27b: mass spectrum m/e 291; ^{1}H NMR δ 7.47–6.73 (AB, 4), 6.03–5.10 (m, 4), 2.60 (m, 2), 2.27 (s, 3), 2.06 (m, 4); ^{13}C NMR as for **27a**.

Reaction with methyl iodide afforded **26a**, **27c**, and **28c**.

27c: mass spectrum m/e 304; ^{1}H NMR δ 7.60–6.93 (AB, 4), 5.87 (m, 4), 2.50 (m, 2), 2.43 (s, 3), 2.13 (m, 4), 1.43 (s, 3); ^{13}C NMR δ 22.78 and 29.73 (CH_3), 39.66 ($C_{7,8}$), 50.20 (C_9), 51.21 ($C_{1,6}$), 126.47 ($C_{3,4}$), 136.39 ($C_{2,5}$).

28c: mass spectrum m/e 304; ^{1}H NMR δ 7.60–6.70 (m, 3), 5.74 (m, 4), 3.54 (t, 1), 2.70 (m, 2), 2.23 (s, 3), 2.23 (s, 3), 2.00 (m, 4).

Reaction of 25 with *n*-BuLi and Water. This reaction afforded starting material and a mixture of *n*-butyl *p*-tolyl selenide (m/e 228), *syn*-9-(*p*-tolylseleno)bicyclo[4.2.1]nonane (m/e 294; 3.5 ppm, t, H_9), and *anti*-9-(*p*-tolylseleno)bicyclo[4.2.1]nonane (m/e 294; 3.6 ppm, s, H_9) which could not be separated by high-pressure LC.

Acknowledgment. The authors are indebted to Dr. J. W. de Haan and L. J. M. van de Ven for the recording and interpretation of the ^{13}C spectra and to Dr. P. A. Leclerq and G. L. Scherpenzeel for measuring the mass spectra.

Registry No. **7a**, 72065-39-5; **7b**, 72065-40-8; **7c**, 72065-41-9; **7d**, 72065-42-0; **8a**, 72065-43-1; **8b**, 72065-44-2; **8c**, 72065-45-3; **8d**, 72065-46-4; **8e**, 72065-47-5; **8f**, 72065-48-6; **8g**, 72065-49-7; **9a**, 72065-50-0; **9b**, 72065-51-1; **9c**, 72065-52-2; **9d**, 72065-53-3; **9e**, 72065-54-4; **9f**, 72065-55-5; **9g**, 72065-56-6; **10b**, 72065-57-7; **10c**, 72065-58-8; **10d**, 72065-59-9; **10e**, 72065-60-2; **10f**, 72065-61-3; **10g**, 72065-62-4; **11a**, 72065-63-5; **11b**, 72065-64-6; *endo*-**11c**, 72065-65-7; *exo*-**11c**, 72065-66-8; **11d**, 72065-67-9; **11e**, 72065-68-0; **11f**, 72065-69-1; **11g**, 72065-70-4; **12a**, 72065-71-5; **12b**, 72065-72-6; **12c**, 72065-73-7; **12d**, 72065-74-8; **12e**, 72065-75-9; **12f**, 72065-76-0; **12g**, 72065-77-1; **13a**, 72065-78-2; **13b**, 72065-79-3; **13c**, 72065-80-6; **13d**, 72065-81-7; **14a**, 72065-82-8; **14b**, 72065-83-9; **14c**, 72065-84-0; **14d**, 72065-85-1; **15b**, 72065-86-2; **15c**, 72065-87-3; **15d**, 72065-88-4; **16a**, 72065-89-5; **16b**, 72065-90-8; **16c**, 72065-91-9; **16d**, 72065-92-0; **17a**, 72065-93-1; **17b**, 72065-94-2; **17c**, 72065-95-3; **17d**, 72065-96-4; **18b**, 72065-97-5; **18c**, 72065-98-6; **19a**, 72065-99-7; **19b**, 72066-00-3; **19c**, 72066-01-4; **20b**, 72066-02-5; **20c**, 72066-02-5; **21a**, 72066-03-6; **21b**, 72066-04-7; *endo*-**21c**, 72120-56-0; *exo*-**21c**, 72066-05-8; **22a**, 72066-06-9; **22b**, 72066-07-0; **22c**, 72066-08-1; **24**, 72066-09-2; **25**, 72066-10-5; **26a**, 72066-11-6; **26b**, 72066-12-7; **26c**, 72066-13-8; **27a**, 72066-14-9; **27b**, 72066-15-0; **27c**, 72066-16-1; **28a**, 72066-11-6; **28b**, 72066-17-2; **28c**, 72066-18-3; **29a**, 72066-19-4; **29b**, 72066-20-7; **29c**, 72066-21-8; **41**, 34733-74-9; **42**, 52902-51-9; **44a**, 645-96-5; **44b**, 37773-23-2; CH_3I, 74-88-4; PhCHO, 100-52-7; Ph_2CO, 119-61-9; DMF, 68-12-2; CO_2, 124-38-9; H_2O, 7732-18-5; D_2O, 7789-20-0.

Addition of Tri-*n*-butyltin Hydride to Conjugated *p*-Menthadienes

Minoru Ukita, Jun Iyoda, and Isao Shiihaha*

Government Industrial Research Institute, Osaka, Midorigaoka 1, Ikeda, Osaka, Japan

Received February 16, 1979

The addition reaction of tri-*n*-butyltin hydride is here adapted to the conjugated 1,3- and 2,4(8)-*p*-menthadienes. The yields of the adducts are considerable for these conjugated *p*-menthadienes. Eight new organotin adduct compounds have been separated and their structures determined by IR and NMR spectra, which show one double bond as in the *p*-menthene ring, as well as the tri-*n*-butylstannyl group. An addition scheme is postulated in which 1,2-addition of tri-*n*-butyltin hydride to the original *p*-menthadienes is favored, followed by isomerization from the original. 1,4-Addition then occurs.

The addition of tri-*n*-butyltin hydride to β-pinene, limonene, and 1(7)-*p*-menthene has been previously reported by the present authors.[1] In these cases, the tri-*n*-butylstannyl group attaches to the outer carbon of the *p*-menthene ring, and the adducts are simple compositions.

In this paper, further investigation, using these techniques, on the conjugated *p*-menthadiene adducts such as 1,3- and 2,4(8)-*p*-menthadienes is presented. In these cases, however, the compositions of adduct mixtures are complex, and thus careful separation and analytical techniques are needed.

It has been found that by using a Golay column we could analyze these organotin adduct components without decomposition even at temperatures as high as 190 °C if proper operating conditions were chosen. Moreover, each component was purified sufficiently to permit the determination of its structure by a combination of two separation techniques, vacuum distillation with a spinning-band column followed by several repetitions of liquid chromatography using a column packed with silica gel at room temperature.

As it was difficult to obtain these terpenes[2] at high purity as starting material, they were used as mixtures containing several percent of other terpenes such as *p*-menthene, *p*-cymene, and 1,4-[3] and 1,4(8)-*p*-menthadienes in which mono- and unconjugated double bonds were absent or far less active in this reaction.

The conditions used for the addition reaction were the same as those in the previous report:[1] azobis(isobutyronitrile) (AIBN) and heating at 200 °C for 24 h or more in a sealed glass tube.

The determination of the structure of each component was made possible by examining the IR and NMR spectra of the purified samples and referring to its retention time in GC and stability in the acid and iodine cleavage reactions.

Experimental Section

The precise GC analysis of the organotin components was carried out on a Hitachi K-53 gas chromatograph with a Golay column of Z-45 (silicone grease SE-30, 0.25 mm i.d. × 45 m, column temperature 190 °C, He 1.0 atm, injection quantity of sample 0.2–0.4 mL). *p*-Menthanes, methenes, methadiens, and iodo-*p*-menthanes were also analyzed by a Golay column of R-45 (polypropylene glycol, up to 140 °C) and HB-2000 (polyethylene glycol, up to 160 °C). A spinning-band fractionation column having 40 theoretical plates was used under a vacuum of 1.0 torr, and high reflux ratios were used for the separation of each com-

(1) J. Iyoda and I. Shiihara, *J. Org. Chem.*, **35**, 4267 (1970).

(2) P. de Mayo, "Mono- and Sesquiterpenoids", Vol. II, Interscience, New York, 1959, p 60. On this page, it is mentioned that α-terpinene (1,3-*p*-menthadiene) has not been obtained in pure form.

(3) The adduct yield for 1,4-*p*-menthadiene was only 9.1% under the same conditions as those used for the other conjugated menthadienes. The dehydrogenation tendency to *p*-cymene of this menthadiene was strongest, and the adduct components were almost the same as those in 1,3-*p*-menthadiene with regard to formation ratios and kinds. Thus, it may be isomerized first to 1,3-*p*-menthadiene in this reaction system and can add Bu_3SnH, but owing to simultaneous side reactions this is consumed and changes to ditin, which causes a low yield.

0022-3263/80/1945-0328$01.00/0

Table I. Yields and Compositions of the Addition Reaction

p-menthadienes[a]	catalysts	total yield, %	adduct compositions, %								
			1	2	3	4	5	6	7	8	9[b]
I	Bu_3SnI	18	45			16	10	13	7	9	
I′	AIBN	28	12		2	7	16	44	7	12	
II	Bu_3SnI	14	8	4	51	3	15		3	4	12
II′	AIBN	29	24	15	29	13	9		2	3	5

[a] I and I′ = 2,4(8)-*p*-menthadiene; II and II′ = 1,3-*p*-menthadiene. [b] **9** is 9-(tributylstannyl)-*p*-menth-1-ene caused by contaminated limonene.[1]

ponent, the purity of which was checked by GC. Liquid chromatography (LC) was carried out with a stationary-phase column of 37 mm i.d. × 0.8 m packed with Merck silica gel 60, using *n*-hexane as eluent at room temperature. One injection of the sample was 0.5–2.0 g, and the flow rate was 95–100 mL/h, adjusted by a head 2 m in height from the hexane level in the reservoir to the column outlet. One elution required about 4.5 h. A JEOL (PS-100) 100-MHz instrument was used for NMR spectra.

Materials: 2,4(8)-*p*-menthadiene (sample I purity 73.4%) accompanied by 1,4(8)-*p*-menthadiene (26.6%) (sample I′, purity 70.8%), 1,4(8)- (9.9%), 1,4- (0.6%), and 1,3-*p*-menthadiene (2.5%), and *p*-menthenes (15.1%); 1,3-*p*-menthadiene (sample II purity 78.7%) accompanied by limonene (2.7%), *p*-cymene (14.4%), and *p*-methenes (4.2%) (sample II′, purity 58.0%), 1,4- (11.7%), 2,4(8)- (8.7%), and 1,8(9)-*p*-menthadiene (4.2%), and *p*-menthenes (17.4%).

Tri-*n*-butyltin hydride (hereafter tributyltin hydride) was prepared by the method proposed by us,[4] and hexabutylditin (abbreviated ditin) was prepared from tributyltin hydride and bis(tributyltin) oxide,[5] and both were of almost 100% purity as indicated by iodometry and GC.

Analyses. Elemental analyses of carbon and hydrogen gave good agreement for several organotin compounds. One example of the adduct analysis by a combination of iodimetry and successive alkalimetry was carried out as follows. A fractionated sample of the adducts mixture from sample II (0.5173 g, composition ratio 1:2:3:4 = 36:24:30:10, with the sum of the reactive adducts known to be 68.8% by GC) was dissolved in 20 mL of benzene and titrated with a 0.1 N iodine–benzene solution (f = 1.00). The titers were 16.0 mL (66.1% to the 100% purity). Ethanol (20 mL) was poured into this end-point solution in order to obtain the solubility of the benzene and water titers of 0.1 N alkali (f = 0.973), and this was then heated to near 40 °C for several minutes to secure smooth reaction of alkaline titration. Phenolphthalein was used as the indicator, and 17.1 mL (16.5 mL for f = 1.000) was required for neutralization. The titers of iodine were seen to be about equal to that of alkali.

The benzene layer after the titration was washed by water and dried, and the benzene was distilled off. The residue was a mixture of terpene and bis(tributyltin) oxide, and this was injected into the HB-2000 column at 100 °C. It was found that 3-, 2-, and 1-menthenes, *p*-cymene, and *p*-menthadienes were detected in a ratio of 35:23:15:22:5 by the peaks at the corresponding relative retention time of each terpene.

Results and Discussion

Addition Reaction. Two *p*-menthadienes (I′ and II′) were used mainly. They were easily obtainable in quantity, the yields were satisfactory, and, by use of AIBN catalyst, enough of the crude adducts were obtained for purification by vacuum distillation (pot capacity 50 mL). Occasionally tributyltin iodide was examined as a cationic catalyst in addition to AIBN.

The results for these addition reactions are listed in Table I with the yields and compositions of the adducts. The adduct components are numbered in the order of appearance. Two examples of the marked contrast caused by using different catalysts are shown for each of the *p*-menthadienes. Besides the adduct components **1–8**, *p*-menthenes, and menthadienes (unreacted and isomerized), tetrabutyltin, terpene dimers, and ditin were recognized separately in the order of their boiling points.

Even if the radical catalyst AIBN was used here, it gave tributyltin cyanide[6] upon reaction with tributyltin hydride which could impose the effect of a cationic mode on this reaction system to even a smaller extent than upon reaction with tributyltin iodide.

There are many *p*-menthadienes, both conjugated and unconjugated. Both 2,4(8)- and 1,3-*p*-menthadienes are popular among them, are stable as the conjugated menthadienes, and are fairly easily obtainable. They are also easily isomerized to many *p*-menthadienes by heating in the presence of an ionic catalyst,[7] and the same isomerizations were encountered under these addition reaction conditions by the tributyltin radical or tributyltin halide.

Ditin was formed in all cases in considerable amounts. This was confirmed by the retention time in GC compared with that of an authentic sample. The largest amounts were found when the adduct yield was poor. Free hydrogen gas evolution was always recognized by the pressure in the sealed tube rather than hydrogenation of the unsaturated compounds.

Separation and Purification of the Adduct Components. About 20–30 g of sample was charged into the 50-mL pot of the distillation column, fractionated into 1.5–2.0-g samples, and tested by GC analysis. 2,4(8)-*p*-Menthadiene by use of AIBN catalyst gave **6** as the stable unique product among the other components which contained the *p*-cymene ring. Compound **6** was cleanly separated by one LC run. Three or four repetitions were needed to obtain satisfactory purity for a difficult separation such as was the case for compounds **4**, **7**, and **8**.

The elution order of the adducts and the byproducts was entirely different from that with GC, and this seemed to be related to the cationic character of the adducts. The order was as follows: $Bu_4Sn \approx (Bu_3Sn)_2 > 1 > 3 \approx 5 > 4 > 2 > 8 > 7 > 6 >$ terpene dimers.

Chemical and Spectral Analyses of the Adducts. The characteristics (relative retention time (RT), bp, and n^{25}_D) and C and H analyses of the adduct components are summarized in Table II, along with their names based on IR and NMR structural analyses (Table III). The relative retention times were calculated by dividing each retention time in GC with that of ditin. Generally, for n^{25}_D values, 3-*p*-menthene derivatives are smaller than those of 7-*p*-menthene, 4(8)-*p*-menthene, and *p*-cymene.

In the IR spectra of these components, the inner double bond appears at 1650–1680 cm^{-1} and at 810–915 cm^{-1}. Components **1–4** have geminal methyls on the *i*-Pr group which are shown as the two peaks at 1378–1360 cm^{-1}. When the $SnBu_3$ group is attached to C^9 such as in com-

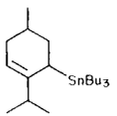
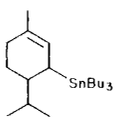
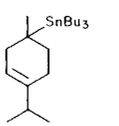
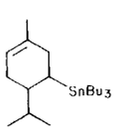
(4) K. Hayashi, J. Iyoda, and I. Shiihara, *J. Organomet. Chem.*, **10**, 81 (1967).
(5) A. Sawyer, *J. Am. Chem. Soc.*, **87**, 537 (1965).
(6) W. Neumann, H. Niermann, and R. Sommer, *Justus Liebigs Ann. Chem.*, **659**, 27 (1962).
(7) R. Bates, E. Caldwell, and H. Klein, *J. Org. Chem.*, **34**, 2615 (1969).

Table II. Characteristics and C and H Analyses of the Adducts[a]

compd no.	names	RT[b] in GC	bp, °C (1 torr)	n^{25}_D
1	5-(tributylstannyl)-3-*p*-menthene	0.424	148	1.4955
2	3-(tributylstannyl)-1-*p*-menthene	0.444	151	1.5018
3	1-(tributylstannyl)-3-*p*-menthene	0.483	151	1.4935
4	5-(tributylstannyl)-1-*p*-menthene	0.514	153	1.4998
5	9-(tributylstannyl)-3-*p*-menthene	0.534	153	1.4930
6	9-(tributylstannyl)-*p*-cymene	0.548	154	1.5089
7	9-(tributylstannyl)-4(8)-*p*-menthene	0.580	154	1.5016
8	2-(tributylstannyl)-4(8)-*p*-menthene	0.595	157	1.5014

[a] Satisfactory combustion analytical data for C and H (±0.4%) were provided for these compounds. [b] Relative retention time (RT) of hexabutylditin = 1.000.

Table III. Spectra of the Adducts

compd no.	structures	IR, cm^{-1}: inner CC=C in *p*-menthene 1-	IR, cm^{-1}: inner CC=C in *p*-menthene 3-	IR, cm^{-1}: gem or single Me, C^9 Me	NMR,[a] τ: CH_2Sn	NMR,[a] τ: Me in Bu_3Sn	NMR,[a] τ: head Me	NMR,[a] τ: Me in C^9	NMR,[a] τ: Me in CH_3C=	NMR,[a] τ: CH_2	NMR,[a] τ: CH_2C=	NMR,[a] τ: C^8H	NMR,[a] τ: HC=
1			1660 (w) 890 (w) 810 (w)	1375 (s) 1360 (m)	9.18 (t, 6 H, J = 7)	9.11 (t, 9 H, J = 6)	9.08 (d, 3 H, J = 6)	9.04 (d, 6 H, J = 6)		8.4-9.0 (m, 15 H)	8.0-8.4 (br, 3 H)	7.89 (sept, 1 H, J = 6)	4.68 (br, 1 H)
2		1660 (w) 915 (w) 810 (w)		1378 (s) 1365 (m)	9.12 (t, 6 H, J = 7)	9.11 (t, 9 H, J = 6.5)		9.08 (d, 6 H, J = 6)	8.42 (s, 3 H)	8.4-9.0 (m, 15)	7.6-8.4 (br, 4 H)		4.7, 4.6 (br, 1 H)
3			1665 (w) 895 (w) 817 (w)	1378 (s) 1361 (w)	9.18 (t, 6 H, J = 7)	9.11 (t, 9 H, J = 6)	9.07 (s, 3 H)	9.04 (d, 6 H, J = 6)		8.4-9.0 (m, 13 H)	8.0-8.4 (br, 5 H)	7.75 (sept, 1 H, J = 6)	4.72 (br, 1 H)
4		1660 (w) 907 (w) 817 (w)		1378 (s) 1360 (m)	9.11 (t, 6 H, J = 7)	9.11 (t, 9 H, J = 6.5)		9.08 (d, 6 H, J = 6)	8.42 (s, 3 H)	8.4-9.0 (m, 15 H)	7.6-8.4 (br, 4 H)		4.7, 4.6 (br, 1 H)

5		1664 (w) 892 (m) 813 (m)	1376 (s)	9.16 (t, 6 H, J = 7)	9.11 (t, 9 H, J = 6.5)	9.08 (d, 3 H, J = 7)	9.02 (d, 3 H, J = 7)	7.9–8.9 (m, 21 H)		7.77 (sext, 1 H, J = 7)	4.71 (br, 1 H)
6		1516 (s)[b] 818 (s)[b] 535 (m)[b]	1376 (s)	9.39 (t, 6 H, J = 7)	9.15 (t, 9 H, J = 6)	7.74 (s, 3 H)	8.78 (d, 3 H, J = 7)	8.4–9.0 (m, 14 H)		7.14 (sext, 1 H, J = 7)	3.03 (s, 4 H)
7			1376 (s)	9.17 (t, 6 H, J = 6)	9.11 (t, 9 H, J = 6)	9.08 (d, 3 H, J = 6)		8.4–9.0 (m, 18 H)	8.39 (s, 3 H)	7.3–8.3 (br, 5 H)	
8			1376 (s)	9.17 (t, 6 H, J = 6)	9.11 (t, 9 H, J = 6)	9.08 (d, 3 H, J = 6)		8.4–9.0 (m, 15 H)	8.39 (s, 6 H)	7.3–8.3 (br, 5 H)	

[a] J values in hertz. [b] From the *p*-cymene ring.

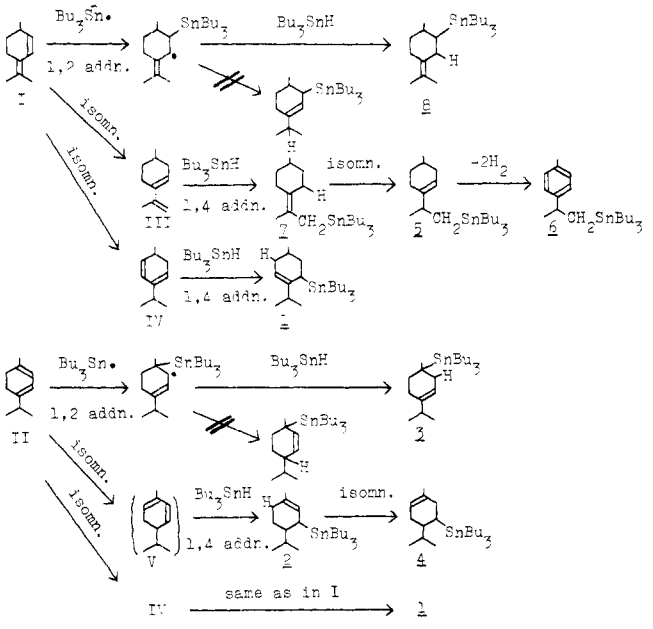
ponents **5** and **7**, it is remarkable that a single methyl peak appears at 1380 cm^{-1}, and the absorption at 1150 cm^{-1} is somewhat stronger than that at 1180 cm^{-1}, contrasting with the equal intensity in those two positions for the free *i*-Pr group.

Only component **6** has the *p*-cymene ring, as shown by the same characteristic absorption band in the IR as in *p*-cymene, and may be assumed to have been derived from the dehydrogenation of **5** and **7**. The UV spectrum of this component also shows maximum absorptions at 265.5, 267.5 (log ϵ 2.773), and 274 nm just as with *p*-cymene.

The peaks of the NMR spectra are classified by τ values with the kind of signal patterns, the number of H atoms, and the coupling constants J (Hz). The number of H atoms is 44 except for **6**, which has 40. A methyl group far from the double bond appears at τ 9.08, and one close to the double bond appears at τ 9.04. By this means the two types of 1- and 3-*p*-menthene derivatives are clearly distinguished. Component **3** is the only adduct in which the Bu_3Sn group attaches to the tertiary carbon (here in C^1), and the NMR (270 Hz) shows no coupling in the head methyl of *p*-menthene, owing to the nonexistence of the hydrogen atom. A hydrogen atom of methine -HC=C< has one peak as in **1**, **3**, and **5**, but two peaks appear in **2** and **4** in the τ 4.5–5.0 region. The latter case may arise from the two isomers shown by different configurations of adducts which have $SnBu_3$ and *i*-Pr cis or trans to each other at C^3 and C^4. Components **7** and **8** have no peaks in the 4–5 region, but the patterns in the τ 7.3–8.5 region are very similar to those of 4(8)-*p*-menthene and 2,4(8)-*p*-menthadiene, especially characteristic to CH_3C= at τ 8.39.

Titration by 0.1 N Iodine–Benzene and Succeeding 0.1 N KOH Ethanol Solutions. Although components **5**, **6**, and **7** had no titers by titration with 0.1 N iodine solution in benzene as assumed from their structures, **1**, **2**, **3**, **4**, and **8** had 2 mol of titer by titration with the iodine solution and also an additional 2 mol of titer from titration with 0.1 N KOH solution formulated as in eq 1–3.

Scheme I



This shows the easy cleavage of those adducts which have a Bu_3Sn group in the *p*-menthene ring by iodine. The iodine derivatives thus obtained are also cleaved by the weak alkaline solution at room temperature either to *p*-menthadienes or to hydroxy-*p*-menthenes, because of the β-positioned or γ-positioned carbon double bond in the *p*-menthene ring and the strong affinity of Bu_3SnOH for halogen. In the second step, the *p*-menthadienes are partially disproportionated to *p*-menthenes and *p*-cymene in equal ratios, and the hydroxy-*p*-menthenes are hydrogenated to *p*-menthenes through the oxidation of Bu_3SnOH to dibutyltin oxide which was recognized as the white powder deposited after the titration and identified by its IR spectrum. Thus, the ratios of the formed *p*-menthenes and *p*-cymeme determined by GC are found to be quite close to those of the original adduct components as far as the allylic adducts are concerned, and the homoallylic ones seem to be the origin of *p*-cymene.

Scheme of the Addition Reaction. As a result of the determination of the structures of components 1–8, the scheme for this addition reaction is now postulated. In explanation of the products from original or isomerized *p*-menthadienes, the work reported by Bates[7] for the equilibration of *p*-menthadienes is quoted.

It seems that the addition products are derived from several competitive reactions such as 1,2-addition of the original *p*-menthadienes (I, II) and 1,4-addition of the isomerized ones (III, IV, V) which may be caused by the cationic catalysts which inevitably existed in this reaction system even when the radical catalyst AIBN is used.[6] Accordingly, the reactions become complicated, and the adducts are formed by the many kinds of components such as 1–8. So the trials to show each of the corresponding routes are limited by choosing the most acceptable ones shown in Scheme I.

The direct addition products of the original *p*-menthadienes (I, II) are only 8 and 3, and 1,2-addition of Bu_3SnH is realized as shown by Cook's results.[8] All others seem to be formed from the isomerized intermediates (III, IV, V) or products (from 7 to 5 and 6 and from 2 to 4). The intermediate free radicals for 8 and 3 may be fairly stable by their allylic nature. The positions of C^3 and C^2 are both open for the approaching Bu_3SnH molecule, and it is possible to abstract its H atom, giving the adducts of 8 and 3. At the same time, the Bu_3Sn·radical is regenerated and is used for new attack so long as the chain reaction continues.

Although, the intermediate radical (shown by ⇿) routes in Scheme I may have the same stability as above, the positions of C^8 and C^4 may cause difficulty in the approach of the Bu_3SnH molecule resulting from the steric hindrance of the *i*-Pr group. Accordingly, none of the product is observed.

Component 1 is formed in considerably rich yields in both cases, which indicates the strong reactivity of IV, especially at the C^5 position. The formation of 2 from II may be explained by assuming the isomerization to V, although there is no direct evidence for its formation. However, it is most probable that V is consumed easily by the dimerization as is recognized in GC analysis of the crude adduct besides the formation of 2 and 4.

As to the other components, the formation of 4 from I is not the inherent product, because when the accompanying 1,4(8)-*p*-menthadiene content in the starting material is small as in I′, the formation of 4 decreases. In I, moreover, there is no formation of 2, which is deemed to be the main origin of 4 in the case of II. In all, it is found that for I an increase in purity of the starting material causes a decrease in the adduct yields (to 5–7%), and the adequate use of the cationic catalyst is positive, thus accelerating the isomerization to the easy addition forms and others. For II an increase of purity favors the yield.

There are marked differences in products between I and II, in that I gives higher RT components in GC such as 5, 6, 7, and 8 (but not 1), while II gives lower RT components 1, 2, 3, and 4. This shows that the double bond in the *p*-menthadiene ring like II does not shift to the outer carbons.

Registry No. I, 586-63-0; II, 99-86-5; 1, 72100-23-3; 2, 72100-24-4; 3, 72100-25-5; 4, 72100-26-6; 5, 72100-27-7; 6, 72100-28-8; 7, 72100-29-9; 8, 72100-30-2; 9, 72100-31-3; tributyltin hydride, 688-73-3; ditin, 813-19-4.

(8) D. Cooke, G. Nickless, and F. Pollard, *Chem. Ind. (London)*, 1493 (1963).