- L. Pauling, The Nature of the Chemical Bond, 3rd edn., Cornell University Press, Ithaca, N. Y. (1960), p. 257.
- 4. N. G. Bokii and Yu. T. Struchkov, Zh. Strukt. Khim., 9, 722 (1960).
- 5. E. A. Chernysev, N. G. Komalenkova, S. A. Bashkirova, and V. V. Sokolov, Zh. Obshch. Khim., 48, 830 (1978).
- 6. W. Hieber and I. Gruber, Z. Anorg. Allg. Chem., <u>296</u>, 91 (1958).

REACTIONS OF HEXAMETHYLDISTANNANE WITH ALLYL ACETATES

AND ALLYL HALIDES CATALYZED BY PALLADIUM COMPLEXES

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In our previous work, we demonstrated the possibility of obtaining allyltrimethyltin by the reaction of hexamethyldistannane (I) with allyl bromide catalyzed by $(\eta^3-C_3H_5PdCl)_2$ [1]. In the present work, this reaction was expanded for a broad range of allylic compounds including allyl acetates and other allyl halides for the preparation of various allyltrimethyl-stannanes.

We have found that the reaction of allyl acetates with (I) in HMPTA at about 20°C in the presence of 5 mole % Pd(PPh₃)₄ (II) gives high yields of the following allyltrimethyl-stannanes (Table 1)*

$$\frac{Me_{\theta}Sn_{2} + AllOAc}{(I)} \frac{5 \text{ mole, } \%_{(II)}}{HMPTA, 20^{\circ}} Me_{3}SnAll + Me_{3}SnOAc$$
(1)

All = $CH_2 = CHCH_2$, trans-PhCH= CHCH₂, and cyclohexen-2-yl.

The data given in Table 1 indicate that the activity of the allyl acetates relative to (I) under the conditions studied increases in the following series: cyclohexen-2-yl acetate < cinnamyl acetate < allyl acetate.

The trans configuration of the allylic fragment in retained in the reaction of cinnamyl acetate with (I) as shown by PMR spectroscopy

$$Ph \land OAc + (1) \xrightarrow{(II), (III)} Ph \land SnMe_3 + Me_3SnOAc$$
(2)

According to our previous work [1], $bis(\pi-allylpalladium chloride)$ (III) is markedly more efficient as a catalyst in the reactions of (I) with aryloids than palladium phosphine complexes. The high efficiency of this catalyst is a result of the reaction of Pd(0) which is formed as the result of the rapid reaction of (I) with (III) with organic halides RX which are active in oxidative addition to form the complex RPdXL₂, while solvent molecules act as the weak ligand L. Since donor solvents are much weaker stabilizing ligands than PPh₃, then RPdXL₂ (L is the solvent) has significantly greater catalytic activity than the corresponding phosphine complex.

An attempt to use (III) as a catalyst in the reactions of (I) was unsuccessful, apparently as a result of the low activity of allyl acetates in oxidative addition reactions and the separation of all the palladium immediately after mixing of the reagents as an inactive black.

The use of allyl halides instead of allyl acetates permits the use of complex (III)

*The ordinary method for the synthesis of allyltrimethylstannanes by the reaction of AllMgBr with Me₃SnX (X = Cl, Br) leads to AllSnMe₃ in low yields: 25% for All = CH₂CH = CH₂ [2], 24% for All = cyclohexen-2-yl [3], and 21% for All = trans-PhCh = CHCH₂ [4].

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TABLE 1. Reactions of Hexamethyldistannane (I) with AllX, 5 mole % Pd(PPh₃)₄ (II), or $(\pi-C_3H_5PdCl)_2$ (III); C(I) = $C_{AllX} = 0.25$ mole/liter, 20°C

AllX	Catalyst	Time, min ^a		Yield,		
			RSnMe ₃	HMPTA	acetone	DMF
$CH_2 = CIICH_2OAC$ $CH_2 = CIICH_2CI$ $CH_2 = CHCH_2Br$ $CH_2 = CIICH_2Br$ $CH_2 = CIICH_2Br$ $CH_2 = CHCH_2I$	(II) (III) (III) (II) (III) (III)	40 10 10 2 h 10	CH ₂ =CHCH ₂ SnMe ₃ same	92 83 80 b 73 85 c		
-OAC	(11)	22 h	-SnMea	26 đ		
Br	(III) (II)	15 22 b	same	83		
Ph OAC	(II) (III)	22 n 10	same	73	97	
∕∖∽∖ _{Br} ₄	(111)	10	SuMe ₃	57	58	42
\mathbf{V}			SnMe,	41f [.]	14 44	43
Ċı	(111)	10	SnMe ₃	traces	12	11

^a Time for the disappearance of (I) in the reaction mixture. ^b 17% $CH_2 = CHCH_2Br$ remained. ^c 12% $CH_2 = CHCH_2I$ remained. ^d (I) and 68% of the starting acetate remained in the reaction mixture. ^f The stereochemistry was not studied. ^f 53% of starting $CH_3CH(C1)CH = CH_2$ remained.

as the catalyst. (Ally1 halides are more active in oxidative addition to Pd(0) complexes.) The reactions of ally1 halides with (I) in the presence of (III) proceed in HMPTA at about 20°C and lead to ally1trimethy1stannanes in high yield (see Table 1).

$$(I) + AllX \xrightarrow{5 \text{ mole}\%(III)}_{\text{HMPTA, 20}} Me_3 SnAll + Me_3 SnX$$
(3)

All = CH_2 = $CHCH_2$, trans-PhCh = $CHCH_2$, cyclohexen-2-yl, CH_3CH = $CHCH_2$, and CH_2 = CHCH (CH_3); X = Cl, Br, and I.

Crotyl bromide reacts with (I) to form two regioisomeric RSnMe₃: crotyltrimethyltin in 57% yield and (1-buten-3-y1)trimethyltin in 16% yield. Upon going from HMPTA to acetone and DMF, the yield of these regioisomers hardly changes (see Table 1, experiment 10). Thus, the major product is the organotin compound, in which the Me₃Sn group is bound to the least substituted carbon atom, and the reaction regioselectivity is only slightly dependent on the nature of the solvent

 $Br + (I) \rightarrow \underbrace{\operatorname{SnMe}_3}_{42-58\%} \operatorname{SnMe}_3 + \underbrace{\operatorname{SnMe}_3}_{13-16\%} + \operatorname{Me}_3 \operatorname{SnBr}$ (4)

The predominant formation of the least substituted product is observed in the reactions of ally1stannanes with ally1 halides and ally1 acetates catalyzed by palladium complexes [5, 6].

2-Chloro-3-butene reacts with (I) in the presence of (III) in HMPTA with transfer of the reaction site to form virtually only one regioisomer, namely, crtoyltrimethyltin in 41% yield

$$\int_{-\infty}^{Cl} + (I) \rightarrow \sum_{e_1}^{e_2} + Me_5 SnCl$$
(5)

Carrying out the reaction in acetone and DMF leads to the appearance of a small amount of a second regioisomer (see Table 1, experiment 11).

It is striking that the yield of the allyltrimethylstannanes in the reaction of allyl halides with (I) does not exced 85%, while it is only 41% in reaction (5). Up to 20% Me₄Sn is formed as a second product of the reactions of (I) with allyl halides, while 100% conversion relative to (I) is found in all cases. Me₄Sn is most likely formed in the disproportionation of (I) catalyzed by trimethyltin halide which arises during the reaction [7]

$$(1) \xrightarrow{\operatorname{Me}_4 \operatorname{Sn} \times} \operatorname{Me}_4 \operatorname{Sn} + (\operatorname{Me}_2 \operatorname{Sn})_n \tag{6}$$

Hence, the starting allyl halides (17% $CH_2 = CHCH_2Br$ and 12% $CH_2 = CHCH_2I$) remain in reaction of allyl bromide and allyl iodide with (I) catalyzed by (III) after the disappearance of (I). The amount of unreacted chloride was 53% in the reaction of (I) with 2-chloro-3-butene.

We should note the possibility of the reaction of $RSnMe_3$ formed with the starting allyl acetate or allyl halide in the presence of the palladium catalyst with the formation of a coupling product [5, 6, 8, 9]

$$//OAc + //SnMe_3 \xrightarrow{(II)} // + Me_3SnOAc$$
 (7)

However, this reaction occurs significantly more slowly than reactions (1) and (3) and the formation of the R-R coupling product is not observed in the preparation of $RSnMe_3$ from either allyl acetates in the presence of (II) or from allyl halides in the presence of (III).

In the reactions of (I) with allyl halides, as in the reactions of (I) with aryl iodides [1], complex (III) is a much more efficient catalyst than complex (II). While the yield of allyltrimethyltin (IV) is 80% after only 10 min after the onset of the reaction of allyl bromide with (I) in the presence of (III), only 73% (IV) is formed after 2 h in the presence of (II). In reactions catalyzed by (II), allyl acetates are significantly more active than allyl halides: The yield of (IV) was 92% in the reaction of (I) with CH₂=CHCH₂OAc 40 min after the onset. In our previous work [8], we showed that a similar decrease in reaction rate in going from CH₂=CHCH₂OAc to CH₂=CHCH₂X (X = Cl, Br, I) is also found in the reaction of p-MeC₆H₄SnMe₃ catalyzed by (II). Since allyl acetates are less active than allyl halides in oxidative addition to Pd(0) complexes, their high reactivity in reactions with organotin compounds is apparently related to the superiority of the acetate ion as a leaving group relative to halide ions upon the attack of the π -allylpalladium intermediate by an organotin compound.

The effect of the nature of the solvent (HMPTA, DMF, acetone, THF, benzene and chloroform) on the yield of (IV) was studied in the case of the reaction of (I) with $CH_2 = CHCH_2OAc$ catalyzed by 1 mole % (II) at about 20°C (Table 2). The most favorable solvent was DMF, in which (IV) is formed in quantitative yield 1.5 h after the reaction onset.

In the reactions of (I) with allyl halides catalyzed by (III), the solvent may affect the ratio of the rates of reactions (3) and (6) and, thus, the yield of $RSnMe_3$. In a number of cases (see Table 1, experiments 9 and 11), a marked increase in the yield of $RSnMe_3$ is found in going from HMPTA to acetone and DMF, which is apparently related to a relative decrease in the rate of side-reaction (6).

By analogy with the mechanism for the allyldemetallation of organotin compounds catalyzed by (II) [5, 6], we may propose the following catalytic cycle for the reactions of (I) with allyl acetates carried out in the presence of (II) TABLE 2. Change in the Yield of Allyltrimethyltin (IV) during the Reaction of $CH_2 = CHCH_2OAc$ with Me_6Sn_2 (I) Catalyzed by 1 mole % Pd(PPh_3), at 20°C; $CCH_2 = CHCH_2OAc = C_{(I)} = 0.25$ mole/liter

		Yield of (IV), %									
Solvent	min		h								
	15	30	ÍЧ	1,5	2,5	4	6				
HMPTA	28	38	54	72	85	85	-+				
Acetone	19	53 57	64 82	70 100	75 _	75	-				
THF	9	13	-	16	21	37	-				
Benzene CHCl ₃	-	-	· _	-	-	-	Traces				

*Not determined.



According to scheme (8), an incompletely coordinated complex, $Pd(PPh_3)_2$ is initially formed upon the dissociation of (II) which then acts as the catalyst. The first step of the catalytic cycle is the oxidative addition of allyl acetate to $Pd(PPh_3)_2$ with the formation of cationic π -allylpalladium intermediate (V). Then, the allylic organotin compound is formed as a result of the nucleophilic attack of (I) on the π -allyl ligand of complex (V) and $Pd(PPh_3)_2$ is regenerated.

In order to confirm the participation of intermediate (V) in the catalytic cycle, we carried out the stoichiometric reaction of the complex $[n^3-C_3H_5Pd(PPh_3)_2]$ ⁺Cl⁻ obtained in situ from (III) and 2 eq. PPh₃ (relative to Pd) with (I) in HMPTA. However, the yield of (IV) determined by gas-liquid chromatography immediately after the disappearance of (I) from the reaction mixture (2 min after mixing of the reagents) was only 32%

$$[\eta^{3}-C_{3}H_{5}Pd(PPh_{3})_{2}]^{+}CI^{-} + (I) \rightarrow (IV) \stackrel{!}{\to} Me_{3}SnCI \stackrel{!}{\to} Pd(PPh_{3})_{2}$$

$$\tag{9}$$

The low yield of (IV) is apparently related to the decomposition of (IV) by the action of the incompletely coordinated complex, $Pd(PPh_3)_2$ at the high temperature of the chromatograph injector. The decomposition of (IV) even occurs at $\sim 20^{\circ}C$: Thin-layer chromatographic analysis with hexane eluant and I₂ developer shows that (IV) entirely disappears from the reaction mixture after 8 h. According to our previous work [10], the decomposition of organotin compounds RSnMe₃ (R = p-MeC₆H₄, PhC=C, and 2-C₄H₃S) occurs in HMPTA at 20°C even in the presence of catalytic amounts of (II).

In order to determine the true yield of (IV) immediately after the disappearance of (I), we added 2 eq. $p-NO_2C_6H_4I$, which reacts with $Pd(PPh_3)_2$ to form the complex, $p-NO_2C_6H_4Pd(PPh_3)_2I$ [11] which reacts with (IV) formed in reaction (9) to give a 79% yield of p-nitroallylbenzene*

$$p-\mathrm{NO}_{2}C_{6}\mathrm{II}_{4}\mathrm{Pd}(\mathrm{PPh}_{3})_{2}\mathrm{I} + (\mathrm{IV}) \rightarrow p-\mathrm{NO}_{2}C_{6}\mathrm{II}_{4} \wedge \mathscr{I} + \mathrm{Me}_{3}\mathrm{SnI} + \mathrm{Pd}(\mathrm{PPh}_{3})_{2}$$
(10)

^{*}An independent experiment showed that $p-NO_2C_6H_4Pd(PPh_3)_2I$ reacts with (IV) in HMPTA at about 20°C to form $p-NO_2C_6H_4CH_2CH = CH_2$ in quantitative yield.

Hence, the true yield of (IV) in stoichiometric reaction (I) is not less than 79%. Thus, the results of our study of stoichiometric reaction (9) confirm the participation of intermediate (V) in the catalytic cycle.

A similar mechanism may also be proposed for the reactions of (I) with allyl halides catalyzed by (III). The role of the stabilizing ligands in this case is played by the solvent molecule, while the initial formation of Pd(0) occurs as a result of the reduction of (III) by hexamethyldistannane.

According to our previous work [8, 9], allylic organotin compounds in the presence of palladium complexes undergo coupling reactions with allyl acetates and allyl halides to give high yields of allyldemetallation products

$$AllSnMe_3 + All'X \xrightarrow{(II), (III)} All - All' + Me_3SnX$$
(11)
X = OAc (II), Hal (III).

This permits us to propose a method for the synthesis of asymmetric 1,5-dienes by the reaction of allyl acetates or allyl halides with allylic tin compounds generated in situ. The synthesis of 1-phenyl-1,5-hexadiene may be given as an example.

$$/ Br + (I) \xrightarrow{5 \text{ mole } .\% (III)}_{HMPTA, 10 \text{ min}} (IV) \xrightarrow{Ph/(Ac,5 \text{ mole}\% (II))}_{HMPTA, 6 \text{ h}} Ph / (12)$$

The same product was also obtained in 85% yield in the reaction of cinnamyltrimethyltin obtained in situ from cinnamyl acetate and (I) in the presence of (II) with allyl bromide catalyzed by (III)

$$Ph \land OAc + (1) \frac{5 \text{ mole.} \% (II)}{HMPTA, 22 h} Ph \land SnMe_3 \xrightarrow{/Br, 5 \text{ mole} \% (III)}{HMPTA, 15 \text{ min}}$$
(13)

Schemes (12) and (13) imply that the optimal method for the preparation of 1,5-dienes is the use of allyl halides in the presence of (III). However, the greater availability of allyl acetates relative to allyl halides in some cases makes the use of allyl acetates preferred.

The most common method for the synthesis of asymmetric 1,5-dienes by the reaction of allylic zinc derivatives AllZnBr with allyl bromides All'Br [12] leads to the preparation of All-All' with yields (taking account of the step involving formation of AllZnBr) not exceeding 50%.

EXPERIMENTAL

Samples of Me₆Sn₂ (I), CH₂ = CHCH₂SnMe (IV), CH₃CH(SnMe₃)CH = CH₂, complexes Pd(PPh₃)₄ (II), $(\pi-C_3H_5PdCl)_2$ (III), and p-NO₂C₆H₄PdI(PPh₃)₂ were synthesized by known methods.

The chromatographic analysis was carried out on a Tsvet-2 chromatograph with a flame ionization detector in a 40 ml/min nitrogen stream using a 2 m \times 3 mm column packed with 3% SE-30 on n-super Chromatone. The tin-layer chromatographic analysis was carried out on Silufol UV-254 plates with development in UV light or iodine vapor. The UV spectra were recorded on a Hitachi-124 spectrophotometer in quartz cells.

Reactions of (I) with Allyl Acetates in the Presence of (II). a) A sample of 0.107 g (0.6 mmole) (I), 0.05 g (0.5 mmole) CH₂ = CHCH₂OAc, and 2 ml HMPTA was added to a flask flushed with argon. A sample of 0.029 g (0.025 mmole) (II) was added to the solution obtained with stirring. The reaction endpoint was found relative to the disappearance of the chromatographic spot for (I) on the chromatogram with heptane eluant and iodine vapor development. After 40 min, the yield of (IV) was found by gas-liquid chromatography using n-nonane as the internal standard. The yield of (IV) was 92%. The product was identified by gas-liquid chromatography using a standard compound. The following reactions were carried out similarly:

b) Reaction of 1.97 g (6 mmoles) (I) with 0.88 g (5 mmoles) cinnamyl acetate catalyzed by 0.29 g (0.25 mmole) (II) in 20 ml HMPTA. After 22 h, 80 ml pentane was added to the reaction mixture. The precipitate of palladium complexes was filtered off to give a transparent solution which was washed with water to remove HMPTA and dried over Na₂SO₄. Thinlayer chromatography on silica gel with 3:1 hexane-ether eluant yielded 1.35 g (96%) cinnamyltrimethyltin [4]. PMR spectrum (CCl₄, δ , ppm): 0.12 s (9H, CH₃), 1.93 d (2H, CH₂), 6.32 m (2H, CH=), 7.23 s (5H, Ar).

c) Reaction of 1.97 g (6 mmoles) (I) with 0.7 g (5 mmoles) 3-acetoxycyclohexene catalyzed by 0.29 g (0.25 mmole) (II) in 20 ml HMPTA. After 22 h, the extent of the reaction found using gas-liquid chromatography relative to the amount of unreacted acetoxycyclohexene was 32%; the chromatogram showed a spot for (I). Then, 80 ml water was added to the reaction mixture which was extracted with three 20-ml portions of ether. The ethereal solution was washed and dried over Na₂SO₄. Fractional distillation gave 0.28 g (26%) (cyclohexene-2-yl) trimethyltin [3], bp 93-95°C (9 mm). PMR spectrum (CCl₄, δ , ppm): 0.18 s (9H, CH₃), 1.74-2.20 m (7H, CH₂ + CH), 5.57 m (2H, CH=).

<u>Reaction of (I) with Allyl Halides in the Presence of (III)</u>. A sample of 0.197 g (0.6 mmole) (I), 0.061 g (0.5 mmole) allyl bromide, and 2 ml HMPTA was placed in a flask flushed with nitrogen. A sample of $4.6 \cdot 10^{-3}$ g (0.025 mmole) (III) was added to the solution with stirring by a magnetic stirrer. The spot for (I) disappeared from the chromatogram after 10 min. Analysis of the reaction mixture was carried out by gas-liquid chromatography using standard compounds. The yield of (IV) was 80% (n-nonane was used as the standard). In addition, 17% starting CH₂ \swarrow CHCH₂Br remained in the reaction mixture. A 73% yield of (IV) was obtained in the same reaction using 0.029 g (0.25 mmole) (II) as the catalyst after 2 h. The reactions of (I) with allyl chloride, allyl iodide, 3-bromocyclohexene, and cinnamyl bromide were carried out similarly. The results are given in Table 1.

A sample of 0.45 g (41%) crotyltrimethyltin [4], bp 69°C (20 mm) was obtained in the reaction of 1.97 g (6 mmoles) (I) with 0.45 g (5 mmoles) 2-chloro-3-butene catalyzed by 0.046 g (0.25 mmole) (III) after the usual water-ether work-up and fractional distillation. PMR spectrum (CCl₄, δ , ppm): 0.04 s (9H, CH₃), 1.70 m (5H, CH₃ + CH₂), 5.40 m (2H, CH=).

The reaction of 1.97 g (6 mmoles) (I) with 0.68 g (5 mmoles) crotyl bromide catalyzed by 0.046 g (0.25 mmole) (III) gave 0.8 g (73%) of a mixture of crotyltrimethyltin (57%) and (1-buten-3-yl)trimethyltin (16%), bp 63° C (18 mm). The amounts of each of the isomers were found by gas-liquid chromatography using n-decane as the internal standard.

Reactions of (I) with $CH_2 = CHCH_2OAc$ Catalyzed by (II) in Various Solvents. A sample of 0.197 g (0.6 mmole) (I), 0.05 g (0.5 mmole) allyl acetate, and 2 ml solvent was placed in a flask flushed with argon. A sample of 5.8 mg (0.005 mmole) (II) was added with stirring to the solution obtained. After the formation of a homogeneous solution, the stirring was stopped and the reaction mixture was maintained at about 20°C. Gas-liquid chromatographic analysis of probes using n-nonane as the standard gave the yields of (IV) at given time intervals. This method was employed to study the reaction of (I) with $CH_2 = CHCH_2OAc$ in HMPTA, DMF, acetone, THF, benzene, and chloroform. The results are given in Table 2.

<u>Reaction of (I) with $[\eta^3-C_3H_5Pd(PPh_3)_2]^+Cl^-$ </u>. a) A sample of 3 ml HMPTA, 0.045 g (0.125 mmole) (III) and 0.131 g (0.5 mmole) PPh₃ was added to a flask flushed with argon and equipped with a magnetic stirrer. A sample of 0.082 g (0.25 mmole) (I) was added to the reaction mixture. This almost immediately resulted in the separation of palladium black and a change in the color of the solution from light yellow to black. After 2 min, the peak for (I) disappeared from the chromatogram. The yield of (IV) as determined by gas-liquid chromatography using n-nonane as the internal standard was 32%.

b) A sample of 0.125 g (0.5 mmole) p-nitroiodobenzene was added in the same reaction after the disappearance of (I) to the solution obtained. After 1.5 h, the peak for p-NO₂C₆H₄I had disappeared from the chromatogram (2:1 hexane-ether eluant). The yields of p-NO₂C₆H₄CH₂-CH = CH₂ (79%) and p-NO₂C₆H₄Pd(PPh₃)₂I (92%) were determined by thin-layer chromatography and UV spectroscopy using standard compounds.

<u>Reaction of (IV) with p-NO₂C₆H₄Pd(PPh₃)₂I.</u> A sample of 3 ml HMPTA, 0.22 g (0.25 mmole) p-NO₂C₆H₄Pd(PPh₃)₂I and 0.051 g (0.25 mmole) (IV) was added to a flask flushed with argon and equipped with a magnetic stirrer. The reaction mixture was stirred at about 20°C and the disappearance of (IV) was monitored using thin-layer chromatography with hexane eluant and I₂ development. The disappearance of p-NO₂C₆H₄Pd(PPh₃)I was followed using chloroform eluant and development in UV light. At the end of the reaction (after about 1 h), the yield of pnitroallylbenzene (94%) was determined by thin-layer chromatography and UV spectroscopy using a standard compound. Allyldemetallation of Allylic Tin Compounds Generated in situ. a) A sample of 0.197 g (0.6 mmole) (I), 0.061 g (0.5 mmole) allyl bromide, and 2 ml HMPTA was added to a flask flushed with argon and equipped with a magnetic stirrer. A sample of 4.6 mg (0.025 mmole) (III) was added with stirring to the solution obtained. The spot for (I) disappeared from the chromatogram after 10 min. Then, 0.088 g (0.5 mmole) cinnamyl acetate and 0.029 g (0.025 mmole) (II) were added to the reaction mixture. The reaction endpoint was evaluated relative to the disappearance of the spots for (IV) and cinnamyl acetate from the chromatogram (3:1) hexane-ether eluant). After 6 h, the yield of trans-1-phenyl-1,5-hexadiene (87%) was determined using thin-layer chromatography with UV spectroscopy and a standard compound.

b) A sample of 0.088 g (0.5 mmole) cinnamyl acetate, 0.197 g (0.6 mmole) (I) and 2 ml HMPTA was added to a flask flushed with argon and equipped with a magnetic stirrer. A sample of 0.029 g (0.025 mmole) (II) was added to the solution obtained. The homogeneous solution was maintained at about 20°C. The reaction was monitored by thin-layer chromatography. The reaction endpoint was evaluated relative to the disappearance for the spots for (I) and cinnamyl acetate. After 22 h, 0.061 g (0.5 mmole) $CH_2 = CHCH_2Br$ and 4.6 mg (0.025 mmole) (III) were added to the reaction mixture. The spot for cinnamyl acetate disappeared 15 min after this introduction. Thin-layer chromatographic analysis using UV spectroscopy indicate that the yield of trans-1-phenyl-1,5-hexadiene was 85%.

CONCLUSIONS

1. A method was developed for the synthesis of allyltrimethylstannanes with high yields by the reaction of Me_6Sn_2 with allyl acetates catalyzed by $Pd(PPh_3)_4$ and with allyl halides catalyzed by $(n^3-C_3H_5PdCl)_2$ in HMPTA at about 20°C.

2. A study of the stoichiometric reaction of Me_6Sn_2 with the complex $[n^3-C_3H_3Pd(PPh_3)_2]^+Cl^$ indicated the participation of a π -allylpalladiumintermediate in the catalytic reactions.

3. A method was proposed for the synthesis of 1,5-dienes by the reaction of allyltrimethylstannanes generated in situ with allyl acetates and allyl halides in the presence of palladium complexes.

LITERATURE CITED

- A. N. Kashin, I. G. Bumagin, N. A. Bumagin, V. N. Bakunin, and I. P. Beletskaya, Zh. Org. Khim., <u>17</u>, 805 (1981).
- 2. M. M. Koton, T. M. Kiseleva, and N. P. Zapevalova, Zh. Obshch. Khim., 30, 186 (1960).
- 3. R. H. Fish, H. G. Kuivila, and I. J. Tyminski, J. Am. Chem. Soc., 89, 5861 (1967).
- 4. C. W. Fong and W. Kitching, J. Organomet. Chem., 22, 107 (1970).
- 5. J. Godschalx and J. K. Stille, Tetrahedron Lett., No. 21, 2595 (1980).
- 6. B. M. Trost and E. Keinan, Tetrahedron Lett., No. 21, 2595 (1980).
- 7. R. Arnold, M. J. Cutbertson, and P. R. Wells, J. Organomet. Chem., 184, 39 (1980).
- 8. N. A. Bumagin, A. N. Kasatkin, and I. P. Beletskaya, Dokl. Akad. Nauk SSSR, <u>266</u>, 862 (1982).
- 9. N. A. Bumagin, I. G. Bumagina, A. N. Kashin, and I. P. Beletskaya, Zh. Obshch. Khim., <u>52</u>, 714 (1982).
- N. A. Bumagin, A. N. Kasatkin, and I. P. Beletskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 912 (1983).
- 11. P. Fitton and E. A. Rick, J. Organomet. Chem., 28, 287 (1971).
- 12. Houben-Weil, Methoden der Organischen Chemie, Vol. 13, Stuttgart (1973), p. 2a, 763.