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SYNTHESIS OF SUBSTITUTED ARYLTRIMETHYLSTANNANES BY THE REACTION OF TRIMETHYLSTANNYLSODIUM WITH ARYL BROMIDES

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Summary

The preparation of substituted aryltrimethylstannanes by the reaction of aryl bromides with trimethylstannylsodium in tetraglyme has been studied. Among the substituents present on the aromatic rings were bromine, chlorine, amino, formyl, acetyl and methoxycarbonyl. Factors affecting the success of these and other preparations are discussed in terms of a previously proposed mechanism involving the formation of arylsodium and bromotrimethylstannane as intermediates. These can react with each other in the solvent cage in which they are formed, or after diffusion into the bulk of the solvent. Side reactions can occur by reaction of the arylsodium with functional substituents.

Organic halides are used in the synthesis of organotin compounds either by conversion to the Grignard reagent, followed by reaction with the organotin halide, eq. 1, or by conversion of an organotin halide to the organostannylalkali compound, followed by reaction with the organic halide, eq. 2 (M = alkali metal). The first application of organostannylalkali derivative to the synthesis of an aryltrimethylstannane was reported by Kraus and Sessions in 1922 who treated

$$R—X + Mg \rightarrow RMgX \xrightarrow{R'_3SnX} R—SnR'_3 + MgX_2 \quad (1)$$

$$R'_3SnX + 2M \rightarrow MX + R'_3SnM \xrightarrow{RX} R—SnR'_3 + MX \quad (2)$$

p-dichlorobenzene with trimethylstannylsodium in liquid ammonia and obtained *p*-bis(trimethylstannyl)benzene in unspecified yield [1]. Two years later Bullard and Robinson [2] prepared phenyltrimethylstannane in 14% yield by a similar procedure. Since these early reports, no others appeared until more than a

(continued on p. 32)

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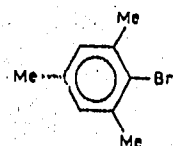
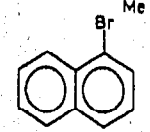
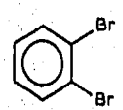
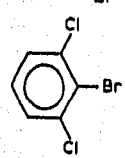
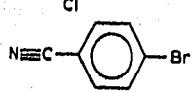
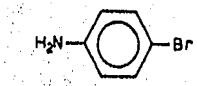
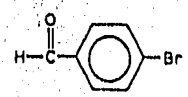
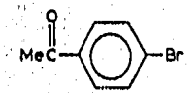
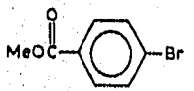
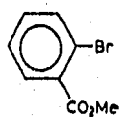
TABLE 1

SYNTHESIS OF ARYLSTANNANES

ArBr	$ArSnMe_3$ (%)	ArH (%)	proton NMR [a]		IR [c]	Elemental analysis found (calcd.) (%)	
			$Sn(CH_3)_3$ (ppm) [b]	$^2J(SnCH)$ (Hz)	cm^{-1} (assignment)	C	H
	88 [d]		0.337 lit. [e] (0.323)	53.0 (53.0)			
	91 [d]		0.425 lit. [f] (0.403)	53.8 (54.1)			
	42 [d,h]	7 [i]	0.306 lit. [m] (0.305)	53.0 (53.0)			
	60 [d]		0.470	56.7	790 (C—Cl)	35.01(34.89)	3.90(3.86)
	82 [d]		0.344 [j]	56.0 [j]	2260 (C≡N)	45.30(45.17)	4.92(4.93)

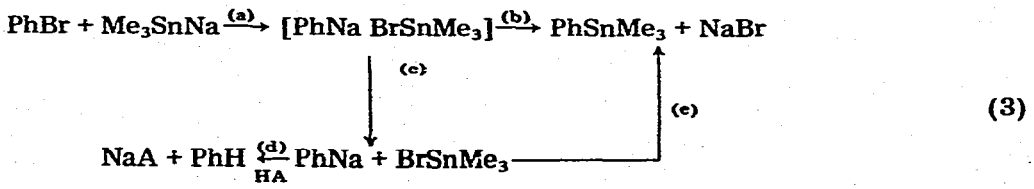
	40[j]	60[j]	0.204	53.5	3350 (NH_2)	42.40(42.24)	5.95(5.91)
	39[k,ll]	—	0.325	55.3	2830 2740 (—C(=O)—H) 1705 (—C(=O)—)	44.75(44.67)	5.27(5.25)
	56[j]	43[j]	0.308	55.0	1680 (—C(=O)—)	46.84(46.70)	5.69(5.70)
	78[j]	2[j]	0.308	55.2	1730 (—C(=O)—O)	44.54(44.20)	5.40(5.40)
	78[d]	—	0.290[l]	55.1[l]	1725 (—C(=O)—O)	44.28(44.20)	5.49(5.40)

[a] Recorded in CCl_4 unless oterwise noted. [b] Relative to internal TMS. [c] Recorded as a thin film between KBr plates. [d] Isolated yield. [e] Ref. 6. [f] Ref. 11. [g] o-Dibromobenzene was added to trimethylstannylsodium in this case. [h] o-Bis(trimethylstannyl)benzene. [i] Trimethylphenylstannane; percentage determined from area on GLC trace; not corrected for response factor. [j] Yield determined by GLC. [k] Isolated as a mixture of benzaldehyde and *p*-formylphenyltrimethylstannae; yield was estimated by NMR integration. [l] Recorded in $CDCl_3$. [m] Ref. 10. [n] See Experimental.

quarter of a century later. These involved the reaction of triphenylstannyllithium with iodobenzene in ether [3], with bromobenzene in tetrahydrofuran [4], and with several substituted iodo- and brom-benzenes in ether [5]. The yields of tetraphenylstannane were 66% and 75% with the unsubstituted halobenzenes, but were below 45% in all of the other examples cited. Perhaps these latter results have acted as a deterrent to the use of reaction 2 as a general method for the preparation of arylstannanes. As a part of a study of the scope and mechanisms of the reactions of organostannylalkalis, we have developed a procedure which is synthetically useful, and can be used for the preparation of organofunctional arylstannanes which could not be prepared by reaction sequence 1.

Reactions were conducted by adding trimethylstannylsodium in tetraglyme (ca. 1 *M*) to an appropriate volume of the aryl bromide (also ca. 1 *M*) in the same solvent maintained at 0°C throughout the period of addition. Compositions of the reaction product mixtures were analyzed by GLC. Products were characterized by their spectral properties and elemental analyses. When the arylstannane was to be isolated this could be done easily by hydrolysis of the reaction mixture with water and extraction of the product into petroleum ether to provide a solution free of tetraglyme, which could be concentrated. The product then was distilled. Results are gathered in Table 1 for ten aryl bromides. In those cases where comparisons are possible, the yields are superior to those obtained by the Grignard method of eq. 1. For example, our yields of stannane obtained from bromomesitylene and 1-bromonaphthalene were 88% and 91%, respectively, whereas the Grignard method has been reported to give yields of 68% [6] and 57% [7] respectively, for these compounds. Not included in the table are the observations that bromobenzene and *p*-bromotoluene provide phenyl- and *p*-tolyltrimethylstannanes in nearly quantitative yield as determined by GLC [8].

The bromides used for the other syntheses for which data are recorded in Table 1 fall into two categories. *o*-Dibromobenzene and 2,6-dichlorobromobenzene would react with magnesium to form Grignard reagents which would undergo loss of magnesium halide to form benzyne before they could be used in the second step of eq. 1. The remainder of the bromides have functional groups which would react with the Grignard reagents. Yet all they provide modest to good yields of arylstannane by the method of eq. 2. A rationale for the pattern of yields which is shown in Table 1 follows directly from consideration of the gross mechanism shown in eq. 3 [8] which accomodates all of the experimental information currently available *. The first step represents a nucleophilic attack by the trimethylstannyl anion on the bromine of the aryl



(3)

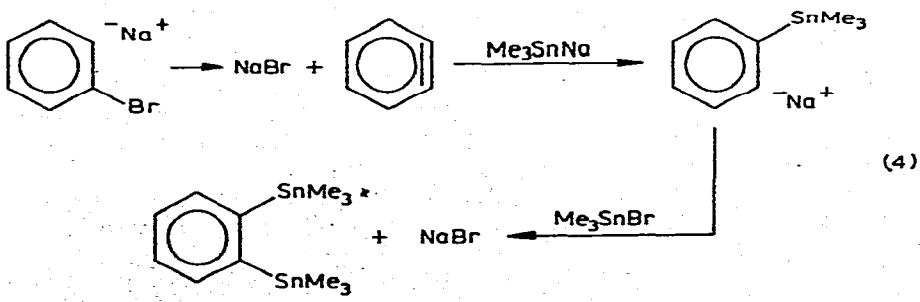
* This mechanism may not be complete in detail, but the evidence for the intermediacy of an aryl anion is compelling [8,9]. The possibility that the first step in the reaction is actually an electron transfer from trimethylstannyl anion to the aryl bromide has not been eliminated.

bromide to form arylsodium and trimethyl bromostannane in a solvent cage represented by the brackets. This reaction occurs much more rapidly than the attack at the carbonyl group or at a proton of the functional group on the benzene ring. The species in the cage react with each other to form product in step b, or they may diffuse apart in step c and form product in step e instead. If a proton source, HA, is present in the medium, then step d may compete with, and may be much faster than, step e. This leads to the formation of the reduction product, here represented by PhH. An alternative competition step is the reaction of PhNa with the carbonyl group of the reactant (or product) in any of the last four examples listed in the table. Steps a and c constitute a conventional halogen—metal exchange which has been shown to occur with *ortho* substituted iodobenzenes [5a].

With this scheme in mind we conclude that, in the case of *p*-bromoaniline, about 40% of caged species couple in reaction b to form substitution product; the remainder diffuse out of the cage and the *p*-aminophenylsodiums abstract protons from the amino groups to form the reduction product, aniline. The last two items in Table 1 indicate that reaction of the arylsodium with ester groups is not a serious side reaction, for the yields of substitution product are quite satisfactory. Interestingly, the major by-product formed from *p*-bromoacetophenone is the reduction product, acetophenone. This indicates that *p*-acetylphenylsodium reacts with the acetyl groups by proton abstraction rather than by attack at the carbonyl carbon. In fact, the latter reaction hardly competes at all for the combined yield of reduction and substitution products is 99%.

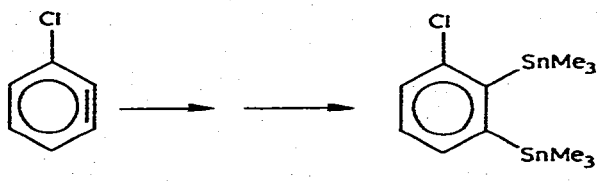
The reaction with *p*-bromobenzaldehyde presents another interesting case, for no substitution product was observed when the reaction was carried out under the conditions used for the other substrates: only polymeric product was formed. This was attributed to reaction of *p*-formylphenylsodium with aldehyde groups of both reactant and product. However, if this species could be removed by reaction with an effective trap HA in reaction d then the coupling product formed within the cage could be salvaged. Indeed when the reaction was conducted in the presence of t-butyl alcohol (see Experimental) the 39% yield of *p*-formylphenyltrimethylstannane shown in Table 1 was obtained.

If arylsodiums are intermediates in these reactions, one would expect that benzynes might be formed when *o*-dibromobenzene and 2,6-dichlorobromobenzene are substrates. To test this possiblity, the reaction of the former with trimethylstannylsodium was carried out in the presence of furan. The reaction product mixture did contain the adduct of benzyne and furan, which was characterized by proton NMR; and it was converted by treatment with acid to 1-naphthol. Reaction sequence 4 accounts for the formation of *o*-bistrimethylstannylbenzene [10] by way of the benzyne intermediate.



(4)

If a benzyne were formed as a major intermediate from 2,6-dichlorobromobenzene it would be expected to react as in eq. 5 as one possibility. The gas chromatogram showed no indication of a product with retention time in the appropriate range. Thus, if a benzene is formed, it suffers a different fate. In



(5)

any case, the major course of reaction is the simple replacement of the bromine by the trimethylstannyl group. This implies that 2,6-dichlorophenylsodium can react with bromotrimethylstannene faster than it loses chloride ion to form benzyne.

The results presented above, taken together with those available in the literature, suggest some guidelines for synthesis of arylstannens by the reaction of aryl bromides with organostannylalkalis. The success of Tamborski and coworkers [4] indicates that preparation of the organostannylalkali from the reaction of the alkali metal with distannane or halostannane in an aprotic solvent is desirable. Our results provide confirmation. If functional groups are present in the aryl substrate, then use of a viscious solvent such as tetraglyme will increase the yield of coupling product formed from the initially formed species within the solvent cage. A protoic solvent such as liquid ammonia would seem to be a questionnable choice, for it can react with the arylalkali formed as an intermediate, and is of low viscosity, a property which will lead to more facile diffusion from the cage and more diversion to reduction product. Poor yields will result unless the organotin halide reacts much faster with the arylalkali than does ammonia.

Experimental

Melting and boiling points are uncorrected. Elemental analyses were performed by Instranal of Rensselaer, New York, Infrared spectra data were recorded on a Beckman IR-8 or IR-10 instrument and are reported in cm^{-1}. Proton magnetic spectra were recorded on a Varian A-60A instrument. Chemical shifts are reported in ppm downfield from internal tetramethylsilane; coupling constants are for $^{119}Sn—^{1}H$.

Trimethylstannylsodium

In a typical preparation, 1.80 g (3.60 mmol) of hexamethyldistannane was added with 0.5 g (22 mmol) of finely cut sodium to 70 ml tetraglyme in a 250 ml three-necked flask fitted with a stopcock at the bottom. The mixture was stirred using a Hirshberg stirrer in an atmosphere of nitrogen for about 4 h. To test for completion of the reaction, a sample was added to bromobenzene to form trimethylphenylstannane, and then analyzed by GLC. The absence of hexamethyldistannane was taken as an indication of complete reaction in the formation of the trimethylstannylsodium; yields were 85—90%. The solution

could then be used immediately if filtered through a plug of cotton; or it could be left to stand overnight whereupon the black suspended solid settled. Samples of the clear greenish yellow supernatant solution were removed by syringe for further use.

1-Naphthyltrimethylstannane

To a cooled solution (0°C) containing 4.510 g (21.78 mmol) of 1-bromonaphthalene (Eastman) in 10 ml of tetraglyme (TG) was added 24 ml (23.7 mmol) of 0.91 *M* trimethylstannylsodium in TG. The reaction mixture was quenched after 2 h with 75 ml of water and 25 ml of saturated ammonium chloride. The aqueous TG layer was then extracted with petroleum ether (3 × 75 ml). The extracts were washed with water (4 × 75 ml), dried ($MgSO_4$) and concentrated to yield 6.52 g of crude product. Fractional distillation through a 15 cm column packed with metal helices afforded 5.79 g (91% yield) of pure 1-napthyltrimethylstannane: b.p. 98—100°C/0.025 Torr (lit. [7] 120—121°C/1.0 Torr); NMR (CCl_4) δ (ppm) 0.425 (s, ^2J(SnCH) 53.8 Hz, 9, $Sn(C\underline{H}_3)_3$), and 7.15—7.85 (m, 7, ArH) (lit. [11] NMR (CCl_4) δ (ppm): 0.403 (s, ^2J(SnCH) 54.1 Hz)].

Mesityltrimethylstannane

Reaction of 4.154 g (20.86 mmol) of bromomesitylene (Aldrich) in 10 ml of TG with 24 ml (21.8 mmol) of 1.91 *M* trimethylstannylsodium was carried out as described above. Distillation of 5.91 g of the crude product through a 15 cm column packed with metal helices provided 5.18 g (88% yield) of pure mesityltrimethylstannane: b.p. 84—86°C/0.27 Torr (lit [6] 65—55°C/0.10 Torr)]; NMR (CCl_4) δ (ppm): 0.337 (s, ^2J(SnCH) 53.0 Hz, 9, $Sn(C\underline{H}_3)_3$), 2.19 (s, 3, *p*-$C\underline{H}_3$), 2.33 (s, $^4J(SnCCH_3)$ 6 Hz, 6, 2, 6 di-$C\underline{H}_3$) and 6.71 (bs, ^4J(SnCCH) 16 Hz, 2, Ar$\underline{H}$).

o-Bis(trimethylstannyl)benzene

A solution containing (4.72 g (20 mmol) of *o*-dibromobenzene (Aldrich) in 10 ml of TG was added to 88 ml of a cooled (0°C) solution of 0.5 *M* (44 mmol) of trimethylstannylsodium in TG. The reaction mixture was worked-up after 8 h by adding 75 ml of water and 25 ml of saturated ammonium chloride and then extracting with petroleum ether (3 × 75 ml). The ether extracts were washed with water (3 × 75 ml), dried ($CaCl_2$) and concentrated to yield 5.94 g of crude product. ELC analysis (6 ft. × 0.25 in. glass column, 5% Apiezon L on 60-80 Chromosorb G, temperature program 50—250°C at 10°C/min, digital integration) of the crude products gave the following compounds in order of elution: compound (% area), $(Me_2Sn)_2$(29%), $Me_3SnC_6A_5$ (5%), *o*-BrC_6H_4Br (5%), not identified (4%). *o*-$BrC_6H_4SnMe_3$ (3%) and *o*-$Me_3SnC_6H_4SnMe_3$ (54%). Distillation through a 15 cm column packed with glass helices provided two fractions. The first fraction contained 0.75 g of impure *o*-bis (trimethylstannyl)benzene (ca. 50% purity): b.p. 50—84°C/0.10 Torr. The second fraction provided 3.49 g (87% purity) of *o*-bis(trimethylstannyl)benzene: b.p. 84°C/0.10 torr (lit. [10] 92—94°C/0.15 Torr); NMR (CCl_4) δ (ppm): 0.306 (s, ^2J(SnCH) 53.0 Hz, 9, $Sn(C\underline{H}_3)_3$) and 7.25 (m, 4, Ar$\underline{H}$ (lit. [10] NMR (CCl_4) δ (ppm): 0.31 (s, ^2J(SnCH) 53 Hz)). Based on the purity of each fraction, the yield of *o*-bis(trimethylstannyl)benzene was 3.42 g (42%).

2,6-Dichlorophenyltrimethylstannane

A solution of trimethylstannylsodium, prepared from 10.43 g (31.84 mmol) of hexamethyldistannane and 3 g (130 mmol) of sodium in 90 ml of TG, was filtered through a cotton plug to remove the excess sodium. This solution was then added to a cooled (—5 to —10°C) solution containing 14.45 g (63.7 mmol) of 1-bromo-2,6-dichlorobenzene (Aldrich) in 40 ml of TG. The reaction mixture was worked up after 12 h by quenching with ethanol and then water. The reaction mixture was then extracted with diethyl ether followed by repeated washing of the ether extracts with water (5 × 100 ml). The dried and concentrated extracts yielded 16.47 g of crude product. GLC analysis (10 ft. × 0.125 in. column, 10% UCW98 on 80-100 Chromosorb W, isothermal at 230°C) of the crude product gave in order of elution: 1-bromo-2,6-dichlorobenzene. TG and 2,6-dichlorophenyltrimethylstannene. Distillation provided 12.35 g (60% yield) of 2,6-dichlorophenyltrimethylstannane: b.p. 74°C/0.10 Torr); NMR (CCl_4) δ (ppm): 0.470 (s, ^2J(SnCH) 56.7 Hz, 9, $Sn(C\underline{H}_3)_2$) and 7.08 (m, 3, Ar$\underline{H}$). Preparative GLC (80 in. × 0.75 in. ss column, 15% Apiezon L on 60-80 Chromosorb W) provided an analytically pure sample.

p-Cyanophenyltrimethylsatannane

To a cooled (0°C) solution containing 3.65 g (20.05 mmol of *p*-bromobenzonitrile (Aldrich) in 20 ml of TG was added 44 ml (22.0 mmol) of 0.5 *M* trimethylstannylsodium in TG. Work-up by extraction with petroleum ether followed by washing with water yielded 5.33 g of crude product. Distillation through a short path distillation apparatus provided 4.39 g (82% yield) of pure *p*-cyanophenyltrimethylatannane: b.p. 97—99°C/0.5 Torr); NMR ($CDCl_3$) δ (ppm): 0.344 (s, ^2J(SnCH) 56.0 Hz, 9, $Sn(C\underline{H}_3)_3$) and 7.58 (m, 4, ArH); IR (thin film) 2260 cm^{-1} (C≡N).

p-Aminophenyltrimethylstannane

To a cooled (0°C) solution containing 3.44 g (20.0 mmol) of *p*-bromoaniline (Eastman) in 20 ml of TG was added 44 ml (22.0 mmol) of 0.5 *M* trimethylstannylsodium in TG. Work-up as above yielded 3.0 g of crude product. GLC analysis (6 ft. × 0.25 in. glass column, 5% Apiezon L on Chromosorb G, temperature program 50—250°C at 10°C/min) of crude product mixture gave in order of elution: $(Me_3Sn)_2$, $C_6H_5NH_2$, *p*-$BrC_6H_4NH_2$ and *p*-$Me_3SnC_6H_4NH_2$. Preparative GLC (80 in. × 0.75 in column, 15% Apiezon L on 60-80 Chromosorb W) afforded pure aniline (NMR identical with authentic sample) and pure *p*-aminophenyltrimethylstannane: NMR (CCl_4) δ (ppm): 0.204 (s, ^2J(SnCH) 53.3 Hz, 9, $Sn(C\underline{H}_3)_3$), 3, 37 (bs, 2, $N\underline{H}_2$) and (6.37—7.13 (A_2B_2 m, 4, ArH); IR (thin film) 3350 cm^{-1} (NH_2).

To obtain absolute yields of aniline and *p*-aminophenyltrimethylstannane, the above reaction was repeated with dodecane added as an internal standard. The reaction mixture was worked-up as above and the pentane extracts concentrated to 2 ml. GLC analysis as above, with digital integration, gave 67% aniline and 40% *p*-aminophenyltrimethylstannane. These values were consistent with those obtained by NMR integration of the crude product mixture.

p-Acetylphenyltrimethylstannane

To a cooled (0°C) solution containing 3.98 g (20 mmol) of *p*-bromoaceto-

phenone (Eastman) in 20 ml of TG was added 44 ml (22 mmol) of 0.05 *M* trimethylstannylsodium in TG. The reaction mixture, worked-up as above after 8 h, provided 4.41 g of crude product. GLC analysis (6 ft. × 0.25 in. glass column, 5% Apiezon L on 60-80 Chromosorb G, temperature program 50—250°C at 10°C/min) of the crude product mixture gave the following compounds in order of elution: $(Me_2Sn)_2$, C_6H_5COMe, *p*-BrC_6H_4COMe and *p*-$Me_3SnC_6H_4COMe$. Distillation through a short path distillation apparatus yielded 1.68 g of impure product: b.p. 100—115°C/1.5 Torr. Purification of the distilled fraction by preparative GLC (80 in. × 0.75 in. column, 15% Apiezon L on 60-80 Chromosorb W, temperature program 150—200° at 10°C/min) provided pure acetophenone (NMR identical with authentic sample) and pure *p*-acetylphenyltrimethylstannane: NMR (CCl_4) δ (ppm): 0.308 (s, ^2J(SnCH) 55.0 Hz, 9, $Sn(C\underline{H}_3)_3$), 2.47 (s, 3, $C\underline{H}_3$) and 7.42—7.88 (A_2B_2 m, 4, Ar<u>H</u>); IR (thin film) 1680 cm^{-1} (C)).

Absolute yields of acetophenone and *p*-acetylphenyltrimethylstannanen were obtained by GLC analysis as above, with digital integration, of a mixture reaction containing dodecane as an internal standard. The yield of acetophenone (43%) was determined before extraction while that for *p*-acetylphenyltrimethylstannane (56%) was obtained after extraction with pentane.

p-Carbomethoxyphenyltrimethylstannane

To a cooled (0°C) solution containing 1.32 g (6.14 mmol) of methyl *p*-bromobenzoate in 6 ml of TG was added 6.75 ml (6.75 mmol) of 1 *M* trimethylstannylsodium in TG. Work-up (as above) after 1 h provided 1.30 g of crude product. Preparative GLC (80 in. × 0.75 in. column, 15% Apiezon L on 60-80 Chromosorb W. isothermal at 200°C) yielded pure *p*-carbomethoxyphenyltrimethylstannane: NMR (CCl_4 δ (ppm): 0.308 (s, ^2J(SnCH) 55.2 Hz, 9, $Sn(C\underline{H}_3)_3$), 3.84 (s, 3, $OC\underline{H}_3$) and 7.39—8.04 (A_2B_2 m, 4, Ar<u>H</u>); IR (thin film) 1730 cm^{-1} (CO_2Me).

The above reaction was repeated with dodecane added as a GLC internal standard. GLC analysis (6 ft. × 0.25 in. glass column, 5% Apiezon L on 60-80 Chromosorb G. temperature program 50—250°C at 10°C/min, digital integration) of the petroleum ether extracts gave 78% yield of substitution product and 2% yield of methyl benzoate.

o-Carbomethoxymethyltrimethylstannane

To a cooled solution (0°C) containing 6.345 g (29.5 mmol) of methyl *o*-bromobenzoate in 30 ml of TG was added 37 ml (29.6 mmol) of 0.8 *M* trimethylstannylsodium in TG. Work-up as above 1.5 h after addition yielded 8.68 g of crude product. Fractional distillation through a 15 cm column packed with glass helices provided 6.90 g (78% yield) of pure substitution product: b.p. 105.5—107°C/1.0 Torr); NMR ($CDCl_3$) δ (ppm): 0.290 (s, ^2J(SnCH) 55.1 Hz, 9, $Sn(C\underline{H}_3)_3$), 3.86 (s, 3, $C\underline{H}_3$) and 7.14—8.22 (m, 4, Ar<u>H</u>); IR (thin film) 1725 cm^{-1} (CO_2Me).

p-Formylphenyltrimethylstannane

Attempts to react trimethylstannylsodium with *p*-bromobenzaldehyde (K & K) under conditions employed with other aryl bromides gave only polymeric products. It was also found that a rapid and very exothermic reaction occurred between trimethylstannylsodium and benzaldehyde. It was of interest to deter-

mine whether reaction at halogen would compete effectively with reaction at the aldehyde. To prevent polymerization due to the arylsodium, reaction was carried out in the presence of t-butyl alcohol.

To a cooled (0°C) solution containing 1.03 g (5.57 mmol) of *p*-bromobenzaldehyde and 0.5 ml (ca. 5 mmol) of t-butyl alcohol in 25 ml of TG was rapidly added 6.2 ml (5.67 mmol) of trimethylstannylsodium in TG. Ten seconds after addition the reaction was first quenched with 5 ml of saturated ammonium chloride and then immediately extracted with petroleum ether (3 × 75 ml). The organic layer was washed repeatedly with water (4 × 75 ml), dried ($MgSO_4$) and concentrated to yield 1.15 g of crude product. The crude product mixture was trap-to-trap distilled (0.025 Torr) to yield 940 mg of volatile product. GLC analysis (6 ft. × 0.125 in. column, 10% Apiezon L on 90-100 Anakrom ABS, temperature program 50—250°C at 10°C/min) gave the following compounds in order of elution: $(Me_3Sn)_2$ + benzaldehyde, and *p*-formylphenyltrimethylstannane. NMR of the volatile product mixture gave: NMR (CCl_4) δ (ppm): 0.22 (s, ^2J(SnCH) 48.5 Hz, ^3J(SnCH) 16 Hz, $(Me_3Sn)_2$), 0.316 (s, ^2J(SnCH) 55.4 Hz, $ArSn(C\underline{H}_3)_3$), 7.30—7.92 (m, Ar<u>H</u>), 10.32 (s, <u>H</u>—CO) and 10.33 (s, <u>H</u>—CO). The estimated yield of *p*-formylphenyltrimethylstannane by NMR integration was 590 mg (38% yield). This value agrees with an estimate obtained by GLC integration. An analytically pure sample was obtained by preparative GLC (6 ft. × 0.25 in. ss column, 5% Apiezon L on 60-80 Chromosorb G, isothermal at 185°C): NMR (CCl_4) δ (ppm): 0.325 (s, ^2J(SnCH) 55.3 Hz, 9, $Sn(C\underline{H}_3)_3$), 7.51—7.96 (m, 4, Ar<u>H</u>) and 9.95 (s, 1, <u>H</u>—CO); IR (thin film), 2930 and 2740 cm^{-1} (<u>H</u>—CO) and 1705 cm^{-1} (C=O).

Trapping of benzyne from the reaction of trimethylstannylsodium with o-dibromobenzene

A 1 *M* solution of trimethylstannylsodium was prepared by stirring 13.3 g (40.6 mmol) of hexamethyldistannane with 3 g (130 mmol) of sodium in 81 ml of TG for 24 h. Dropwise addition of 46 ml (ca. 46 mmol) of trimethylstannylsodium to a cooled (0°C) solution of 5.23 g (22.2 mmol) of *o*-dibromobenzene in 20 ml of furan caused total consumption of the dihalide. The progress of reaction was followed by GLC (6 ft. × 0.25 in. glass column, 5% Apiezon L on 60-80 Chromosorb G temperature program 50—250°C at 10°C/min). The following components, in order of elution, were found: furan, $(Me_3Sn)_2$, $Me_3SnC_6H_5$, 1,4-epoxynaphthalene, TG, and *o*-bis(trimethylstannyl)benzene. The reaction mixture was worked-up by adding water, extracting with petroleum ether and washing the ether extracts with water to remove the TG. The dried ($CaCl_2$) and concentrated extracts yielded 6.0 g of a crude product mixture. Hexamethyldistannane was identified by NMR: (CCl_4) δ (ppm) 0.21 (s, ^2J(SnCH) 48 Hz, ^3J(SnSnCH) 16 Hz, $(Me_3Sn)_2$). The other components were isolated by GLC collection (chromatographic conditions as above): trimethylphenylstannane, NMR (CCl_4) δ (ppm): 0.26 (s, ^2J(SnCH) 54 Hz, 9, $Sn(C\underline{H}_3)_3$) and 7.2 (broad, s, 5, Ar<u>H</u>); *o*-bis(trimethylstannyl)benzene, NMR (CCl_4) δ (ppm): 0.30 (s, ^2J(SnCH) 52 Hz, 18, $Sn)C\underline{H}_3)_3$) and 6.97—7.48 (m, 4, Ar<u>H</u>) (identical with lit. [10]), 1,4-epoxynaphthalene, NMR (CCl_4) δ (ppm): 5.51 (broad, s, 2, bridgehead <u>H</u>) and 6.57—7.17 (m, 6, Ar<u>H</u> and vinylic <u>H</u>), mass spectrum molecular ion, *m/e* 144. Evaporation of the CCl_4 from the NMR tube yielded impure 1,4-epoxy-

naphthalene: m.p. 51—53°C (lit. [12] m.p. 56°C). The crystals were then dissolved in methanol containing two drops of concentrated HCl. After 24 h the NMR spectrum showed the same signals as that of 1-naphthol recorded under similar conditions.

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