unstable 1-azido-2-naphthylamine began to decompose. The solution was quickly poured into ice water and made strongly basic with sodium hydroxide. The cold solution was extracted three times with benzene. The benzene solution was extracted several times with dilute hydrochloric acid. These acid extracts were immediately cooled by addition of ice and diazotized by addition of 0.53 g of sodium nitrite in water. The solution was filtered, and the filtrate was treated with an aqueous solution of sodium azide (0.50 g). After standing overnight, filtration gave 0.15 g of crude 1,2-diazidonaphthalene, mp 100–104°. Recrystallization from petroleum ether (bp 60–90°) raised the melting point to 108°.

***cis,cis*-1,4-Dicyano-1,3-butadienes and *cis*-2-Cyanocinnamylnitrile.** In order to minimize the possibility of explosive decomposition, all of the 1,2-diazides were decomposed in dilute solution. The following procedure is typical. 4-Methoxy-1,2-diazidobenzene (2.06 g, 0.0108 mole) was dissolved in 15 ml of decalin. This solution was added dropwise over a period of 1 hr to 25 ml of refluxing decalin. After standing overnight at room temperature, the crude solid was filtered and washed thoroughly with petroleum ether (bp 30–60°). Recrystallization (charcoal) from 50 ml of carbon tetrachloride gave 1.24 g of *cis,cis*-2-methoxy-1,4-dicyano-1,3-butadiene. An additional 0.07 g was obtained by concentration of the filtrate.

Preparation of the Isomeric 1,4-Dicyano-1,3-butadienes by Elimination. To a mixture of 300 ml of 95% ethanol, 20 ml of water, and 26.4 g (0.3 mole) of anhydrous sodium acetate was added 26.6 g (0.1 mole) of 2,3-dibromo-1,4-dicyanobutane. The mixture was refluxed for 23 hr. Ethanol was distilled out of the reaction mixture until the volume was reduced to 100 ml. Chilling of this solution in ice gave a precipitate which was filtered and washed with solid alcohol and then with water; yield 3.06 g (29%) of *trans,-trans*-1,4-dicyano-1,3-butadiene, mp 156–157° (lit.[5] mp 161–162°). The infrared spectrum indicated that this compound was free from the other two isomers.

The water-alcohol filtrates after removal of the *trans,trans* isomer were boiled until all of the alcohol had distilled. An oil separated which solidified on cooling. The solid was filtered and washed with water. This solid was dissolved in benzene and placed on an alumina (100 g of Fisher A-540) column. Elution of the column with 50 ml of benzene gave 0.19 g (1.8%) of *cis,cis*-1,4-dicyano-1,3-butadiene, mp 127–128°. Its infrared spectrum was identical with that prepared by decomposition of 1,2-diazidobenzene. Continued elution of the column with an additional 300 ml of benzene gave 3.28 g (33%) of crude *cis,trans*-1,4-dicyano-1,3-butadiene, mp 58–68°. After several recrystallizations from carbon tetrachloride, a pure product, mp 69–70° (lit.[5] 65–66°), was obtained.

Acknowledgment. I am indebted to Dr. Donald Moore, U. S. Naval Ordinance Test Station at China Lake, Calif., for the theoretical calculations of the nmr spectra of the isomeric 1,4-dicyano-1,3-butadienes.

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

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Abstract: The free radical catalyzed addition of trimethyltin hydride to 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, cyclopentadiene, 1,3-cyclohexadiene, 4-vinylcyclohexene-1, 1,3-cyclooctadiene, and 1,5-cyclooctadiene has been studied. Structures and configurations of all the adducts have been assigned on the basis of infrared and nmr spectroscopy, degradation, or comparison with authentic samples prepared by other methods. Information regarding direction of addition and stereochemistry thus obtained is discussed in terms of a probable mechanism and the roles which electronic and steric factors play in determining the course of the reactions.

The addition of electrophilic free radicals such as halogens and thiyl radicals to dienes has been studied extensively.[4] On the other hand, parallel studies involving radicals which might be nucleophilic have received little attention. While the work reported in this paper was in progress, Neumann and Sommer[5] reported on the addition of organotin hydrides to dienes. This reaction has been shown[6] to proceed by a free-radical mechanism with reactions 1 and 2 as the probable chain-carrying steps.[6,7] The organotin radical might be expected to display nucleophilic character.

$$\mathrm{Sn\cdot + RCH{=}CH_2 \longrightarrow R\dot{C}HCH_2Sn} \qquad (1)$$

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

We have examined the products of addition of trimethyltin hydride to six conjugated dienes and two un-

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(2) Taken in part from the Ph.D. dissertations of R. H. F. (1965) and I. J. T. (1967) submitted to the Graduate School of the University of New Hampshire, Durham, N. H.

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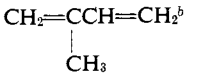
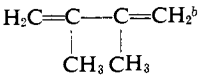
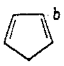
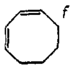
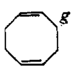
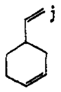
(4) (a) M. S. Kharasch, E. T. Margolis, and F. R. Mayo, *J. Org. Chem.*, 1, 393 (1936); (b) M. S. Kharasch, J. Kritchevsky, and F. R. Mayo, *ibid.*, 2, 489 (1937); (c) A. A. Oswald, K. Griesbaum, W. A. Thaler, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **84**, 3897 (1962), references therein; (d) J. A. Reeder, Ph.D. Thesis, University of Colorado, Boulder, Colo., 1958; (e) A. A. Oswald, B. E. Hudson, Jr., G. Rodgers, and F. Noel, *J. Org. Chem.*, 27, 2438 (1962); (f) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 1262 (1963); (g) A. A. Oswald, K. Griesbaum, and B. E. Hudson, Jr., *ibid.*, **28**, 2355 (1963); (h) M. S. Kharasch and M. Sage, *ibid.*, **14**, 537 (1949); (i) M. S. Kharasch, E. Simon, and W. Nudenberg, *ibid.*, **18**, 328 (1953); (j) M. S. Kharasch and H. N. Friedlander, *ibid.*, 14, 239 (1949); (k) C. S. H. Chen and R. F. Stamm, *ibid.*, **28**, 1580 (1963); (l) C. S. H. Chen and E. F. Hosterman, *ibid.*, **28**, 1585 (1963); (m) W. A. Thaler, A. A. Oswald, and B. E. Hudson, Jr., *J. Am. Chem. Soc.*, **87**, 311 (1965); (n) R. Dowbenko, *Tetrahedron*, 20, 1843 (1964); *J. Am. Chem. Soc.*, **86**, 946 (1964); (o) L. Friedman, *ibid.*, **86**, 1885 (1964); (p) G. Pregaglia and G. Gregorio, *Chim. Ind.* (Milan), **45**, 1065 (1963); *Chem. Abstr.*, **59**, 12658 (1963); (q) J. M. Locke and E. W. Duck, *Chem. Commun.*, 151 (1965).

(5) (a) W. P. Neumann and R. Sommer, *Angew. Chem.*, **76**, 52 (1964). (b) These authors kindly provided us with a prepublication copy of the manuscript of their full paper: *Ann.*, in press.

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

(7) H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 47 (1964).

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

Diene	Yield, %	Product distribution[a] Compd	Product distribution[a] %	Bp, °C (mm)	n_D (°C)	Calcd, % C	Calcd, % H	Found, % C	Found, % H	Prominent infrared bands, cm^{-1} [k]
CH_2=CHCH=CH_2[b]	60	**1**[c]	37.5	69–72 (25)						3010(m), 1650(m), 1430(s), 1185(m), 960(s), 765(s)
		2	7.1		1.4685 (25)	38.39	7.31	38.28	7.36	3075(m), 2975(s), 2925(s), 1649(s), 1450(m), 1185(s), 990(s), 910(s), 765(s)
		3[c]	55.4							3012(m), 1648(s), 1450(m), 1400(m), 1190(s), 770(s), 725(w)
 $CH_2{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}CH{=}CH_2$[b]	66	**4**	5.4	36–37.5 (2)		41.25	7.73	41.45	7.93	3075(m), 2950(s), 2920(s), 1638(m), 1450(m), 1360(m), 1185(m), 990(s), 910(s), 765(s)
		5	45.5		1.4766 (25)	41.25	7.73	41.53[l]	7.61[l]	3015(m), 2960(s), 2910(s), 1655(m), 1335(m), 1370(m), 1185(m), 960(m), 820(w), 760(s)
		6	5.5			41.25	7.73	41.53[l]	7.61[l]	885(m)
		7	43.6		1.4823 (25)	41.25	7.73	41.54	7.82	3015(w), 2960(s), 2915(s), 1655(m), 1450(m), 1375(m), 1190(m), 845(m), 765(s)
 $H_2C{=}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{-}\underset{\displaystyle CH_3}{\underset{\vert}{C}}{=}CH_2$[b]	66	**8**	23	46–48.5 (1.2)	1.4748 (25)	43.77	8.10	44.06	8.43	3065(m), 2950(s), 2910(s), 1645(m), 1450(m), 1370(m), 1185(m), 890(s), 765(s)
		9	77		1.4850 (25)	43.77	8.10	43.92	8.12	2975(s), 2905(s), 1650(w), 1440(m), 1365(m), 1185(s), 1150(s), 1100(m), 760(s)
 [b]	67	**10**	57	30 (0.3)	1.5031 (25)	41.61	6.94	41.85	7.14	3050(m), 2965(s), 1590(m), 1190(s), 900(s), 760(s), 710(w)
		11	43		1.4935 (25)	41.61	6.94	41.42	7.06	3040(m), 2960(s), 1610(m), 1185(m), 975(m), 890(m), 765(s), 670(s)
	58[d]	**10**	>89	36–38 (1.2)						
		11	⩽11							
	55	**12**[e]	66	30–30.5 (0.08)		44.11	7.35	44.30	7.33	3010(m), 2965(s), 1625(m), 1185(m), 880(m), 762(s)
		13[e]	34		1.5032 (25)	44.11	7.35	43.90	7.20	3017(m), 2975(s), 1655(m), 1440(s), 900(m), 870(m), 765(s), 700(w), 650(s)
 [f]	28	**14**	87.5	65 (0.5)	1.5172 (25)	48.36	8.12	48.38	8.30	3034(w), 3000(s), 1630(m), 1450(m), 1185(m), 835(w), 780(s), 765(s), 705(m)
		15	12.5		1.5125 (25)	48.36	8.12	48.38	8.28	3050(w), 3005(m), 2850(s), 1625(w), 1450(m), 1185(m), 910(w)
 [g]	36	**16**	29.4	51 (0.25)	1.5028 (26)	48.36	8.12	48.48	8.07	3000(w), 2936(s), 2858(s), 1440(m), 1185(m), 920(w), 805(w), 760(s), 700(m)
		17	5.9							3000(w), 2974(m), 2936(s), 2858(s), 1440(m), 1190(w), 1185(m), 1050(w), 965(w), 850(w), 762(s), 705(m)
		18	64.7		1.5127 (24.5)	48.36	8.12	48.17	7.96	3010(m), 2970(m), 2845(s), 1640(w), 1440(m), 1185(m), 880, 762(s), 720(s)
	38[h]	**16**	44.4							
		17	11.1							
		18	44.4							
	50[i]	**16**	⩽3							
		17								
		18	⩾97							
 [j]	40	**19**	100	70 (0.85)	1.5000 (23)	48.36	8.12	48.12	7.93	3013(s), 3000(s), 1650, 1450(m), 800(m), 762(s), 712(s)

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[a] All products were separated on a 20 ft × 3/8 in. silicone nitrile (GE XF1150) column on Chromosorb P (60–80 mesh). [b] Twofold excess diene at 100° for 10–13 hr with AIBN catalysis (2 mole %). [c] See ref 8. [d] 1:1 diene to hydride at 175° for 7 hr without AIBN catalysis. [e] Based on trimethyltin proton peak areas in nmr spectrum. [f] 100% excess diene at 80° with 18 mole % AIBN or photochemically (36°) for 34 hr (see Experimental Section for description of photolysis experiment). [g] 100% excess diene at 80° with 14 mole % AIBN. [h] 100% excess diene at 175° for 12 hr without AIBN catalysis. [i] Photochemically at 36° for 34 hr (see Experimental Section). [j] 100% excess diene at 80° for 8 hr with 6 mole % AIBN or photochemically for 34 hr at 36° (68% yield). [k] Neat liquids. [l] Mixture of **5** and **6**.

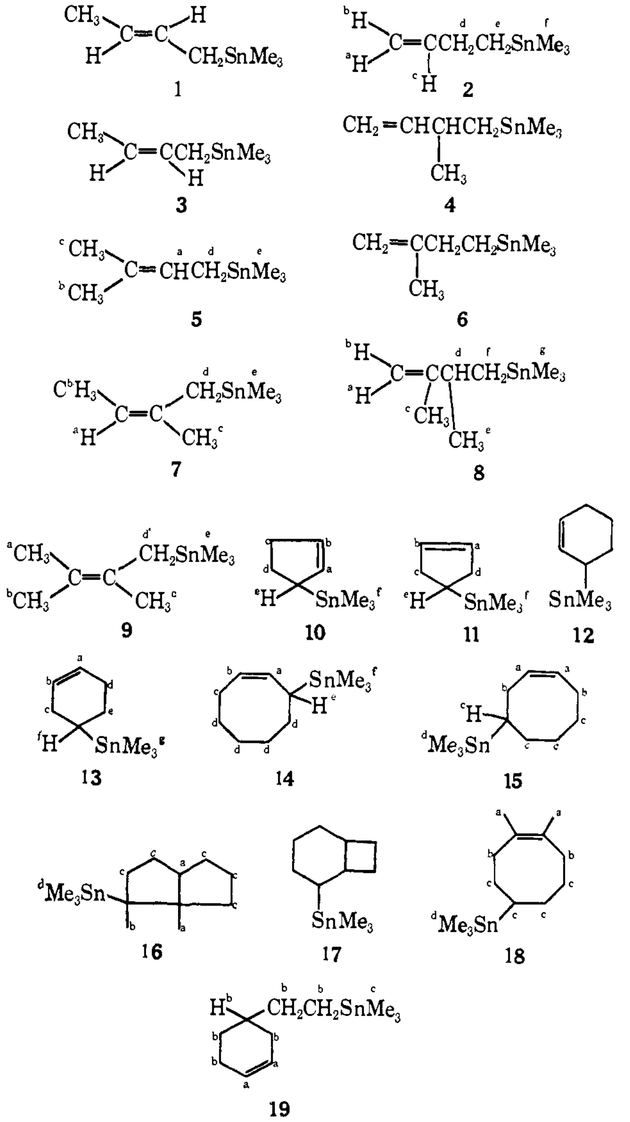
Table II. Nmr Spectral Data on Trimethyltin Hydride–Diene Adducts[a,b]

Adducts	Concn in CCl₄, %	Proton a	b	c	d	e	f	g	J_{a-b}	J_{a-c}	J_{b-c}	J_{c-b}	J_{c-d}	J_{e-d}	J_{d-f}	J_{a-d}
2	Neat	5.10(m)	5.14(m)	4.3(m)	7.80(4)	9.12(3)	9.95(1)		1.5	6.0		10.5	7.5	7.5		
5[c]	Neat	4.68(3)	831(m)	8.31(m)	8.31(m)	9.90(1)										9.0
7	50	5.07(4)	8.22–8.75(m)			9.90(1)			6.5							
8	30	5.42(m)	5.47(m)	8.31(2)	7.61(6)	8.95(2)	8.99(2)	9.95(1)	1.0	0.5	0.5				7.0	
9	50	8.42(1)	8.35(1)	8.42(1)	8.28(1)	9.93(1)										
10	Neat	4.35(m)	4.35(m)	7.80(m)	7.80(m)	7.80(m)	9.95(1)									
11	Neat	4.35(m)	4.35(m)	7.75(m)	7.75(m)	7.75(m)	9.97(1)									
13	35	4.47(m)	4.47(m)	~7.9(m)	~7.9(m)	~8.1(m)	~8.1(m)	9.99(1)								
14	25	4.25–4.75(m)		~7.75(m)	~8.2(m)	~8.4(m)	9.97(1)									
15	30	~4.5(m)	~7.7(m)	~8.5(m)	9.97(1)											
16	50	~7.7(m)	7.95(m)	~8.5(m)	10.00(1)											
18	30	4.39(5)	7.9(m)	~8.4(m)	10.00(1)											
19	Neat	4.46(m)	7.88–9.38(m)	10.00(1)												

[a] See Chart I for structure and proton designation. [b] Valves in τ units measured to the center of each multiplet; J valves in cycles per second or width of multiplet given. [c] Contaminated with compound **6**.

conjugated dienes in order to ascertain the pattern of addition with respect to both direction of addition and stereochemistry of products as functions of diene structure.

Chart I



Results

The addition reactions, initiated by heat, by azobis(isobutyronitrile), or by light from a medium-pressure mercury vapor lamp, were carried out under a variety of conditions. Products were first analyzed by gas–liquid partition chromatography (glpc) to determine relative amounts of isomeric adducts, and total yields of adducts were then determined by isolation.

Individual adducts were separated by glpc when possible, subjected to elemental analysis, and assigned structures on the basis of infrared and nuclear magnetic resonance (nmr) spectra. In several cases, structures were assigned after comparison of properties with authentic amples. The structures of all the products are given in Chart I. Yields, product distributions, analytical data, and characteristic infrared bands are given in Table I. Nmr data, including chemical shifts in τ units, coupling constants in cycles per second, and assignments, are given in Table II.

1,3-Butadiene. The azobis(isobutyronitrile) (AIBN) catalyzed addition of trimethyltin hydride to 1,3-butadiene provided, in 60% yield, a mixture containing 37.5% of *trans*-crotyltrimethyltin (**1**), 7.1% of allylcarbinyltrimethyltin (**2**), and 55.4% of *cis*-crotyltrimethyltin (**3**). Compounds **1** and **2** could not be separated by glpc, but the proportion of **1** could be determined by ultraviolet absorption spectroscopy using the molar extinction coefficient of **1** at 225 mμ previously determined by Verdone.[8] It is well documented that allylic organometallics react much more rapidly with electrophilic reagents than do simple alkyl derivatives.[9] This fact was exploited to obtain pure **2**: treatment of the product mixture with trifluoroacetic acid destroyed **1** and **3**, leaving **2** which could then be isolated.

Compounds **1** and **3** were identified by comparison with known samples prepared by Verdone,[8] and **2** was characterized by its infrared and nmr spectra as well as

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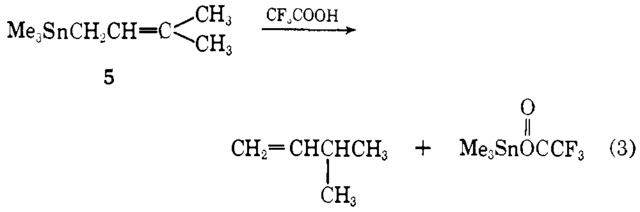
(8) J. A. Verdone, Ph.D. Dissertation, University of New Hampshire, Durham, N. H., 1963, p 46.

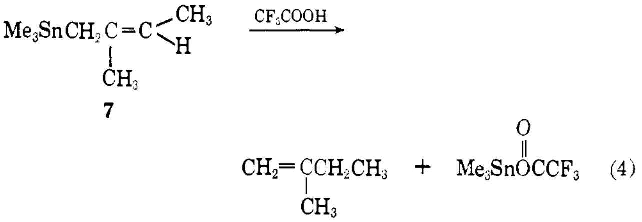
(9) (a) L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948); (b) D. Grafstein, *ibid.*, **77**, 6650 (1955); (c) S. D. Rosenberg, E. Debreczeni, and E. I. Weinberg, *ibid.*, **81**, 972 (1959); (d) P. D. Sleezer, S. Winstein, and W. G. Young, *ibid.*, **85**, 1890 (1963); (e) H. G. Kuivila and J. A. Verdone, *Tetrahedron Letters*, 119 (1964); (f) A. D. Petrov and V. F. Mironov, *Angew. Chem.*, **73**, 59 (1961).

by independent synthesis (by the reaction of allylcarbinylmagnesium bromide with trimethyltin chloride).

2-Methyl-1,3-butadiene. The mixture obtained in 65% yield using AIBN catalysis contained four components to which structures were assigned as follows. 2-Methylbut-3-en-1-yltrimethyltin (**4**) (5.4%) showed the strong bands at 990 and 910 cm^{-1} characteristic of a terminal vinyl group. 3-Methylbut-2-en-1-yltrimethyltin (**5**) (45.5%) was partially separated by glpc from 3-methylbut-3-en-1-yltrimethyltin (**6**) (5.5%) and was assigned this structure because of an infrared band at 885 cm^{-1}, characteristic of a terminal methylene group. An nmr spectrum of a mixture of **5** and **6** contained a multiplet at τ 5.30 which is attributed to the terminal methylene protons of **6**. Compound **5** had an infrared band at 845 cm^{-1} characteristic of a trisubstituted ethylene. The nmr spectrum of **5** showed a vinyl proton triplet at τ 4.86 (J_{a-d} = 9.0 cps); a multiplet at τ 8.41 was attributed to the protons of the two remaining methyl groups and the methylene group, and the sharp singlet at τ 9.90 was attributed to the protons of the trimethyltin group. 2-Methylbut-2-en-1-yltrimethyltin (**7**) (43.6%) was identified by infrared bands at 3015 and 820 cm^{-1} characteristic of a trisubstituted double bond. (The configuration shown is not necessarily correct.) Its mnr spectrum contained a vinyl proton quartet at τ 5.07 ($J_{a,b}$ = 6.5 cps); a multiplet at τ 8.42 was assigned to the remaining two methyl and the methylene protons; the singlet at τ 9.90 was due to the protons of the trimethyltin group. In order to provide further substantiation of the structure of **5** and **7**, trifluoroacetic acid was added to the mixture of products. If an SE2′ mechanism[9e] is assumed, the 4,1 addition product **5** would give 3-methyl-1-butene, and **7** would give 2-methylbut-1-ene (eq 3 and 4). The results of the cleavage reaction were not quantitative since 2-methylbut-1-ene was found to react with trifluoroacetic acid. Both 3-methylbut-1-ene (94.5%) and 2-methylbut-1-ene (5.5%) were identified by comparison of their retention times (glpc) with authentic samples and by an infrared spectrum which was consistent with 3-methylbut-1-ene being the predominant product.



$$\underset{\textbf{5}}{Me_3SnCH_2CH{=}C(CH_3)_2} \xrightarrow{CF_3COOH} CH_2{=}CHCH(CH_3)CH_3 + Me_3SnOC(=O)CF_3 \quad (3)$$



$$\underset{\textbf{7}}{Me_3SnCH_2C(CH_3){=}CHCH_3} \xrightarrow{CF_3COOH} CH_2{=}C(CH_3)CH_2CH_3 + Me_3SnOC(=O)CF_3 \quad (4)$$

2,3-Dimethyl-1,3-butadiene. The product obtained in 66% yield with AIBN catalysis was a mixture of two components of which 23% was 2,3-dimethylbut-3-en-1-yltrimethyltin (**8**) and 77% was 2,3-dimethylbut-2-en-1-yltrimethyltin (**9**). Compound **8** had infrared bands at 3065 and 890 cm^{-1} characteristic of a terminal methylene group. Its nmr spectrum revealed multiplets at τ 5.42 and 5.47 ($J_{a,b}$ = 1.0 cps) assigned to the terminal methylene protons. A methyl doublet τ 8.95 and a methylene doublet τ 8.99 were coupled with a tertiary proton τ 7.61 split into a sextet (J = 7.0 cps). The trimethyltin group proton signal appeared at τ 9.93. Compound **9** produced singlets at τ 8.42 (six protons), τ 8.35 (three protons), τ 8.23 (two protons), and τ 9.93 (nine protons) as expected from the assigned structure.

Cyclopentadiene. The mixture which formed at 100° in 67% yield (AIBN catalysis) comprised 57% of cyclopent-2-en-1-yltrimethyltin (**10**) and 43% of cyclopent-3-en-1-yltrimethyltin (**11**). Compound **10** was identified by its infrared spectrum which showed a double bond stretching band at 1590 cm^{-1}, and its nmr spectrum, which showed multiplets at τ 4.35 (two protons), τ 7.80 (five protons), and τ 9.95 (nine protons). Upon treatment of a mixture of **10** and **11** with trifluoroacetic acid **10** was completely destroyed. Compound **21** was prepared independently (eq 5) and had infrared spectrum, nmr spectrum, and glpc retention times identical with those of the product isolated (glpc) from the trifluoroacetic acid reaction. It is of interest that at 175° the uncatalyzed reaction produced **10** in greater than 89% yield. When a mixture of **10** and **11** (57:43) was heated at 175° with and without a catalytic amount of trimethyltin hydride, no appreciable change in the ratio of the two isomers occurred. Thus it is established that isomerization of **11** to **10** does not take place at 175°.

(5)

11

1,3-Cyclohexadiene. This diene provided a 54.5% yield (AIBN catalysis) of a mixture we could not separate by glpc. The nmr spectrum, however, indicated two trimethyltin singlets at τ 9.91 and 9.96 with areas in the ratio 66:34. A mixture of **12** and **13** was subjected to trifluoroacetic acid cleavage and then examined by nmr spectroscopy. The trimethyltin proton singlet at τ 9.91 disappeared and this was assigned to **12**. Compound **13** was collected by preparative glpc and had infrared and nmr spectra that were identical with those of **13** prepared by independent synthesis.

1,3-Cyclooctadiene. The products from AIBN and photochemically initiated addition, obtained in 26% yield, were cyclooct-2-en-1-yltrimethyltin (**14**) and cyclooct-3-en-1-yltrimethyltin (**15**) in the ratio 87.5:12.5. Compound **14** had infrared bands at 1630 cm^{-1} due to the double bond stretching frequency, and the nmr spectrum had vinyl hydrogen multiplets around τ 4.5 and a signal at τ 7.75 which was assigned to the allylic methylene protons. The proton on the carbon bearing the trimethyltin group was credited with producing a singlet at τ 8.4; the remaining ring methylene and trimethyltin group protons produced a broad singlet at τ 9.97. This compound had infrared and nmr spectra and retention time identical with those of the known compound prepared by an independent method. Further proof was the fact that **14** was destroyed when a mixture of **14** and **15** was treated with trifluoroacetic acid.

1,5-Cyclooctadiene. Three products formed in different ratios depending upon the reaction conditions.

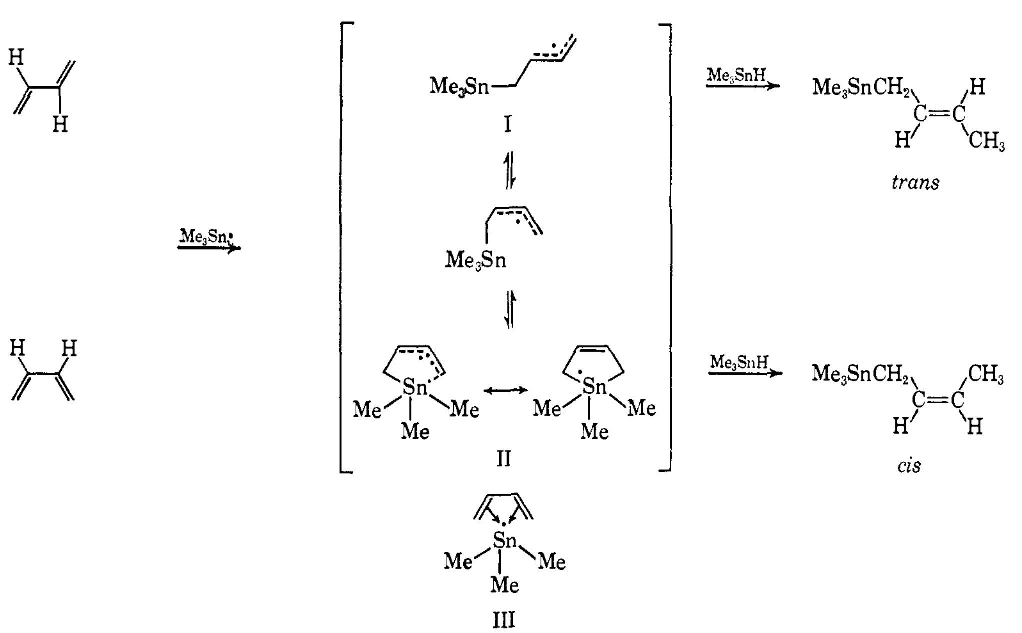


Figure 1. Possible intermediates in the trimethyltin hydride–1,3-butadiene reaction.

The AIBN-catalyzed reaction at 100° gave a 36% yield of bicyclo[3.3.0]oct-2-yltrimethyltin (**16**), bicyclo[4.2.0]-oct-2-yltrimethyltin (**17**), and cyclooct-4-en-1-yltrimethyltin (**18**), in the ratio 29.4:5.9:64.7. At 175°, without AIBN, **16**, **17**, and **18** were formed in the ratio 44.4:11.1:44.4 and an over-all yield of 38%. Under the influence of ultraviolet light, the product **18** formed in 50% yield while only traces of **16** and **17** could be detected by glpc.

The structure of **16** was assigned on the basis of its nmr spectrum which showed the two bridgehead protons as a multiplet, τ 7.7; a sharp singlet at τ 7.95 was assigned to the single proton on the carbon bearing the trimethyltin group. The remaining methylene protons were assigned to the broad signal centered at τ 8.5 and the sharp singlet at τ 10.0 to the nine trimethyltin protons. These assignments are consistent with the nmr spectra of the parent hydrocarbon bicyclo[3.3.0]-octane[10] and *exo,cis*-N-*t*-butylbicyclo[3.3.0]octane-2-carboxamide.[4n]

Compound **17** had an infrared spectrum which showed no unsaturation. Unfortunately, attempts to prepare **17** by an independent method were unsuccessful and enough sample for an nmr spectrum was not obtained. We tentatively take it to be the other bicyclic isomer **17**. Compound **18** had an nmr spectrum with the olefinic protons producing a pentuplet τ 4.39, the methylene and methine and the allylic protons were credited for the multiplets at τ 8.4 and 7.9, respectively, and the trimethyltin group for a singlet at τ 10.0. The nmr spectrum of **18** is consistent with those of several cyclooctenes that have been reported.[4q,11] It was found that no isomerization of **16** and **17** occurred when photolyzed for 77 hr whether or not a catalytic amount of trimethyltin hydride was present.

4-Vinylcyclohexene. The only product from the reaction of this diene, initiated by AIBN or photochemically, was 2-(cyclohex-3-en-1-yl)ethyltrimethyltin (**19**). This was assigned on the basis of the infrared spectrum which showed no bands at 3087, 995, or 913 cm^{-1} indicative of a terminal vinyl group. The nmr spectrum was also consistent with **19**.

Discussion

It has been shown that addition of trimethyltin radicals to *cis*- and *trans*-2-butenes and to *cis*- and *trans*-1-deuterio-1-hexenes is highly reversible.[12] On the other hand, addition of these radicals to *cis*- and *trans*-1-deuteriostyrene[12] and to *cis*- and *trans*-piperylenes[13] is only partially reversible. Thus, it may be concluded that the point of attachment of the trimethyltin group on the dienes with isolated double bonds will be thermodynamically controlled. With the conjugated dienes kinetic control may be the major determinant. All that is known about organotin hydrides indicates that step 2 is irreversible: it must be highly exothermic because the tin–hydrogen bond is much weaker than the carbon–hydrogen bond (this is attested by the very high efficiency with which organotin hydrides function as hydrogen-transfer agents); although the 2-butenes undergo addition of trimethyltin hydride and isomerization into a mixture containing 75% *trans* and 25% *cis*, there is no indication of the formation of 1-butene; there is no evidence for reversibility of the over-all reaction; indeed, when tetraisobutyltin is heated at 300° in an atmosphere of hydrogen 79% of the isobutyl groups appear as isobutane and only 9% as isobutylene.[14]

The addition of trimethyltin hydride to 1,3-butadiene gave a predominance of 1,4 addition along with 7.1% of 1,2 addition. The predominance of the *cis* product in the 1,4 addition is unusual because free-radical addition to this diene usually gives predominantly *trans* products.[4c-g] A scheme which accounts for these results is shown in Figure 1. Its major feature is the formation of the bridged radical II in which a d orbital of the tin atom serves to delocalize the odd electron while two others form bonds with the carbons at the ends of the four-carbon chain. II may form from open-chain radicals as shown in the brackets or *via* the π complex III in-

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[10] Kindly supplied by Professor L. Friedman.

[11] K. B. Wiberg and J. Nist, *J. Am. Chem. Soc.*, **83**, 1226 (1961).

[12] H. G. Kuivila and R. Sommer, *ibid.*, **89**, 5616 (1967).

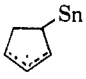
[13] W. P. Neuman, H. J. Albert, and W. Kaiser, *Tetrahedron Letters*, 2041 (1967).

[14] L. L. Gershbein and V. N. Ipatieff, *J. Am. Chem. Soc.*, **74**, 1541 (1952).

volving the butadiene serving as a bidentate ligand on the organotin radical. The addition of trichlorosilane,[15] trimethylgermane,[16] and trimethyltin hydride to norbornadiene[17] and of trimethylgermane to butadiene[16] also yields products whose structure or stereochemistry can be rationalized by assuming formation of precursive bridged intermediates.

Isoprene also gave only products resulting from attack by the trimethyltin radical on the terminal carbons: 51% at C-4 and 49% at C-1. These results can be easily, but not profitably, explained in terms of steric (preferred attack at C-4) and electronic (preferred attack at C-4 by a nucleophilic free radical) effects, and relative stabilities of the intermediate allylic radical (preferred attack at C-1 due to formation of a tertiary–primary *vs.* a secondary–primary allylic radical from attack at C-4).

Cyclopentadiene yielded more of the allylic isomer at 175° (89%) than at 100° (57%). It was shown that this is not due to isomerization of **11** to **10**. These results may be attributed to the partitioning of initial attack by the trimethyltin radical as a function of temperature. More of the allylic radical **20** is formed at 100° than at 175°. It can provide either **10** or **11** in the product-forming step. The isomeric radical **21**, which should appear in greater amount at the higher temperature, provides *only* **10** in the product-forming step. Thus, if attack by the organotin radical on the diene (eq 1) has a higher activation energy than the subsequent hydrogen abstraction (eq 2), as would be expected, the observed change in product distribution is to be expected.



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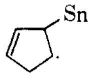

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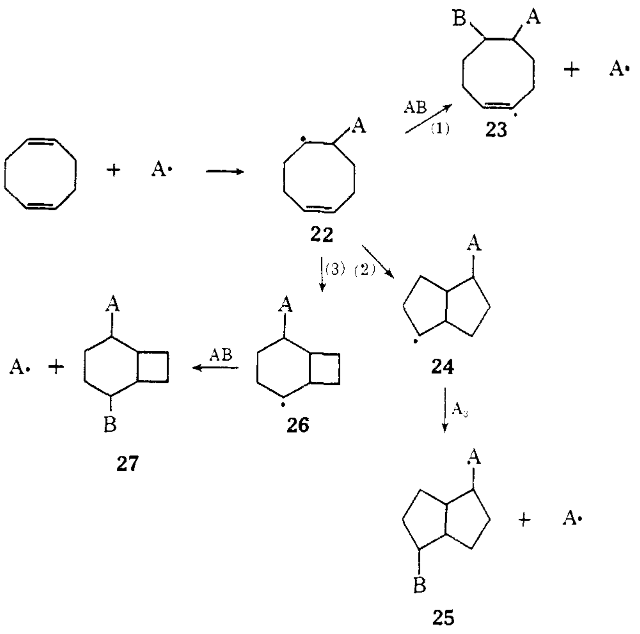
Both 1,3-cyclohexadiene and 1,3-cyclooctadiene show a strong tendency toward 1,4 or (less probably) 2,1 addition, the product mixtures containing 66% **12** and 87.5% **14**, respectively. Neither cyclohexene nor cyclooctene adds trimethyltin hydride under the conditions of these experiments. Thus, it appears that the reactivity of these dienes is a consequence of the double bonds not being coplanar[18,19] and of the stability of the intermediate allylic radicals.

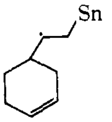
1,5-Cyclooctadiene gave results which are of particular interest in light of recent reports on the free-radical additions to this diene.[4n–q] The first reports described addends such as acetic acid,[4p] dimethylformamide,[4n] carbon tetrachloride,[4n] acetaldehyde,[4o] and diethyl phosphonate,[4o] among others. The uniform conclusion was that free-radical additions to this substrate lead to bicyclo[3.3.0]octane derivatives. However, Locke and Duck[4q] observed that addition of thiolacetic acid, thiolbenzoic acid, and benzenethiol yielded only the simple 1,2 adducts. They suggested that the results could be rationalized by the following reaction scheme.



Initial attack forms the simple cyclooctenyl radical **22**. In the presence of a poor B donor, step 2 occurs, and the product is **25**. If a good B donor such as a thiol is present step 1 occurs more rapidly than 2 and the simple adduct **23** is formed. Our results provide convincing confirmation of this interpretation. At low temperatures, step 1 occurs virtually exclusively yielding more than 97% **18**. As the temperature is raised, the rate of step 2, having a higher activation energy, increases faster than that of step 1 with the result that at 175° **16** and **18** are formed in equal amounts. At this temperature, there was formed 11% of a third product whose structure was not established, but which is believed to be **17**. Formation of bicyclo[4.2.0]octanes has not been reported previously.

The bond dissociation of the S–H bond in hydrogen sulfide is about 90 kcal/mole; that for the Sn–H bond is certainly considerably less. Nonetheless, the thiols used by Locke and Duck appear to be at least as good hydrogen donors as trimethyltin hydride. They used thiolacetic acid, thiolbenzoic acid, and benzenethiol. The S–H bond dissociation energies in these compounds are undoubtedly less than those in simple thiols and hydrogen sulfide due to resonance stabilization of the thioacyl and benzenethiyl radicals. This is borne out by the very high chain-transfer constant of benzenethiol compared with that for *n*-dodecylmercaptan, for example.[20] Apparently, this factor is substantial enough to make these thiols as good hydrogen donors as trimethyltin hydride.

The product (**19**) obtained with 4-vinylcyclohexene is that expected if steric effects and intermediate radical stability are important in determining the course of reaction. Of interest in this case is the absence of any bicyclic product which might form *via* intramolecular addition of the initial radical **28** to form either **29** or **30**.



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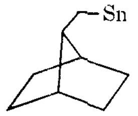

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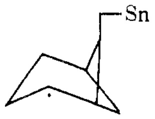

30

Neumann and Sommer[5] examined the direction, but not stereochemistry, of addition of triethyltin hydride, among others, to three of the dienes used in our investi-

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(15) H. G. Kuivila and C. R. Warner, *J. Org. Chem.*, **29**, 2845 (1964).

(16) R. H. Fish and H. G. Kuivila, *ibid.*, 31, 2445 (1966).

(17) O. R. Khan, I. J. Tyminski, and F. L. Pelczar, unpublished observations.

(18) A. W. Burgstahler, H. Ziffer, and U. Weiss, *J. Am. Chem. Soc.*, **83**, 4661 (1961); A. Moscowitz, E. Charnery, U. Weiss, and H. Ziffer, *ibid.*, **83**, 4660 (1961).

(19) C. Y. Chen, R. J. Lefevre, and K. M. S. Sunderam, *J. Chem. Soc.*, 553 (1965).

(20) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 319.

gation: 1,3-butadiene, isoprene, and 1,3-cyclopentadiene. Their reactions were carried out at 70° and are not strictly comparable with ours which were carried out at 100°. However, it is worth pointing out that we find more 1,4 addition with 1,3-butadiene and isoprene than was observed with triethyltin hydride, whereas the reverse is true with 1,3-cyclopentadiene.

Experimental Section

Boiling points are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer with sodium chloride optics. The nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument with tetramethylsilane as an internal standard.

Materials. 1,3-Butadiene (Matheson Co.) was used directly from the cylinder. 2-Methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene (Matheson Coleman and Bell) were distilled before use. 1,3-Cyclohexadiene (Aldrich Chemical Co.) was checked for purity (glpc) on a 4-ft, 17% silicone nitrile column and used without further purification. 4-Vinylcyclohexene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene (a gift from Cities Service Research and Development Company) were distilled before use. Dicyclopentadiene (Distillation Products, Inc.) was cracked to give cyclopentadiene. 2,2-Azobis(isobutyronitrile) (AIBN), mp 102–104° dec, was supplied by Matheson Coleman and Bell.

Preparation of Trimethyltin Hydride. In a three-necked flask equipped with a dropping funnel, stirrer, and distilling head was placed 10.5 g (0.282 mole) of lithium aluminum hydride suspended in 300 ml of bis(2-ethoxyethyl) ether. To this solution was added, over a 2-hr period, 112.3 g (0.565 mole) of trimethyltin chloride[21] dissolved in 100 ml of bis(2-ethoxyethyl) ether. The flask was heated with an oil bath so that distillation of trimethyltin hydride occurred simultaneously with addition of trimethyltin chloride. The trimethyltin hydride obtained was redistilled, 80.32 g (87%), bp 60° (760 mm), and stored in sealed glass ampoules under nitrogen.

Hydrostannations. Typical Procedures. To 8.2 g (0.050 mole) of trimethyltin hydride was added 5.4 g (0.10 mole) of 1,3-butadiene along with 0.18 g (1×10^{-3} mole) of AIBN in a glass ampoule. The ampoule was sealed at −78° and then heated in a bomb at 100° for 13 hr. The crude mixture was analyzed by glpc on a 20 ft × $^{3}/_{8}$ in., 20% silicone nitrile column (GE XF 1150) on Chromosorb P (60–80 mesh), isothermally at 125°, flow rate 200 cc/min, revealing the presence of *cis*-crotyltrimethyltin (55.4%, **3**) and *trans*-crotyltrimethyltin (4.6%, **1**) which was found to contain 7.1% allylcarbinyltrimethyltin (**2**). Distillation gave 6.56 g of product, bp 69–72° (25 mm) (60% yield based on trimethyltin hydride).

Additions to isoprene, 2,3-dimethylbutadiene, 1,3-cyclopentadiene, and 1,3-cyclohexadiene were carried out by the same procedure.

The other three dienes reacted more sluggishly at 80°. Hence, 2 mole % increments of AIBN were added to the reaction mixture at 3-hr intervals. Minimum amounts in mole per cent required to consume all of the trimethyltin hydride as determined by disappearance of an infrared absorption band at 1838 cm^{-1} (olefin in 100% excess) were 6 for 4-vinylcyclohexene, 17 for 1,3-cyclooctadiene, and 11 for 1,5-cyclooctadiene. The precipitate which appeared upon cooling of the reaction product mixture was filtered off before distillation.

Uncatalyzed hydrostannations were carried out under argon using an excess of the olefin in sealed tubes. Pyrex tubes were used for the photochemical reactions which were initiated by irradiation from a 400-w, high-pressure mercury vapor lamp.

Characterization of Adducts. Reaction of the 1,3-Butadiene Adducts with Trifluoroacetic Acid. Into a flask fitted with a side arm which was sealed with a serum cap were transferred 1.78 g (8.15 mmoles) of the product mixture and 2 ml of pentane. To this was added with stirring from a syringe 0.872 g (7.65 mmoles) of trifluoroacetic acid over about 5 min. Immediate precipitation of trimethyltin trifluoroacetate occurred. Water was then added to dissolve the trimethyltin trifluoroacetate. The pentane layer was separated, dried over magnesium sulfate, and distilled to give 0.35 g of a liquid which was analyzed by glpc (4 ft × 0.25 in. column of 17% silicone nitrile on Chromosorb P isothermally at 100°) showing the presence of pentane and another component. The latter was collected, and its infrared spectrum was found to be superimposable on that of an authentic sample of 1-butene.

Preparation of Allylcarbinyltrimethyltin (2). To a 100-ml flask equipped with condenser, dropping funnel, and stirrer was added 50 ml of ether and 0.96 g (39.6 g-atoms) of magnesium turnings followed by 5.35 g (39.6 mmoles) of allylcarbinyl bromide.[22] The reaction proceeded smoothly, and addition was complete in 30 min. To the Grignard reagent was added 10 g (0.05 mole) of trimethyltin chloride in 25 ml of ether. Addition was complete in 15 min, and the mixture was stirred overnight at reflux. The mixture was hydrolyzed with a saturated ammonium chloride solution, then dried over magnesium sulfate. Distillation gave 3.0 g (35%) of product, bp 48–50° (15 mm). Glpc analysis on a 4-ft column of 17% silicone nitrile on Chromosorb P isothermally at 100° gave one peak having the same retention time as the mixture of **1** and **2**.

Reaction of the Isoprene–Trimethyltin Hydride Adducts with Trifluoroacetic Acid. In a flask equipped with a serum cap and gas outlet connected to a trap immersed in Dry Ice–acetone was placed 1.33 g (5.72 mmoles) of isoprene–trimethyltin hydride adduct mixture (compounds **4**, **5**, **6**, and **7**). The flask was cooled in an ice bath and 0.65 g (5.5 mmoles) of trifluoroacetic acid was added from a syringe. The flask was heated to 60° and the product collected in the trap. Glpc analysis (20 ft × $^{3}/_{8}$ in., 20% silicone nitrile on Chromosorb P at room temperature) of the contents in the trap showed two products, 3-methyl-1-butene (94.5%) and 2-methyl-1-butene (5.5%). (In a separate experiment, 2-methyl-1-butene was found to react with trifluoroacetic acid.) The 3-methyl-1-butene and 2-methyl-1-butene were identified by comparing glpc retention times with known samples and, in the former case, by its infrared spectrum which was superimposable on that of authentic 3-methyl-1-butene.

In another experiment, 2.9 g (12.5 mmoles) of adduct dissolved in pentane was allowed to react with 1.36 g (11.9 mmoles) of trifluoroacetic acid. After water was added to dissolve the trimethyltin trifluoroacetate, the pentane layer was separated and analyzed by glpc (4-ft column of 17% silicone nitrile on Chromosorb P isothermal at 100°) showing two peaks. The first peak was the 1,2 adduct **4** (5.4%) and the second was assumed to be the 4,3 adduct **6** (5.5%), shown to be present in the nmr spectrum of **5**.

Reaction of the Cyclopentadiene–Trimethyltin Hydride Adducts with Trifluoroacetic Acid. Into a 25-ml flask equipped with a side arm containing a septum, magnetic stirring bar, and a drying tube was placed 0.74 g (3.2 mmoles) of a mixture of **10** and **11** dissolved in 2 ml of pentane. To this solution was added dropwise from a syringe 0.218 g (1.9 mmoles) of trifluoroacetic acid over 5 min; water was added to dissolve the trimethyltin trifluoroacetate, and the pentane layer was separated and dried over magnesium sulfate.

Pentane was distilled off and the remaining liquid was analyzed by glpc (20 ft × $^{3}/_{8}$ in., 20% silicone nitrile column, isothermally at 140°) showing one peak. The product was collected and had an infrared spectrum superimposable on that of cyclopent-3-en-1-yltrimethyltin (**11**) whose preparation is described below.

Preparation of Cyclopent-3-en-1-yltrimethyltin (11). To 0.98 g (40.6 g-atoms) of magnesium in 50 ml of anhydrous ether was added with stirring 5.68 g (39 mmoles) of 4-bromocyclopentene[23] dissolved in 25 ml of ether over 45 min. To the Grignard reagent was added 8.15 g (41 mmoles) of trimethyltin chloride dissolved in 25 ml of ether over 25 min. The mixture was heated under reflux 8 hr and then hydrolyzed with a saturated ammonium chloride solution. The ethereal layer was separated and washed five times with water and then dried over magnesium sulfate. Distillation gave 2.53 g, 27.8%, bp 35–37° (1.2 mm), of product. Glpc analysis on a 4-ft, 17% silicone nitrile column, isothermally at 100°, showed only one product whose infrared and nmr spectra were identical with those of **11**.

Attempted Isomerization of Cyclopent-3-en-1-yltrimethyltin (11). Sealed tubes containing, respectively, **11** alone, **11** plus 2 mole % of trimethyltin hydride, and a mixture containing 57% of **10** and 43% of **11** were heated for 6 hr at 175° and then analyzed by glpc using the 20 ft × $^{3}/_{8}$ in. silicone nitrile column. In no case was there any change in the composition of the cyclopentenyltin derivative.

Reaction of the 1,3-Cyclohexadiene–Trimethyltin Hydride Adducts with Trifluoroacetic Acid. To a 25-ml flask with a side arm containing a septum and a magnetic stirrer was added 0.54 g (2.2 mmoles) of a mixture containing 66% **12** and 34% **13** in 2 ml of carbon tetrachloride. To this stirring mixture was added by a syringe 0.171 g (1.54 mmoles) of trifluoroacetic acid. Water was then added and the carbon tetrachloride layer was separated and

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(21) A gift from M & T Chemicals, Inc., Rahway, N. J.

(22) J. D. Roberts and R. Mazur, *J. Am. Chem. Soc.*, 73, 2507 (1951).

(23) P. D. Bartlett and M. R. Rice, *J. Org. Chem.*, 28, 3351 (1963).

dried over magnesium sulfate. Preparative glpc (20 ft × $^{3}/_{8}$ in., 20% silicone nitrile on Chromosorb P, 60–80 mesh; isothermal at 150°) was used to collect the remaining product. Its infrared and nmr spectra were superimposable on those of an authentic sample of **13** prepared by an independent synthesis described below.

Preparation of Cyclohex-3-en-1-yltrimethyltin (13). To 0.43 g (17 g-atoms) of magnesium turnings in 50 ml of anhydrous ether was added, dropwise, over a period of 5 min, 2.8 g (17 mmoles) of 4-bromocyclohexene-1[24] dissolved in 10 ml of ether. The solution was stirred for 0.5 hr, and then 3.4 g (17 mmoles) of trimethyltin chloride was added over a 10-min period. The mixture was refluxed for 8 hr and then hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated, washed five times with water, and dried over magnesium sulfate. The ether was removed on a rotary evaporator and the product purified by preparative glpc (20 ft × $^{3}/_{8}$ in., 20% silicone nitrile on Chromosorb P, 60–80 mesh, isothermally at 150°, flow rate 200 cc/min) to give 1.0 g (24%) of product.

Preparation of Cyclooct-2-en-1-yltrimethyltin (14). Amalgamated magnesium (3.04 g, 0.125 g-atom) was placed into a flask with 150 ml of ether. To this was added 1 ml of ethylene bromide which reacted rapidly. This was followed by a solution of 3-bromocyclooctene[25] (5.0 g; 25 mmoles) and trimethyltin chloride (10.0 g; 50 mmoles) in 10 ml of ether. After the addition was completed (1.5 hr), the reaction mixture was refluxed for 1 hr, cooled, and filtered, and the residue was washed well with dry ether. To remove excess trimethyltin chloride, the ether solution was washed with a saturated potassium fluoride–water solution, followed by water. The organic layer was dried, concentrated, and distilled to give hexamethylditin (1.47 g, 4.0 mmoles) and cyclooct-2-en-1-yltrimethyltin (2.16 g, 8.0 mmoles; 32%), bp 63.5–68.5° (0.25 mm).

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[24] C. A. Grob and W. Baumann, *Helv. Chim. Acta*, **38**, 594 (1955).

[25] A. C. Cope and L. L. Ester, Jr., *J. Am. Chem. Soc.*, **72**, 1129 (1950).

Acylation of Cyclooctatetraene Dianion and the Chemistry of Its Products

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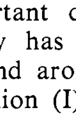
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received April 27, 1967*

Abstract: Cyclooctatetraene dianion (I) reacts as a 1,2- and a 1,4-dicarbanionic reagent with various acyl halides. Thus I and acetyl chloride give 3,5,7,9-dodecatetraene-2,11-dione (III), *syn*-9-acetoxy-9-methylbicyclo[4.2.1]-nonatriene (V), *syn*-9-hydroxy-9-methylbicyclo[4.2.1]nonatriene (IV), and *syn*-9-acetoxy-9-methylbicyclo[6.1.0]-nonatriene (VI). Benzoyl chloride and I yield *trans,cis,cis,trans*-1,10-diphenyl-2,4,6,8-decatetraene-1,10-dione (XIV) and *syn*-9-benzoyloxy-9-phenylbicyclo[4.2.1]nonatriene (XV); similar products (XIX and XX) are obtained from *p*-bromobenzoyl chloride and I. The lactone XXV of 9-(2-carboxyphenyl)-9-hydroxybicyclo-[6.1.0]nonatriene is obtained from I and phthaloyl chloride. The structures of these products are proven by combination of chemical degradation and synthesis. Pyrolysis of the bicyclo[4.2.1]nonatrienes (V and XV) gives 2-substituted indenes; the bicyclo[6.1.0]nonatriene (VI) yields 3-methylindene. The mechanisms of these pyrolyses are discussed.

One of the important developments of modern structural theory has been the demonstration of the existence[2a,b] and aromatic character[2b,3] of the cyclooctatetraene dianion (I). That I is planar and possesses a delocalized π-electron system has been firmly established[3] and provides a dramatic confirmation of the Hückel rule.



I

There has been little systematic investigation, however, of the chemistry of the cyclooctatetraene dianion (I). Reppe and his colleagues, in their original work on cyclooctatetraene, report that cyclooctatetraene forms a dilithium derivative which gives on carbonation a dicarboxylic acid assigned the structure 2,5,7-cyclooctatriene-1,4-dicarboxylic acid.[2a] Cope and Hochstein prepared dilithium and disodium derivatives of cyclooctatetraene; these yield mixtures of 1,3,5- and 1,3,6-cyclooctatrienes on treatment with proton sources.[4]

Alkylation and acylation of cyclooctatetraene dianion (I) were initially described by Azatyan and coworkers.[5,6] Reactions of I with methyl, allyl, and benzyl halides give disubstituted cyclooctatrienes as high-boiling material. Acylation with acetyl chloride is said to yield diacetylcyclooctatriene, a viscous product; benzoyl chloride forms a solid dibenzoylcyclooctatriene, mp 123°.[5,6] The positions of the substituents in all of these products were not specified in the above studies.

Condensation of cyclooctatetraene dianion (I) with acetone, methyl ethyl ketone, benzophenone, benzaldehyde, and cyclohexanone is reported to yield the respective 7,8-bis(α-hydroxyalkyl)-1,3,5-cyclooctatrienes; dehydration of these diols to tetrahydrofuran derivatives is described.[6,7] The product of reaction of cyclooctatetraene dianion with benzophenone is assigned the structure 7,8-bis(α-hydroxybenzhydryl)-1,3,5-cyclooctatriene.[8]

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[1] (a) Abstracted in part from the Ph.D. dissertation of T. S. Cantrell, The Ohio State University, Columbus, Ohio, 1964. (b) National Science Foundation Cooperative Fellow, 1961–1962 and 1963–1964. National Science Foundation Graduate Fellow, 1962–1963.

[2] (a) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann.*, **560**, 1 (1948); (b) T. J. Katz, *J. Am. Chem. Soc.*, **82**, 3784, 3785 (1960); (c) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, Chapter 10.

[3] (a) T. J. Katz, W. H. Reinmuth, and D. E. Smith, *J. Am. Chem. Soc.*, **84**, 802 (1962); (b) H. L. Strauss, T. J. Katz, and G. K. Fraenkel, *ibid.*, **85**, 2360 (1963); (c) H. Keller and H. P. Fritz, *Z. Naturforsch.*, **16b**, 234 (1961); (d) H. P. Fritz and H. Keller, *Ber.*, **95**, 158 (1962).

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[7] V. D. Azatyan and R. S. Gyuli-Kevkhyan, *Izv. Akad. Nauk Arm. SSR, Otd. Khim. Nauk*, **14**, 451 (1961); *Chem. Abstr.*, **58**, 3327 (1963).