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THE PREPARATION OF ALLYLIC DERIVATIVES OF TIN BY WITTIG REACTIONS OF β-TRIMETHYLSTANNYLETHYLIDENETRIPHENYLPHOSPHORANE *

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Summary

The reaction of β-trimethylstannylethylidenetriphenylphosphorane, prepared by the action of methylenetriphenylphosphorane on iodomethyltrimethyltin, followed by deprotonation of the resulting $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ with lithium diisopropylamide, with aldehydes and ketones provides a route to allylic organotin compounds, $Me_3SnCH_2CH{=}CHR$ and $Me_3SnCH_2CH{=}CRR'$. Alkylation of $Ph_3P{=}CHCH_2SnMe_3$ with iodomethane, followed by deprotonation of the resulting phosphonium salt and reaction of the latter with propionaldehyde gave $Me_3SnCH_2C(CH_3){=}CHCH_2CH_3$.

Introduction

In recent years allylic derivatives of tin have found increasing applications in organic and organometallic synthesis [2,3]. Among the methods used previously to prepare allyltin compounds, the reaction of an allylic halide-derived Grignard reagent, preformed or generated in situ by the Barbier procedure, with a tin halide, the reaction of an allylic halide with an organotin-lithium or -sodium reagent, and the radical-initiated 1,4-addition of a tin hydride to a 1,3-diene are the most important [3].

Our need for a 3,3-difluoroallylstannane, whose preparation by the first two of these routes was not possible because of the lack of a facile route to the required allylic halide, $CF_2{=}CHCH_2X$, has led us to develop a new and general procedure for the preparation of allylic derivatives of tin.

Previous syntheses of allylic tin compounds were based on processes in which the carbon skeleton of the allylic group was already formed before the

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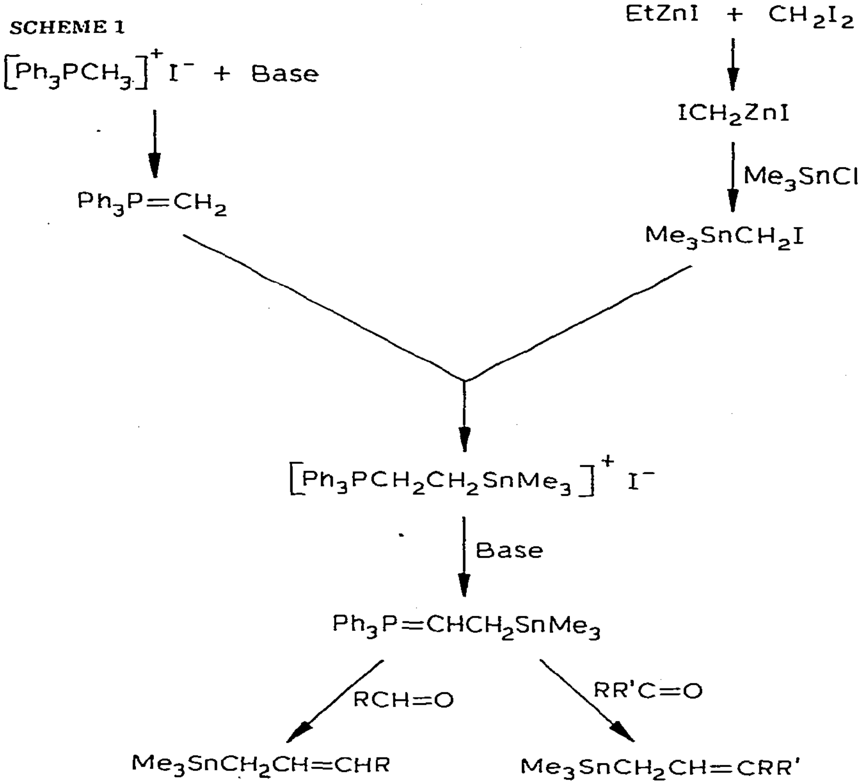
* Preliminary communication, see ref. 1.

Sn—C bond formation step. Our synthesis starts with a compound containing a tin—carbon bond and forms a new C—C bond in the construction of the allyl substituent. The organotin starting materials for this synthesis, iodomethyl- and α-iodoalkyl-derivatives of tin are readily prepared, providing the needed *gem*-diiodides are available (eq. 1) [4], generally in good yield, by a route developed earlier in these laboratories.

$$CH_2I_2 \xrightarrow[THF]{EtZnI} ICH_2ZnI \xrightarrow{Me_3SnCl} Me_3SnCH_2I \qquad (1)$$

Phosphorus ylides are known to displace halide ion from alkyl bromides and iodides, giving a phosphonium halide, e.g., $[Ph_3PCH_2R]^+ X^-$ in the case of the reaction of $Ph_3P{=}CH_2$ with RX [5]. Thus the action of methylenetriphenylphosphorane on iodomethyltin compounds would be expected to give β-stannylethyltriphenylphosphonium iodides, $[Ph_3PCH_2CH_2SnR_3]^+ I^-$. Subsequent deprotonation of the latter with an appropriate base should form the respective β-stannylethylidenetriphenylphosphoranes. These, on reaction with aldehydes and ketones, then should give the desired allyltin compounds. We report here the realization of this proposed chemistry, as outlined in Scheme 1.

SCHEME 1



Results and discussion

(1) Preparation of β-trimethylstannylethyltriphenylphosphonium iodide

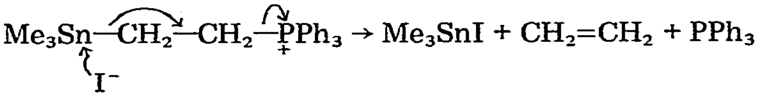
The addition, with stirring, of a solution of methylenetriphenylphosphorane in diethyl ether (prepared by the reaction of a methyltriphenylphosphonium halide with phenyllithium in diethyl ether) to a cold (0°C) solution containing 1.1 molar equivalents of iodomethyltrimethyltin resulted in precipitation of a white solid and formation of a red-orange solution. After the reaction mixture had been stirred for 15 h at room temperature, a light amber slurry was present. Filtration gave a white solid whose NMR spectrum showed it to be the desired product contaminated with 11% of $[Ph_3PCH_3]^+ I^-$. This solid was recrystallized from EtOH/EtOAc (1/4) to provide a pure sample of $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ which was characterized by analysis and infrared and proton NMR spectroscopy. The crude product in such preparations usually is contaminated with 10—20% of methyltriphenylphosphonium iodide, and it may be used in further Wittig reactions without further purification. Base converts the impurity to $Ph_3P{=}CH_2$ whose subsequent reaction with a carbonyl compound gives the much more volatile $RR'C{=}CH_2$ olefin (compared to $RR'C{=}CHCH_2SnMe_3$ in the present case) which is easily and efficiently separated from the desired allyltin product. The provenance of the $[Ph_3PCH_3]^+ I^-$ impurity remains to be established *.

It was not at all certain in advance that $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ would be stable at room temperature. Previous workers had found analogous ammonium and sulfonium salts to be unstable. Thus, attempted quaternization of $Ph_3SnCH_2CH_2NMe_2$ and of $Ph_3SnCH_2CH_2SAr$ compounds with iodomethane resulted in a β-elimination process (eq. 2, 3) [6,7]. On this basis, $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ possibly and $[Ph_3PCH_2CH_2SnPh_3]^+ I^-$ certainly would

$$Ph_3SnCH_2CH_2NMe_2 + MeI \rightarrow Ph_3SnI + CH_2{=}CH_2 + Me_3N \qquad (2)$$

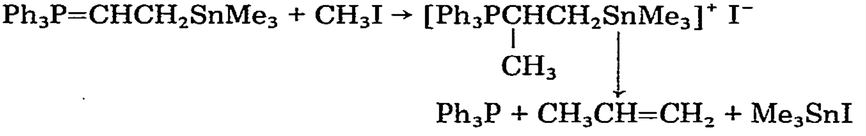
$$Ph_3SnCH_2CH_2SAr + MeI \rightarrow Ph_3SnI + CH_2{=}CH_2 + CH_3SAr \qquad (3)$$

be expected to be unstable. However, the former was stable up to its melting point of 123°C; at this temperature, decomposition occurred, evolving ethylene and forming trimethyltin iodide and triphenylphosphine, presumably by way of nucleophilic attack by iodide ion at tin (eq. 4).



$$Me_3\underset{I^-}{Sn}{-}CH_2{-}CH_2{-}\overset{}{\underset{+}{P}}Ph_3 \rightarrow Me_3SnI + CH_2{=}CH_2 + PPh_3 \qquad (4)$$

A methyl-substituted salt, $[Ph_3PCH(CH_3)\ CH_2SnMe_3]^+ I^-$, was found to be unstable at room temperature. It was prepared by the methylation with iodomethane of the ylide derived from $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ (eq. 5). At room temperature this salt decomposed with formation of a gas and trimethyltin iodide. However, a stable Reineckate salt of this cation,



$$\begin{aligned} &Ph_3P{=}CHCH_2SnMe_3 + CH_3I \rightarrow [Ph_3P\underset{CH_3}{C}HCH_2SnMe_3]^+ I^- \\ &\qquad\qquad\qquad\qquad\qquad \downarrow \\ &\qquad\qquad\qquad\qquad Ph_3P + CH_3CH{=}CH_2 + Me_3SnI \end{aligned} \qquad (5)$$

$[Ph_3PCH(CH_3)\ CH_2SnMe_3]^+ [Cr(NH_3)_2(SCN)_4]^- \cdot H_2O$ could be prepared and

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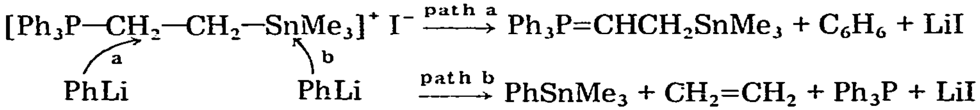
* This question has been considered in more detail in the analogous $Ph_3P{=}CH_2/Me_3SiCH_2I$ reaction [17].

characterized, and the iodide could be converted to the respective ylide, $Ph_3P{=}C(CH_3)\,CH_2SnMe_3$, by in situ treatment with base (see below).

(2) Generation and Wittig reactions of β-trimethylstannylethylidenetriphenylphosphorane

Addition of a molar equivalent of lithium diisopropylamide to a slurry of $[Ph_3PCH_2CH_2SnMe_3]^+\ I^-$ in THF at 0°C resulted in the formation of a homogeneous, deep red-orange solution of the ylide. When an excess of n-heptaldehyde was added to this solution, its color faded to a light amber. After a 3 h reflux period the reaction mixture was worked up and subsequent GLC analysis established that the Wittig product, $Me_3SnCH_2CH{=}CHC_6H_{13}$-n, had been produced in 83% yield. Its NMR spectrum showed two Me_3Sn resonances, indicative of the presence of *cis* and *trans* isomers, and a strong absorption in its infrared spectrum at 960 cm^{-1} showed that the *trans* isomer predominated.

Other bases were examined for applicability in the deprotonation step. Lithium bis(trimethylsilyl)amide gave equally good results, but phenyllithium was not sufficiently selective. When $[Ph_3PCH_2CH_2SnMe_3]^+\ I^-$ was treated with phenyllithium, the ylide was formed in lower yield (as indicated by its subsequent Wittig reaction) and trimethylphenyltin was formed (in 20% yield) as well. Thus phenyllithium reacts as a nucleophile, attacking at tin, as well as a base (eq. 6). The other products of this reaction were not isolated.



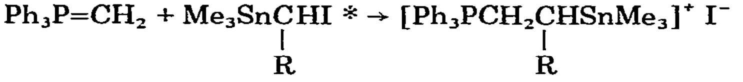
$$\begin{array}{lll} [Ph_3P{-}CH_2{-}CH_2{-}SnMe_3]^+\ I^- & \xrightarrow{\text{path a}} & Ph_3P{=}CHCH_2SnMe_3 + C_6H_6 + LiI \\ \quad \overset{a}{\nearrow}\qquad\qquad \overset{b}{\nwarrow} & & \\ PhLi \qquad\qquad PhLi & \xrightarrow{\text{path b}} & PhSnMe_3 + CH_2{=}CH_2 + Ph_3P + LiI \end{array} \qquad (6)$$

Similar Wittig reactions of β-trimethylstannylethylidenetriphenylphosphorane were carried out with cyclohexanone and benzaldehyde to give 2-cyclohexylideneethyltrimethyltin (79%) and 3-phenylallyltrimethyltin (*trans* isomer) (40%).

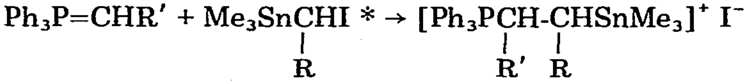
As mentioned above, the phosphonium iodide obtained by addition of iodomethane to β-trimethylstannylethylidenetriphenylphosphorane, $[Ph_3PCH(CH_3)\,CH_2SnMe_3]^+\ I^-$, could not be isolated as the pure solid at room temperature. However, treatment of the reaction mixture in which it was formed with lithium diisopropylamide gave the expected ylide, $Ph_3P{=}C(CH_3)\,CH_2SnMe_3$. Treatment of this reagent with propionaldehyde produced $Me_3SnCH_2C(CH_3){=}CHCH_2CH_3$ (1/1 *E*/*Z* isomer mixture) in 39% yield.

The yields obtained in these allyltin syntheses were not all high, but it is likely that they can be improved. On the basis of the examples given above it is clear that a wide variety of allylic tin compounds can be prepared by this procedure. The reaction of $Ph_3P{=}CHCH_2SnMe_3$ with aldehydes and ketones appears to present no problems and should be of broad applicability. Ylides of type $Ph_3P{=}C(R)\,CH_2SnMe_3$ can be prepared by alkylation of $Ph_3P{=}CHCH_2SnMe_3$ followed by deprotonation of the resulting α-substituted β-trimethylstannylethyltriphenylphosphonium halide. Alternatively, they should be accessible via reactions of substituted ylides, $Ph_3P{=}CHR$, with iodomethyltrimethyltin, followed by deprotonation of the phosphonium halide thus formed. In either route, on the basis of what was observed with

$[Ph_3PCH(CH_3)\,CH_2SnMe_3]^+\,I^-$, one may expect that the α-substituted phosphonium halide will be unstable and that an in situ procedure will have to be used. Phosphonium halides of type $[Ph_3PCH_2CH(R)\,SnMe_3]^+\,I^-$ and $[Ph_3PCH(R')\,CH(R)\,SnMe_3]^+\,I^-$ also may be prepared (eq. 7 and 8), and these will provide the ylides $Ph_3P{=}CHC(R)\,SnMe_3$ and $Ph_3P{=}C(R')\,CH(R)\,SnMe_3$.



$$Ph_3P{=}CH_2 + Me_3Sn\underset{R}{\underset{|}{C}}HI\,{}^{*} \rightarrow [Ph_3PCH_2\underset{R}{\underset{|}{C}}HSnMe_3]^+\,I^- \qquad (7)$$



$$Ph_3P{=}CHR' + Me_3Sn\underset{R}{\underset{|}{C}}HI\,{}^{*} \rightarrow [Ph_3P\underset{R'}{\underset{|}{C}}H\text{-}\underset{R}{\underset{|}{C}}HSnMe_3]^+\,I^- \qquad (8)$$

Again, it is possible that the phosphonium salts will not be stable and that an in situ procedure will need to be used.

In conclusion, we take note of an alternate route to $Ph_3P{=}CHCH_2SnMe_3$ reported by Hannon and Traylor [8] who added trimethyltinlithium to vinyltriphenylphosphonium bromide (eq. 9). The ylide thus produced was treated

$$Me_3SnLi + [CH_2{=}CHPPh_3]^+\,Br^- \xrightarrow{-95^\circ C} Ph_3P{=}CHCH_2SnMe_3 + LiBr \qquad (9)$$

with sufficient cyclohexanone to discharge the red ylide color. Cyclohexylideneethyltrimethyltin was obtained and a yield of 90%, based on cyclohexanone used, was reported. Since the quantity of cyclohexanone used was not disclosed, it is impossible to evaluate the effectiveness of this procedure. In our hands this procedure gave moderate yields of the expected allylic tin product (44% yield, Wittig reaction at −95°C; 48% yield, Wittig reaction at room temperature), based on the 1/1 $Me_3SnLi/[CH_2{=}CHPPh_3]^+\,Br^-$ stoichiometry used. Furthermore, the reaction was complicated by the formation of substantial quantities of hexamethylditin (31% yield in the room temperature reaction).

As noted in the Introduction, the impetus for this work was provided by our need for a practical synthesis of a 3,3-difluoroallylstannane. *β-Trimethylstannylethylidenetriphenylphosphorane proved to be a useful reagent for the synthesis of* $Me_3SnCH_2CH{=}CF_2$ [9a]. Details of this aspect of our work will be provided in a subsequent paper.

One of the useful synthetic applications of allylic tin compounds is their conversion, by transmetalation with an organolithium reagent, to allyllithium compounds. A separate paper describes the preparation of the respective allylic lithium reagents from the allylic tin compounds reported here and some of their reactions [9b].

Experimental

General comments

All reactions were carried out in flame-dried glassware under an atmosphere of dry argon or nitrogen. All solvents were rigorously dried, diethyl ether by distillation from lithium aluminum hydride, tetrahydrofuran (THF) from sodium benzophenone ketyl.

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* Such compounds where $R = CH_3$ and Me_3Si have been prepared [4].

Infrared spectra were recorded using a Perkin—Elmer Model 457A grating infrared spectrophotometer, proton NMR spectra using a Varian Associates T60 spectrometer. Chemical shifts are reported in δ units, ppm downfield from internal tetramethylsilane. Internal standards used were tetramethylsilane, chloroform and dichloromethane. Gas-liquid chromatography (GLC) was used in product analysis, yield determinations and for isolation of pure product samples for analysis and spectroscopy.

Starting materials

Iodomethyltrimethyltin [4b], trimethyltinlithium [10] and vinyltriphenylphosphonium bromide [11] were prepared by literature procedures. Methylenetriphenylphosphorane was prepared by the action of phenyllithium on methyltriphenylphosphonium iodide or bromide [12]. or salt-free, by the reaction of sodamide in liquid ammonia with methyltriphenylphosphonium bromide [13].

Preparation of β-trimethylstannylethyltriphenylphosphonium iodide

A one-liter, three-necked, round-bottomed flask equipped with a paddle stirrer, a 250 ml addition funnel and a nitrogen inlet tube was charged with 113.3 g (0.318 mol) of methyltriphenylphosphonium bromide and 500 ml of diethyl ether. Subsequently 338 ml of 0.99 *M* phenyllithium in diethyl ether (0.334 mol) was added dropwise over a period in 1 h and the resulting mixture was stirred overnight at room temperature to give a solution of methylenetriphenylphosphorane.

A two-liter, three-necked, round-bottomed flask equipped with a paddle stirrer, a 500 ml addition funnel and a nitrogen inlet tube was charged with 105.0 g (0.345 mol) of iodomethyltrimethyltin and 200 ml of diethyl ether and the solution was cooled in an ice bath. The clear $Ph_3P{=}CH_2$ solution was cannulated into the addition funnel and then was added dropwise to the Me_3SnCH_2I, with stirring, over a period of 2 h. The resulting slurry, consisting of a fine, light yellow precipitate and an orange supernatant solution, was stirred at room temperature overnight. Subsequent filtration gave an off-white solid which was washed thoroughly with diethyl ether and dried in vacuum at room temperature. The solid thus obtained (170.0 g, 92%) was a fine, off-white powder, m.p. 115—118°C (dec.). Proton NMR analysis of a sample in $CDCl_3$ showed it to be a mixture of $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ and $[Ph_3PCH_3]^+ I^-$. The composition was determined by examining the integration of the methyl and methylene protons on the carbon atoms adjacent to phosphonium function in the δ 3—4 ppm region. A ratio of 3.88/1 was observed by comparing the integration of the PCH_2 group of the tin compound to the PCH_3 group of the impurity. Correcting for the different numbers of protons in the two groups gave a 5.82/1 mole ratio of the tin-substituted phosphonium salt to the $[Ph_3PCH_3]^+$ impurity, or an 85 mol.% purity of the the $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$. This is equivalent to an 89 weight% purity. In a number of such preparations, carried out on scales of 15 to 350 mmol, product purities of 80—90 mol.% were obtained.

A pure sample of the product was obtained by adding a sufficient quantity of ethanol/ethyl acetate (1/4) to dissolve approximately one-half of the sample used. The mixture was warmed to 50°C and filtered hot. As the filtrate cooled, analytically pure $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ slowly crystallized, m.p. 122.5—123.5°C (dec.). (Anal.: Found: C, 47.53; H, 4.89. $C_{23}H_{28}IPSn$ calcd.: C, 47.54; H, 4.86%). IR ($CHCl_3$): 3030w, 2930s (br), 1590m, 1480m, 1440s, 1390w, 1310w, 1205m (br), 1110s, 990m cm^{-1}. NMR($CDCl_3/CHCl_3$): δ 0.27 (s, 9 H, $J(^{119}Sn—^1H)$ 55 Hz, $J(^{117}Sn—^1H)$ 53 Hz, Me_3Sn), 0.60—1.32 (broad, complex m, 2 H, $SnCH_2$), 3.33—4.13 (broad, complex m, 2 H, PCH_2), 7.60—7.66 (m, 15 H, Ph_3P).

In such syntheses methyltriphenylphosphonium bromide and iodide gave comparable results. The use of salt-free methylenetriphenylphosphorane [13] offered no particular advantages in product yield or purity.

Thermal decomposition of β-trimethylstannylethyltriphenylphosphonium iodide

A 100 ml one-necked flask equipped with a magnetic stirbar was charged with 1.324 g (2.28) mmol of $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ (97% pure). The flask was fitted to a three-way stopcock, which was connected, with all-glass connections, to a high vacuum line and a mercury manometer, and the system was evacuated. The stopcock then was turned to connect only the flask and the manometer and the flask was heated to 160°C. Gas evolution started at about 120°C and was complete after 30 min at 160°C. The system was cooled to room temperature and the quantity of gas was determined to be 1.85 mmol (109.5 ml, 312 mmHg, 23°C, 81% yield). In separate experiments the gas was characterized as ethylene by IR spectroscopy and by bromination to give 1,2-dibromoethane.

The contents of the flask were extracted with 20 ml of hot benzene. Filtration left 0.406 g of red, benzene-insoluble residue whose NMR spectrum showed the presence of a methyltin species (δ 1.36, J(Sn—H) 74 Hz, 43% of total H); a multiplet (δ 1.75—2.05, 8% of total H); a multiplet characteristic of a Ph_3PCH_x species (δ 3.38—3.9, 8% of total H) and a $(C_6H_5)_3P$ moiety (δ 7.53—7.78, 68% of total H). The benzene extracts were treated with 1 ml of iodomethane and stirred for 24 h at room temperature to give 0.433 g (1.07 mmol, 47% yield) of $[Ph_3PCH_3]^+ I^-$, m.p. 184—187°C, whose NMR spectrum was identical to that of an authentic sample. The filtrate was analyzed by GLC (10% Carbowax 20M on Chromosorb W at 150°C) and it was determined that 0.976 mmol (43%) of trimethyltin iodide ($n^{25}D$ 1.5706) was present. The IR spectrum and the GLC retention time of this product were identical with those of an authentic sample.

Wittig reactions of β-trimethylstannylethylidenetriphenylphosphorane

(1) With n-heptaldehyde. Lithium diisopropylamide was prepared by the method of Creger [14]. A 250 ml, one-necked, round-bottomed flask equipped with a magnetic stirbar and a no-air stopper was charged with 7.7 ml (55 mmol) of diisopropylamine (distilled from $LiAlH_4$) and 100 ml of THF and then was cooled to 0°C in an ice bath. A 2.07 *M* (by double titration) solution of n-butyllithium (26.6 ml, 55 mmol) was added dropwise over a 10 min period. The resulting pale yellow solution was stirred at room temperature at 0°C for 30 min.

A 500 ml three-necked, round-bottomed flask equipped with a paddle stirrer, a nitrogen inlet tube and a no-air stopper was charged with 29.0 g of $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ (89% purity by weight, equivalent to 44.5 mmol) and 150 ml of THF. This slurry was cooled in an ice bath and then the i-Pr_2NLi solution was cannulated into it all at once. The red-orange color characteristic of the ylide was formed immediately and after 10 min a homogeneous solution had resulted. The deep orange-red solution was stirred for 45 min and then 9.0 ml (65 mmol) of freshly distilled n-heptaldehyde was added in one portion. The color of the solution faded to a light amber and after a few minutes a light-colored precipitate began to form. The reaction mixture was stirred and heated at reflux for 3 h. Subsequently it was transferred by cannula to a flame-dried, nitrogen-flushed 500 ml round-bottomed flask which was fitted to a vacuum system. Trap-to-trap distillation (room temperature at 0.03 mmHg) into a receiver cooled to —78°C was followed by concentration of the distillate. Distillation of the residue gave 8.85 g (69%) of product. GLC analysis of an aliquot of the trap-to-trap distillate showed the product had been formed in 83% yield.

2-Nonenyltrimethyltin: b.p. 63—68°C at 0.25 mmHg, n_D^{25} 1.4796. (Anal.: Found: C, 49.96; H, 9.04. $C_{12}H_{26}Sn$: C, 49.87; H, 9.07%). NMR (CCl_4): δ 0.05 (s; 9H, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz, Me_3Sn), 0.68—2.55 (m, 15H, all alkyl protons, including 1.68, d, J 9Hz, $SnCH_2$, and other maxima at 0.87 and 1.27), 4.82—5.78 ppm (m, 2H, CH=CH). Close examination of the NMR spectrum showed two CH_3—Sn resonances, at 0.02 as well as at 0.05 ppm, presumably due to the presence of both *cis* and *trans* isomers. By analogy with 3-phenylallyltrimethyltin (see below) and 2-butenylstannanes and silanes [15], the higher field resonance of lower intensity may be attributed to the *cis* isomer and the lower field resonance to the *trans* isomer. The NMR peak height ratio indicated a *trans/cis* isomer ratio of 70/30. The two isomers could not be separated using a variety of boiling point and polarity GLC columns. The predominance of the *trans* isomer was confirmed by the presence of a medium-to-strong absorption at 960 cm^{-1} in the infrared spectrum of the mixed isomers [16].

Use of $(Me_3Si)_2NLi$ in place of i-Pr_2NLi in the generation of the ylide gave 2-nonenyltrimethyltin in 71% yield.

(2) With Cyclohexanone. Essentially the same procedure was used in the reaction of $Ph_3P{=}CHCH_2SnMe_3$ (from 29.0 g of $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ of 89 weight% purity, equivalent to 44.5 mmol) and cyclohexanone (65 mmol) (3 h at reflux in THF). Vacuum distillation of the trap-to-trap distillate gave 6.64 g (55%) of 2-cyclohexylideneethyltrimethyltin, b.p. 59—60°C at 62 mmHg, n_D^{25} 1.5138 (62% yield by GLC analysis of the trap-to-trap distillate). (Anal.: Found: C, 48.24; H, 8.26. $C_{11}H_{22}Sn$ calcd.: C, 48.40; H, 8.12%). NMR (CCl_4): δ 0.05 (s, 9H, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz, Me_3Sn), 1.32—2.28 (complex m, 12H, includes 1.60, d, J 9 Hz, m at 1.32—1.58, ring protons on carbon atoms adjacent to the double bond, and m at 1.85—2.28, other ring protons), 5.18 ppm (t, J 9 Hz, 1H).

In another such reaction carried out using 8.63 mmol of the phosphonium salt in THF/Et_2O medium, a 2 h reaction time at room temperature, and in which the filtered reaction mixture was hydrolyzed with water, the GLC yield of 2-cyclohexylideneethyltrimethyltin was 79%.

(3) With Benzaldehyde. The procedure described in (1) above was used in the reaction of the ylide prepared from 29.0 g of $[Ph_3PCH_2CH_2SnMe_3]^+ I^-$ of 89 weight% purity (44.5 mmol) and 65 mmol of benzaldehyde. A reaction time of 2.5 h at reflux was used. Distillation of the trap-to-trap distillate at reduced pressure gave 4.80 g (40%) of *trans*-3-phenylallyltrimethyltin, b.p. 84—86°C at 0.23 mmHg, n_D^{25} 1.5743 (44% yield by GLC analysis of the trap-to-trap distillate). (Anal.: Found: C, 51.46; H, 6.51. $C_{12}H_{18}Sn$ calcd.: C, 51.30; H, 6.46%). NMR (CCl_4): δ 0.12 (s, 9H, $J(^{119}Sn—^1H)$ 53 Hz, $J(^{117}Sn—^1H)$ 51 Hz, Me_3Sn), 1.90 (d, J 9 Hz, 2H, $SnCH_2$), 6.17—6.30 (m, 2H, CH=CH), 7.18 ppm (s, 5H, Ph). The infrared spectrum showed a strong band at 960 cm^{-1}, indicative of the *trans* structure.

In another experiment, diethyl ether, rather than THF, was employed as the solvent for the Wittig reaction. In this case, a *cis*/*trans* isomer mixture of 3-phenylallyltrimethyltin was formed. According to the NMR spectrum and GLC analysis, the *trans*/*cis* ratio was 62/38. The predominant isomer showed a strong absorption at 960 cm^{-1} in its IR spectrum and its Me_3Sn resonance was at lower field than that of the *cis* isomer. NMR, *cis* isomer (CCl_4): δ 0.08 (s, 9H, Me_3Sn), $J(^{119}Sn—^1H)$ 53 Hz, $J(^{117}Sn—^1H)$ 51 Hz), 2.07 (d, J 9 Hz, 2H, $SnCH_2$), 5.53—6.70 (m, 2H, CH=CH), 7.23 (s, 5H, Ph).

Attempted preparation of β-trimethylstannylisopropyltriphenylphosphonium iodide, $[Ph_3PCH(CH_3)CH_2SnMe_3]^+ I^-$

A solution of $Ph_3P=CHCH_2SnMe_3$ was prepared from 37.5 mmol of the phosphonium salt in 150 ml of diethyl ether as described above.

A one-liter, three-necked, round-bottomed flask equipped with a paddle stirrer, a nitrogen inlet tube and a 500 ml pressure equalizing addition funnel was charged with 6.2 ml (ca. 100 mmol) of iodomethane and 200 ml of diethyl ether and then was cooled in an ice bath. The clear, deep red ylide solution was cannulated into the addition funnel and then was added dropwise to the rapidly stirred iodomethane solution over a period of 30 min. The red ylide color was discharged immediately and a light yellow precipitate was formed. After the reaction mixture had been stirred at 0°C for 30 min, it consisted of a fine, light yellow precipitate and a light yellow supernatant liquid. The ice bath then was removed. As the mixture warmed to room temperature the powder began to stick to the walls of the flask and to darken in color. The supernatant solution was cannulated away and the reaction vessel was evacuated and maintained at 0.1 mmHg overnight. The syrupy solid appeared to "dry out", forming a dry yellow powder. After it had been kept at room temperature under nitrogen for a while, this powder again became syrupy and darker in color. NMR analysis showed the presence of Me_3SnI and during the obvious decomposition a gas appeared to be evolved.

A stable derivative of the β-trimethylstannylisopropyltriphenylphosphonium cation was prepared as follows.

β-Trimethylstannylethylidenetriphenylphosphorane was prepared from 49 mmol of the phosphonium salt in THF solution. Subsequently the clear ylide solution was evaporated at 30°C and 0.09 mmHg. The dark red residue was dissolved in 200 ml of diethyl ether, cannulated into a 500 ml centrifuge bottle and centrifuged. A clear, red, amine-free solution of $Ph_3P{=}CHCH_2SnMe_3$ resulted.

A 500 ml, three-necked flask equipped with a paddle stirrer, a 250 ml pressure equalizing addition funnel and a nitrogen inlet tube was charged with 3.75 ml (ca. 60 mmol) of iodomethane and 150 ml of diethyl ether and cooled to —20° C. Then 84 ml of the ylide solution (ca. 19 mmol) was syringed into the addition funnel and added dropwise with stirring. The resulting suspension was stirred at —20° C for 30 min and subsequently the supernatant solution was removed by cannulation. The solid residue was dissolved in 100 ml of chilled (0° C) absolute ethanol. To this solution was added a solution of 7.08 g (20 mmol) of Reinecke's salt, $[NH_4]\ [Cr(NH_3)_2(SCN)_4] \cdot H_2O$, in 300 ml of absolute ethanol. A fine red precipitate began to form, and the mixture was stirred at 0° C overnight. Filtration gave a fine red powder which was washed with cold ether and dried over P_2O_5 at 0.1 mmHg. A total of 8.70 g was obtained. A portion was recrystallized from ethanol/water to to give long, fine red needles, m.p. 83—85° C (dec.). (Anal.: Found: C, 41.85; H, 4.77. $C_{28}H_{36}N_6S_4PCrSn \cdot H_2O$ calcd.: C, 41.80; H, 4.76%).

Wittig reaction of β-trimethylstannylisopropylidenetriphenylphosphorane with propionaldehyde

The $Ph_3P{=}CHCH_2SnMe_3$ solution prepared from 94.0 mmol of the phosphonium salt in 300 ml of THF was added, as described above, to a solution of 7.32 ml (115 mmol) of iodomethane in 200 ml of THF at —20° C, dropwise with stirring. To the resulting suspension of $[Ph_3PCH(CH_3)\ CH_2SnMe_3]^+\ I^-$ was added in one portion a solution of 127 mmol of $i\text{-}Pr_2NLi$ in THF. After it had been stirred at —20° C the reaction mixture again became a homogeneous, deep red solution. After 45 min at room temperature, this solution was treated with 10.1 ml (140 mmol) of propionaldehyde and the resulting mixture was stirred at reflux for 90 min. Subsequent trap-to-trap distillation at 0.1 mmHg into a receiver at —78° C was followed by GLC analysis of the distillate (20% SE 30 on Chromosorb P) which showed the presence of 2-methyl-2-pentenyltrimethyltin, $Me_3SnCH_2C(CH_3){=}CHCH_2CH_3$ in 39% yield. Vacuum distillation gave this product, b.p. 41—44°C at 3.0 mmHg, n_D^{25} 1.4835, in 31% yield. (Anal.: Found: C, 43.89; H, 8.27. $C_9H_{20}Sn$ calcd.: C, 43.77; H, 8.16%). The NMR spectrum (in CCl_4) indicated that a 1/1 mixture of *E* and *Z* isomers was present: δ 0.13 and 0.17 (2s, 9H total, Me_3Sn, both isomers, $J(^{119}Sn—^1H)$ 52 Hz, $J(^{117}Sn—^1H)$ 50 Hz), 0.97 (t, *J* 7 Hz, 3H, CH_2CH_3), 1.45—2.32 (m, 7H), 4.85 and 4.97 (2t, *J* 7 Hz, 1H total, =CH of both isomers).

Preparation of β-trimethylstannylethylidenetriphenylphosphorane by addition of trimethyltinlithium to vinyltriphenylphosphonium bromide

A 250 ml three-necked flask equipped with a drain containing a medium frit and stopcock, a Hershberg stirrer, an argon inlet tube and a no-air stopper was flame-dried, flushed with argon and charged with 23.6 g (0.118 mol) of trimethyltin chloride and 125 ml of THF. To the stirred solution was added 2.5 g (0.35 g atom) of finely cut lithium. An exothermic reaction took place and the reaction mixture became yellow-green after it had been stirred for 5 min. Stirring was continued at room temperature for 15 h and then the mixture was filtered into a flame-dried, argon flushed flask connected to an argon source and bubbler. An aliquot of the resulting solution of Me_3SnLi was quenched with an excess of n-butyl bromide and then analyzed for n-butyltrimethyltin by GLC (10% DC 200 on Chromosorb W, 100°C). A 71% yield of the latter was obtained. GLC analysis also demonstrated the absence of hexamethylditin in the Me_3SnLi solution.

A 200 ml three-necked flask equipped with a dropping funnel, an argon inlet tube, a pentane thermometer and a magnetic stirbar was charged with 6.604 g (17.88 mmol) of $[Ph_3PCH{=}CH_2]^+ Br^-$ and 40 ml of diethyl ether and the resulting slurry was cooled to —95°C. Trimethylstannyllithium (37.5 ml of THF solution containing 17.9 mmol) was added dropwise over a 30 min period. A red solution formed immediately. After the mixture had been stirred at —93°C for 5 min most of the salts had been consumed. Cyclohexanone was added to the reaction mixture until a color change to bright yellow took place (1.34 g, 13.6 mmol, added). Subsequently, another 0.65 g (20.5 mmol total) was added and the mixture was allowed to warm to room temperature and then stirred for another hour. Filtration was followed by washing of the filtrate with two 75 ml portions of water, drying and concentration at atmospheric pressure. The residue was analyzed by GLC (10% DC 200 on Chromosorb W, 100°C); present were hexamethylditin (30% yield based on Me_3SnLi) and 2-cyclohexylideneethyltrimethyltin (44%). Both products were identified by comparison of their NMR spectra and GLC retention times with those of authentic samples.

A similar reaction carried out at room temperature instead of at —95 to —93°C gave hexamethylditin in 31% yield and 2-cyclohexylideneethyltrimethyltin in 48% yield.

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