (60–80 mesh). The retention times for the products are in the order listed, i.e., 1 shorter time, 14 longest time. [b] 100% excess allene. [c] All physical constants were in accord with those reported by D. Seyferth and L. G. Vaughan, J. Organometal. Chem. (Amsterdam), 1, 138 (1963). [d] J. A. Verdone, Ph.D. Dissertation, University of New Hampshire, 1963. [e] 46% excess allene. [f] 14% excess allene. [g] 7% excess allene. [h] 46% cis and 53.9% trans, based on trimethyltin proton peak areas in n.m.r. spectrum. [i] 10% excess allene. [j] 12.3% cis and 42.2% trans, based on trimethyltin proton peak areas in n.m.r spectrum. [k] Liquid smears.

Table II. N.m.r. Spectral Data on Trimethyltin Hydride–Allene Adducts[a,b]

Adduct	Concn. in CCl₄, %	(a)	(b)	(c)	(d)	(e)	J_{a-b}	J_{a-c}	J_{b-c}	J_{c-d}
1	50	4.37 (m)	4.90 (m)	8.08 (3)	9.9 (1)		1.5–1.6	1.5–1.6	1.5–1.6	
3	50	4.33 (m)	4.88 (m)	7.65 (4)	8.95 (3)	9.82 (1)	1.3	1.3	1.3	7.5
4	50	4.36 (16)	8.33 (2)	8.17 (m)	9.95 (1)		7.0	2.0	1.0	
5	35	3.96 (16)	8.30 (2)	8.15 (m)	9.84 (1)		6.6	1.8	1.4	
8	50	4.33 (m)	4.82 (m)	7.58 (m)	9.0 (2)	9.86 (1)	2.0	1.0	1.0	6.5
9	Neat	8.28 (1)	8.35 (1)	9.25 (1)						
10	Neat	4.35 (4)[c]	8.45 (2)	7.85 (4)	9.1 (3)	9.93 (1)[c]	6.5	1.0		7.2–7.5
11	Neat	3.95 (4)[c]	8.45 (2)	7.85 (4)	9.1 (3)	9.86 (1)[c]	6.5	1.0		7.2–7.5
12	50	4.46 (4)	8.31 (2)	7.61 (m)	9.05 (2)	9.90 (1)	7.0	1.1		7.0
13	50	3.96 (4)	8.31 (2)	7.61 (m)	9.05 (2)	9.82 (1)	7.0	1.1		7.0
14	50	8.27 (1)	8.20 (1)	7.80 (4)	9.12 (3)	9.85 (1)				7.5

[a] See Chart I for structure and proton designation. [b] Values reported in τ-units and measured to the center of each multiplet. J values in c.p.s. [c] $J_{e-a} = 1.2$ c.p.s.

Discussion

The dissociation energy of the carbon–tin bond is about 50 kcal. per mole.[16,17] Since the energy required to convert a double bond to a single bond is about 60 kcal. per mole, reaction 1 may be endothermic or exothermic depending on the stability of the resulting carbon free radical. The dissociation energy of the tin–hydrogen bond appears not to have been determined. However, organometallic hydrides undergo thermal decomposition with preferential cleavage of the tin–hydrogen bonds[13] indicating that the energy is probably less than 50 kcal. per mole. Thus, reaction 2 should be exothermic by over 50 kcal. per mole and should be very fast.

These energy relations account for several important characteristics of the addition of organotin hydrides to olefins[13]: (a) telomers have never been observed (because reaction 2 is much faster than reaction of the carbon radical with an olefin); (b) only terminal olefins, such as styrene, acrylonitrile, and acrylate esters, which can form resonance-stabilized radicals undergo thermal addition readily and in high yields (because step 1 may be exothermic and chains are extremely long); (c) simple terminal olefins such as 1-octene require initiation by free-radical sources (because step 1 may be endothermic and chains are now shorter, but still long enough to provide good yields of adducts); (d) simple internal olefins in general do not react, unless they are strained[18] (because steric effects make step 1 more endothermic).

The energetics of reactions 1 and 2 do not permit any *a priori* statement as to whether the products formed are the result of kinetic control in the formation of intermediate radicals or of the more complex situation which arises if the reverse of reaction 1 competes with, or is fast compared with, reaction 2. However, some inferences regarding orientation in addition to allenes can be drawn by comparison of the present results with those of Jacobs and Illingworth[8] on the addition of ethanethiol to allenes. They observed that allene, 1,2-butadiene, and 3-methyl-1,2-butadiene provided products resulting from attack by the ethanethiyl radical at the central carbon of the allenic triad amounting to 12.8, 48.2, and 100%, respectively. These results may be compared with the figures 45, 86.5, and 100%, respectively, observed for addition of trimethyltin hydride. Furthermore, 2,3-pentadiene and 2-methyl-2,3-pentadiene yield only products resulting from attack at the central carbon by the trimethyltin radical. As the ethanethiyl radical is electrophilic and the trimethyltin radical is nucleophilic, it is clear that polar effects are not of major importance in determining the direction of addition. It is suggestive, rather, of an increasing tendency toward the formation of an allylic radical intermediate with increasing methyl substitution.[8] This would be the result of decreasing reactivity at the methyl-substituted terminal carbons of the allenic triad due to steric effects, as observed for the addition of methyl radicals to olefins,[19] and in-

creasing stability of the allylic radicals due to hyperconjugation with the methyl groups.

An allylic radical formed from an unsymmetrically substituted allene can yield two different products when it abstracts a hydrogen atom from a donor, H–A. The intermediate from 1,2-butadiene in the ethanethiol addition yielded only one product, whereas that in the trimethyltin hydride addition yielded both of the possible products as shown in I. With 3-methyl-1,2-butadiene also only the product of addition of hydrogen
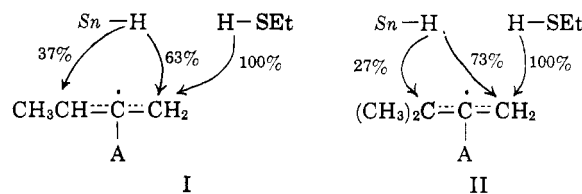
to the terminal atom of the allylic intermediate was formed in thiol addition, while both adducts appeared in the trimethyltin hydride adduct mixture; see II. The major product is the more highly substituted olefin, which is also the product of hydrogen transfer to the less hindered end of the allylic triad. The considerably higher selectivity in the thiol addition is attributable to the higher energy of the sulfur–hydrogen bond over that of the tin–hydrogen bond. The activation energy for the less exothermic reaction should be greater in the absence of significant entropy differences; the transition state should bear a closer resemblance to products[20]; and the tendency toward formation of the more stable olefin should be greater.

2-Methyl-2,3-pentadiene gives 54.5% of the products, **12** and **13,** of transfer of hydrogen from trimethyltin hydride to the more highly substituted end of the allylic group, and 45.5% of the isomeric olefin, **14.** This reversal in direction of addition could be due in part to **12** and **13** being trisubstituted ethylenes and, therefore, less sterically hindered than **14** which is a tetrasubstituted ethylene. On the other hand, the transition state for the reaction between the highly reactive allylic radical and trimethyltin hydride should resemble the reactants in geometry. In this event an explanation may be found by consideration of the structure of the allylic radical. It should exist in the planar configurations III and IV for maximum overlap of the π-orbitals.[21] Strain is present in III due to nonbonded interactions between the methyl groups
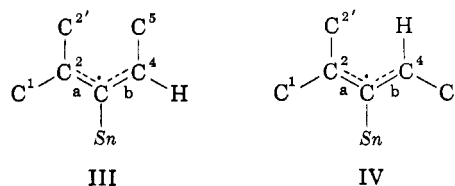
denoted by $C^{2'}$ and C^5 as well as the C^1 methyl and the trimethyltin group. In IV the most serious interactions are between the trimethyltin group and both C^1 and C^5. The resulting strains can be relieved by rotation

(16) J. B. Pedley, H. A. Skinner, and C. L. Chernick, *Trans. Faraday Soc.*, **53**, 1612 (1957).

(17) I. B. Rabinovitch, V. I. Tel'noi, P. N. Nikolaev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **138**, 852 (1961).

(18) O. R. Khan and I. J. Tyminski (unpublished observations from these laboratories) have observed ready addition of trimethyltin hydride to norbornadiene.

(19) R. P. Buckley, F. Leavitt, and M. Szwarc, *J. Am. Chem. Soc.*, **78**, 5557 (1956).

(20) G. S. Hammond, *ibid.*, **77**, 334 (1955).

(21) Since the bond order in the allylic free radical is 1.707 according to MO calculations, it is assumed that rotation about the bonds will be slow compared with reaction with the tin hydride. C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961), have shown that the allylic radicals which are intermediates in the chlorination of butenes by *t*-butyl hypochlorite do not undergo interconversion by rotation about the bonds in the allylic group.

about bonds a and b. Rotation about bond a would require less energy because, in the extreme of rotation about 90°, the result would be a vinyl-substituted tertiary radical, whereas rotation about bond b would yield a vinyl-substituted secondary radical. Thus, to the extent that the radical deviates from planarity, the unpaired electron will be concentrated on C^2 and hydrogen abstraction will tend to occur at this carbon on either III or IV.

The distribution of geometrical isomers in the products from three of the allenes is of some interest. 1,2-Butadiene yields the trimethylcrotyltins 6 and 7 in 10.0 and 3.5% yields, respectively, a result which would be expected if the intermediate vinyl radical is able to undergo interconversion V ⇌ VI. If kinetic control were determining, V would also be expected to predominate, provided a radical attack at a double bond

V   VI
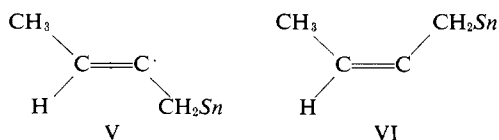
involves electron redistribution as shown in VII; and the trimethyltin radical attacks preferentially from below.

VII
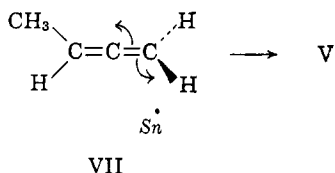
The products resulting from attack by the trimethyltin radical at the central carbon atom of 1,2-butadiene are 3 and the cis and trans pair, 4 and 5. In this case the cis isomer predominates over the trans in the ratio 38.6:16.3. This is explicable in terms of the intermediate allylic radicals VIII and IX. The former will yield 4 upon hydrogen abstraction by the terminal carbon and the latter will yield 5. The main source of


VIII   IX

strain energy in VIII is due to the nonbonded interaction between C^4 and H^1 and should be less (because the bond angles are those of trigonal carbon) than the 1.8 kcal. per mole[22] for methylcyclohexane with the methyl group axial. That in IX should be less, for reasons given below, than that in an ethylene with a methyl group and a t-butyl group cis, which amounts to 4.3 kcal.[23] The results would appear to indicate VIII as the more important of the two isomeric radicals in determining product formation.

2,3-Pentadiene yields the geometrical isomers 10 and 11 in the ratio 46:54. Similarly 2-methyl-2,3-penta-diene provided the isomers 12 and 13 in the ratio 12.3: 42.2. If stability of product is important in determin-

ing the course of these additions, the inference to be drawn is that the trimethyltin group has a steric effect little different from that of the methyl group. This is not entirely unreasonable. The length of the tin-carbon bond (2.17 Å. vs. 1.54 Å. for the carbon-carbon bond) should place the bulk of the trimethyl-tin group further away from the vinyl carbon, thereby decreasing interactions with other proximate groups.[24] Steric strains should also be more easily relieved by bending of the weaker carbon-tin bond. The results can also be interpreted with reference to the geometry of the intermediate allylic radical and application of the Hammond postulate.[20] The radical from 2,3-penta-diene can have the configuration X or XI. The interaction energy between the methyl groups denoted by C^1 and C^5 in XI should be similar to that between 1,3-

X   XI
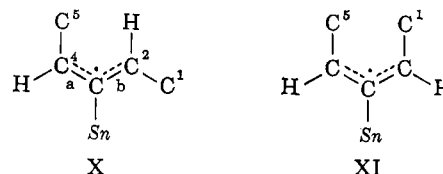
diaxial methyls in cyclohexane (5.4 kcal.[22]). That between the C^1 methyl and the trimethyltin group should be less than the 4.3 kcal.[23] interaction energy in cis-1-methyl-2-t-butylethylene for reasons indicated above. As a result X will be the predominant isomer. Hydrogen abstraction at C^2 will yield 10 and at C^4 will yield 11. There is little to choose a priori between these two positions. To the extent that the interaction between the C^1 methyl and the trimethyltin group is important, strain would be introduced which could be relieved by twisting about bond b, thus placing the higher unpaired electron density on C^2 and favoring attack by hydride at this bond. The slight predominance of 11 in the product is consistent with the idea that there is little interaction between these groups or that it is relieved by bending of the carbon-carbon and carbon-tin bonds in the plane of the allylic triad. Of course, all of the 10 could be formed from the less stable, and therefore more reactive XI.

Similar arguments would lead to the conclusion, that, of the radicals formed from 2-methyl-2,3-pentadiene IV should be more stable than III. However, some of the product must be formed via III because all of the 12 (12%) which is formed (by hydrogen abstraction at C^2) must be derived from it.

Since the polar effect appears not to be the major factor in determining the direction of radical additions to allenes the cause must be sought elsewhere. Although bromine atoms and thiyl radicals attack olefins reversibly,[25] Abell and Anderson[26] have reported that addition of bromine atoms to allene is not reversible.

(22) E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 214.

(23) R. B. Turner, D. E. Nettleton, and M. Perelman, J. Am. Chem. Soc., 80, 1430 (1958).

(24) Although appropriate data are not available for the trimethyltin group, F. R. Jensen and L. H. Gale, ibid., 81, 6337 (1959), have shown that the linear bromomercury group, HgBr, shows no preference for an equatorial conformation on cyclohexane reflecting an apparent bulk comparable to that of hydrogen. The carbon-mercury bond length in methylmercuric bromide of 2.074 Å. [W. Gordy, W. V. Smith, and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953, Table A.9] is actually shorter than the approximately 2.17 Å. given for the carbon-tin bond in methyltin halides [H. A. Skinner and L. E. Sutton, Trans. Faraday Soc., 40, 164 (1944)].

(25) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, Chapter 7.

(26) P. I. Abell and R. S. Anderson, Tetrahedron Letters, No. 49, 3727 (1964).

They therefore suggest that the bromine atom attacks a terminal carbon of allene to form a bromine–allene radical which rapidly rearranges to the allylic radical. This, in turn, abstracts hydrogen from hydrogen bromide to form 2-bromopropene. Direct formation of the allylic radical is not excluded by their results, but is considered unlikely, presumably because of the known pattern of additions to allene. A third alternative which appears not to have been considered is the direct formation of a bridged radical which could react directly or undergo opening of the three-membered ring to form a vinyl radical or an allylic radical (or both) depending on the nature of the substituents on the carbon atoms (eq. 3). The thiyl group, bromine, and the organotin group are capable of forming bridged radicals, whereas

$$CH_2{=}C{=}CH_2 + X\cdot \longrightarrow CH_2{-}C{=}CH_2 \rightleftharpoons CH_2{-}C{=}CH_2$$

$$CH_2{=}C{=}CH_2 \quad (3)$$
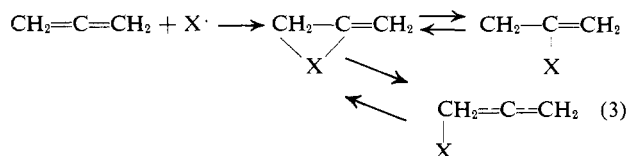
the trifluoromethyl group is not because the unpaired electron must be accommodated in a d-orbital on the bridging atom.

Experimental

Boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer (sodium chloride optics). The n.m.r. spectra were recorded on a Varian A-60 instrument with tetramethylsilane as an internal standard. The g.l.c. analyses were carried out with Aerograph A-700 and F and M Model 300 instruments. Peak areas were used to calculate percentages of the isomeric products.

Materials. Allene (Matheson Co.) was 98.5% pure with 1.5% propylene as the only impurity noted (g.l.c. on a 15 ft. × 0.25 in. dimethylsulfolane column on firebrick at room temperature). 1,2-Butadiene (K and K Laboratories) was 75% pure, containing 17% 1-butene and 8% 2-butene (g.l.c. on a 15 ft. × 0.25 in. dimethylsulfolane column at room temperature). The 1,1-dimethylallene, 1,3-dimethylallene, and the 1,1,3-trimethylallene were prepared by a previously described method[27,28] and were of greater than 98% purity. Propyne (Matheson Co.) was free of allene (g.l.c. and infrared). 2,2'-Azobisisobutyronitrile (AIBN), m.p. 102–104° dec. was supplied by Matheson Coleman and Bell. Trimethyltin hydride was prepared by

adding trimethyltin chloride[29] to a solution of lithium aluminum hydride in bis(2-ethoxyethyl) ether and distilling the trimethyltin hydride in 87% yield, b.p. 60°, from the reaction mixture.

A Typical Trimethyltin Hydride–Allene Reaction.[30] To 4.41 g. (0.027 mole) of trimethyltin hydride was added 2.08 g. (0.052 mole) of allene along with 0.09 g. (5.4 × 10⁻⁴ mole) of AIBN in a glass ampoule. The ampoule was sealed at −78° and then heated in a bomb at 100° for 9 hr. The crude mixture was analyzed by g.l.c. on a 20-ft. 20% silicone nitrile column (G.E. XF 1150) on Chromosorb P (60–80 mesh), isothermally at 90°, flow rate 200 ml./min., revealing the presence of allyltrimethyltin (54.8%) and prop-2-enyltrimethyltin (45.2%). Distillation gave 3.14 g. of product, b.p. 123.5–124.5° (760 mm.) and 0.53 g., b.p. 38° (25 mm.). The total was 3.67 g. (67% yield based on trimethyltin hydride). The excess allene which was collected in a trap cooled by solid carbon dioxide–acetone showed no-methylacetylene (g.l.c. and infrared).

Trimethyltin Hydride–Propyne Reaction. To 5.88 g. (0.035 mole) of trimethyltin hydride was added 3.0 g. (0.075 mole) of methylacetylene in a glass ampoule along with 0.1 g. (7 × 10⁻⁴ mole) of AIBN. The sealed ampoule was heated in a bomb at 100° for 9 hr. The crude mixture was subjected to g.l.c. analysis on a 20 ft. × 3/8 in. 20% silicone nitrile column (isothermally at 90° with flow rate of 200 ml./min.) and showed the presence of prop-1-enyltrimethyltin (70.4%), *cis*-prop-1-enyltrimethyltin (29.0%), and prop-2-enyltrimethyltin (*ca.* 0.6%). The contents of the ampoule was distilled giving 3.0 g. (43%, b.p. 125–126° at 760 mm.) of product.

Reaction of cis-But-2-en-3-yltrimethyltin and Trifluoroacetic Acid. To 0.1337 g. (6.1 × 10⁻⁴ mole) of *cis*-but-2-en-3-yltrimethyltin in a flask equipped with a serum cap and a gas outlet connected to a trap immersed in a solid carbon dioxide–acetone bath was added, with a syringe, 0.06 g. (6.1 × 10⁻⁴ mole) of trifluoroacetic acid. The reaction was very exothermic; trimethyltin trifluoroacetate precipitated immediately. The gas was analyzed by g.l.c. (15-ft. dimethylsulfolane on Chromosorb P column, at room temperature) giving 94% of a component with the same retention time as *cis*-2-butene and 6% with the same retention time as *trans*-2-butene. The trimethyltin trifluoroacetate had m.p. 122–124° dec. undepressed when admixed with an authentic sample.[31]

(27) W. R. Moore and H. R. Ward, *J. Org. Chem.*, **25**, 2073 (1960).
(28) L. Skattebol, *Tetrahedron Letters*, 167 (1961).
(29) A gift from M & T Chemicals, Inc.
(30) This procedure, with the minor modifications indicated in Table II was used for the other additions of trimethyltin hydride to allenes.
(31) Prepared by O. R. Khan.