

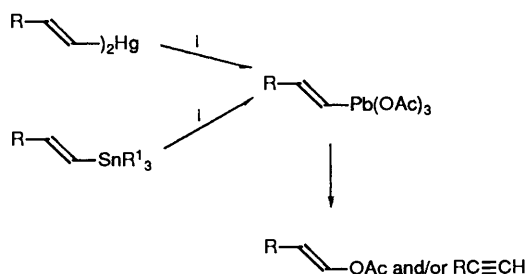
## Vinyl Cation Formation by Decomposition of Vinyllead(IV) Triacetates. Part 2.<sup>1</sup>

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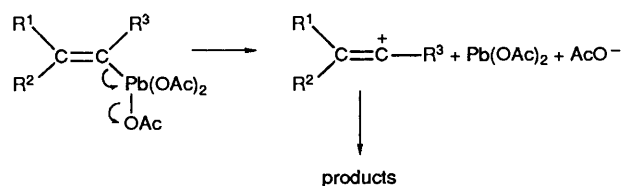
The products resulting from the reductive elimination of lead(II) acetate from four *E*- and *Z*-pairs of vinyllead triacetates have been examined for evidence that these highly unstable lead compounds are a potential source of vinyl cations, including the less stable primary vinyl cations. The vinyllead triacetates which incorporated either methoxy or phenyl groups for intramolecular cation trapping, were generated by reaction of the corresponding tributyl(vinyl)stannanes with lead tetraacetate. In four cases participation by methoxy and phenyl groups occurred to produce cyclic compounds, strongly implicating vinyl cation formation.

In part 1 of this series<sup>1</sup> we presented evidence that the treatment of trialkyl(vinyl)stannanes or divinylmercury compounds with lead tetraacetate (LTA) yields vinyllead triacetates. In most cases these compounds are very unstable and, in the absence of added nucleophiles, they undergo decomposition with elimination of lead(II) acetate to yield the corresponding vinyl acetate and/or acetylene (see Scheme 1).



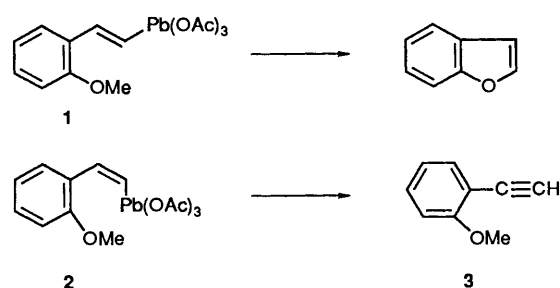
Scheme 1 Reagent: i, LTA

In that earlier work we examined the reactions of a wide range of vinylstannanes and vinylmercurials with LTA, and found that in many cases the decompositions of vinyllead triacetates and solvolyses of the corresponding vinyl triflates (or nonaflates)<sup>2</sup> gave similar products. Thus, there was compelling evidence that, like the solvolyses of the vinyl esters, the decompositions of many vinyllead triacetates proceed by formation of a vinyl cation as indicated in Scheme 2.

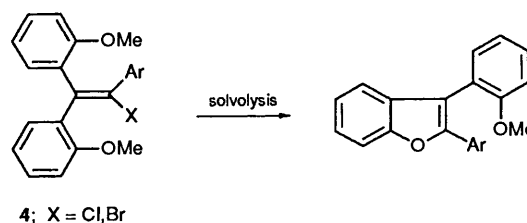


Scheme 2

Of special interest was the finding that some primary vinyl cations, which were inaccessible by ester solvolysis because of their high energy, may be generated by vinyllead triacetate decomposition. In that work we showed that the (*E*)-*o*-methoxystyryl derivative **1** produced benzofuran on decomposition, while the (*Z*)-isomer **2** afforded *o*-methoxyphenylacetylene **3** (see Scheme 3). The reaction of the (*E*)-isomer **1** indicated the formation of an intermediate primary vinyl cation which then underwent attack by the neighbouring oxygen, with subsequent loss of the methyl group as methyl acetate. Similar benzofuran formation has been observed in solvolyses of a number of vinyl halides of type **4** (Scheme 4), and strong evidence for vinyl cation intermediates has been presented.<sup>3</sup> Significantly, in that



Scheme 3



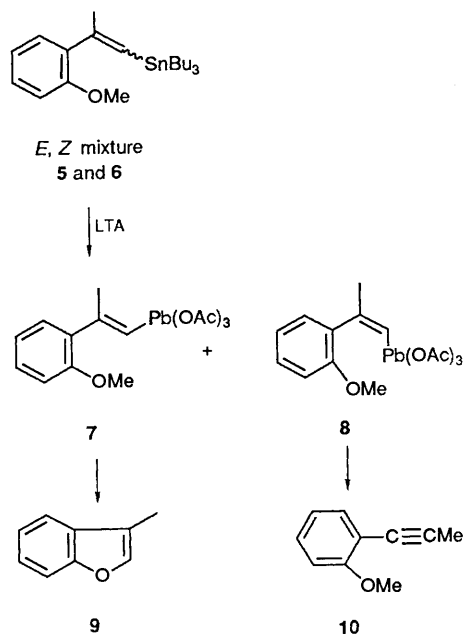
Scheme 4

work it was found that when the cation-stabilising  $\alpha$ -aryl group was replaced by hydrogen or a methyl group there was no cyclisation, and indeed solvolyses were not observed in these cases.

The formation of the acetylene **3** from the corresponding (*Z*)-isomer **2** could be rationalised in terms of an E2-type elimination; however, here also a mechanism involving initial formation of a primary vinyl cation, in a conformation precluding furan ring formation, followed by loss of a proton, could not be discounted.<sup>1</sup>

To further examine the participation of a neighbouring methoxy group and the difference in the behaviour of stereoisomers in the decomposition of vinyllead triacetates, we selected the (*E*)-styryl derivative **7** and its (*Z*)-isomer **8**, in which there was no possibility of a  $\beta$ -elimination. The lead compounds **7** and **8** were generated by the reaction of the corresponding tributyl(vinyl)stannanes **5** and **6**, respectively, with LTA in chloroform. Although neither of the stannanes **5** and **6** could be obtained free of the other isomer, the reaction pathways for each could be readily outlined (see Scheme 5) by employing mixtures containing different ratios of **5** and **6** (see later). When the reaction with LTA was carried out on a mixture in which the *E*:*Z* ratio was 2:3, the major products were 3-methylbenzofuran **9** and 1-(*o*-methoxyphenyl)prop-1-yne **10**, which were obtained in yields of 31 (36 by <sup>1</sup>H NMR spectroscopy) and 25% respectively. Also present in the mixture were butyl acetate (9%), produced by the alternative Sn-C cleavage, and 2-(*o*-

methoxyphenyl)prop-1-ene (10%), which resulted from the high moisture sensitivity of the stannanes. Analysis by GLC showed that no 2-methylbenzofuran was produced. The  $^1\text{H}$  NMR spectroscopic study of the reaction yielded only a small amount of useful information. It showed that metal-metal exchange was considerably more rapid for the (*E*)-stannane **5** than the (*Z*)-isomer **6**, and as a result only the (*E*)-vinyllead compound **7** could be observed.

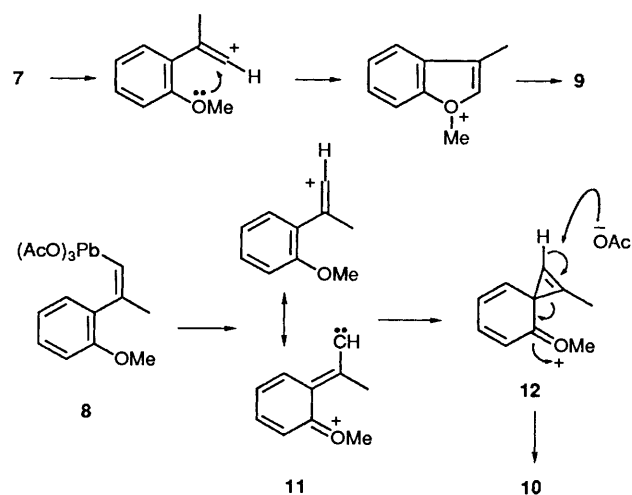


Scheme 5

When the above reaction was repeated using a 1:9 ratio of stannanes **5** and **6**, the yield of the benzofuran **9** was only 4%, while 71% of the acetylene **10** was produced. Thus, it would appear that the (*E*)-stannane **5** is the precursor of 3-methylbenzofuran **9**, while the (*Z*)-isomer **6** gives rise to 1-(*o*-methoxyphenyl)prop-1-yne **10**, as indicated in Scheme 5. These results complement those obtained for the decompositions of the isomeric vinyllead compounds **1** and **2** (Scheme 3), and support our view that the reductive elimination of lead(II) acetate from vinyllead triacetates provides an important new route to vinyl cations, even primary vinyl cations.

The formation of the benzofuran **9** is most readily rationalised as proceeding by the mechanism previously outlined for compounds **1** and **4**; *i.e.*, by collapse of the vinyllead compound **7** to a primary vinyl cation, which then undergoes intramolecular attack by oxygen (see Scheme 6); participation by the neighbouring oxygen as the positive charge develops must, of course, also be considered a possibility. The decomposition of the (*Z*)-lead compound **8** to yield the acetylene **10** appears to us to be even stronger support for primary vinyl cation formation. The geometry of the molecule precludes a concerted breaking of the C-Pb bond and migration of the aryl group, a rationalisation which has been proposed for some solvolyses which would otherwise result in generation of a primary vinyl cation.<sup>2</sup> We tentatively propose that, like the (*Z*)-isomer **2**,<sup>1</sup> compound **8** undergoes reductive elimination in the conformation shown in Scheme 6 to produce the vinyl cation **11**, which can then give rise to the bridged phenonium ion **12**. The acetylene **10** would result from collapse of this ion and proton abstraction as indicated. It should be noted that the absence of 2-methylbenzofuran from the products (see above) requires that the secondary vinyl cation **17** is not on the pathway to the acetylene **10**.

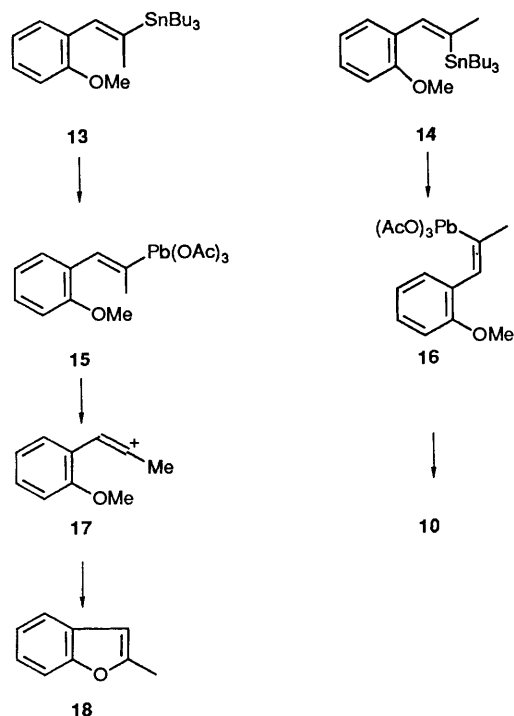
To complete our study of vinyl cation trapping by a neighbouring methoxy group, we examined the reaction of the



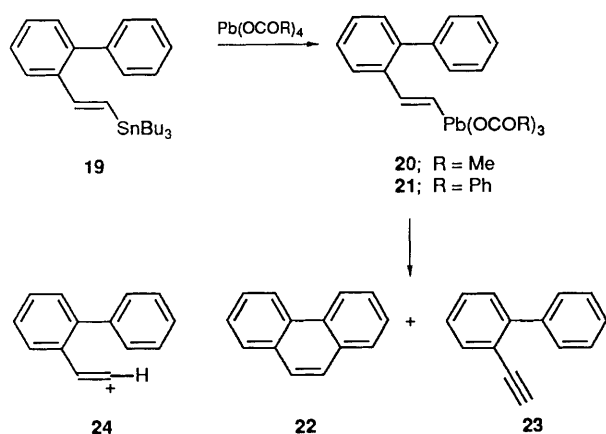
Scheme 6

$\alpha$ -methyl substituted *o*-methoxystyrylstannanes **13** and **14** with LTA. Here again, although the compounds **13** and **14** could not be obtained free of the other isomer, reaction pathways could be outlined (see Scheme 7) by the use of mixtures containing different ratios of them (see later). Both of the isomers **13** and **14** were slow to react with LTA, and thus the corresponding intermediate vinyllead triacetates **15** and **16** could not be observed by NMR spectroscopy. As a result of this slower reaction at the  $\text{sp}^2$  centre there was significant (20–30%) butyl-tin cleavage by LTA to produce butyl acetate. From the reaction of a mixture of the stannanes **13** and **14** in which the *E*:*Z* ratio was 7:93, 2-methylbenzofuran **18** and 1-(*o*-methoxyphenyl)prop-1-yne **10** were produced in yields of 7 and 64% respectively, while a mixture in which the *E*:*Z* ratio was 9:10 gave compounds **18** and **10** in yields of 20 and 27% respectively. Thus, in the light of the results outlined in Scheme 4 and in our earlier paper,<sup>1</sup> it would appear reasonable to propose that the (*E*)-stannane **13** reacts with LTA to give the (*E*)-vinyllead triacetate **15**, which undergoes reductive elimination of lead(II) acetate to give the benzofuran **18** via the vinyl cation **17** (see Scheme 7). As indicated above in the formation of benzofuran **9**, this ion may not fully develop before attack by the neighbouring oxygen. The results also point to the (*Z*)-stannane **14** being the precursor of the acetylene **10**, and in analogy with the behaviour of the (*Z*)-compounds **1** and **8** we propose the pathway outlined in Scheme 7; thus, the (*Z*)-vinyllead compound in conformation **16** could undergo reductive elimination to produce a cation, from which intramolecular proton abstraction may occur. There is, however, also the possibility that an *E2*-type elimination produces the acetylene.

We have examined the possibility of the intramolecular trapping of vinyl cations by a neighbouring phenyl group in two cases. In the first of these, (*E*)-vinyllead triacetate **20** was generated by reaction of the (*E*)-vinylstannane **19** with LTA in chloroform (Scheme 8). Compound **20** was readily observed by  $^1\text{H}$  NMR spectroscopy, and shown to produce phenanthrene **22** and the acetylene **23** in overall yields of 23 and 36%, respectively. Interestingly, when LTA was replaced by lead tetrabenzoate (LTB) in the above experiment, the yields of phenanthrene and the acetylene **23** were 46 and 20%, respectively. These results indicate that the products **22** and **23** arise by two different pathways, and not from the same vinyl cation. Since the formation of phenanthrene would appear to be most likely occurring through the vinyl cation **24**, it is tentatively proposed that the acetylene results from a *cis* *E2*-type elimination. The difference in the ratios of products **22** and **23** from the two reactions is possibly explained by the presence of



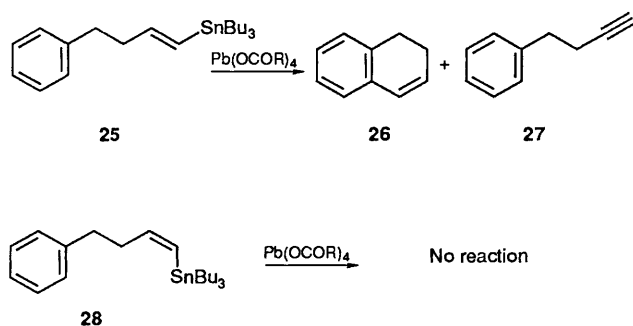
Scheme 7



Scheme 8

the more electron-withdrawing tribenzoyloxyplumbyl group in the vinyllead intermediate **21**, increasing the rate of decomposition to the vinyl cation **24**.

The (*E*)-stannane **25** was the second compound examined for phenyl group participation, and it was found to mirror the behaviour of stannane **19** when treated in separate experiments with LTA and LTB (Scheme 9). It was obtained as an 81:19

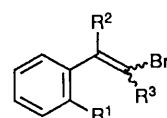


Scheme 9

(*E:Z*) mixture; however, in a separate experiment it was established, by employing a 10:90 (*E:Z*) mixture, that the (*Z*)-isomer **28** was inert under the normal reaction conditions. The mixture containing 81% of the (*E*)-stannane **25** was treated with LTA in chloroform to give 1,2-dihydronaphthalene **26** and 4-phenylbutyne **27** in yields of 19 and 62%, respectively. When LTA was replaced by LTB in the reaction, the yield of cyclic compound **26** increased to 36%, while relatively less (43%) of the acetylene **27** was produced. Due to the relatively slow tin-lead exchange of compound **25**, the intermediate vinyllead tricarboxylates were not observed by NMR spectroscopy; however, we rationalise the production of the dihydronaphthalene **26** and the acetylene derivative **27** as we did in the case of the formation of compounds **22** and **23** respectively.

*Synthesis of Tributyl(vinyl)stannanes.*—The vinylstannanes **5**, **6**, **19**, **25** and **28** were prepared by treatment of the corresponding Grignard reagent with tributyltin chloride, while reaction of the appropriate acetylene with tributyltin hydride was used to produce the stannanes **13**, **14**, **25** and **28**.

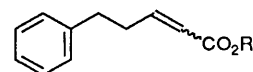
The vinyl bromides *E*-**29** and *Z*-**29**, which were required for the synthesis of stannanes **5** and **6**, were obtained as a 2:3 (*E:Z*) mixture by reaction of *o*-methoxyacetophenone with (bromo-methyl)triphenylphosphonium bromide. This mixture of bromides yielded stannanes **5** and **6** in a similar ratio by the Grignard route. When the mixture of isomeric stannanes was irradiated through Pyrex glass with UV light, equilibration occurred to produce a 1:9 (*E:Z*) mixture.



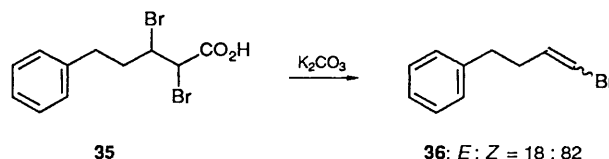
**29**; R<sup>1</sup> = OMe, R<sup>2</sup> = Me, R<sup>3</sup> = H  
**30**; R<sup>1</sup> = Ph, R<sup>2</sup> = R<sup>3</sup> = H

Of interest in the synthesis of (*E*)-vinylstannane **19**, was our finding that a 28:72 (*E:Z*) mixture of the vinyl bromides *E*-**30** and *Z*-**30**, prepared as previously described,<sup>4</sup> gave none of the (*Z*)-stannane. Although isomerisation can occur in oxidative metallation reactions,<sup>5</sup> it is rare and this was the only case of inversion of configuration during vinylmagnesium halide formation which we encountered here or in our earlier work.<sup>1</sup>

The 1:9 (*E:Z*) mixture of stannanes **25** and **28** was also produced by the above Grignard route, and the synthesis of the mixture of vinyl bromides **36** employed is shown in Scheme 10.



**31**; *E*, R = Et  
**32**; *Z*, R = Et  
**33**; *E*, R = H  
**34**; *Z*, R = H



Scheme 10

The required  $\alpha,\beta$ -unsaturated carboxylic acid **33** was obtained by reaction of  $\beta$ -phenylpropionaldehyde with (ethoxycarbonylmethylene)triphenylphosphorane; this gave an approximately 7:1 (*E:Z*) ratio of esters **31** and **32**. The esters were readily

separated by chromatography, and hydrolysis of each produced the corresponding carboxylic acids **33** and **34**. Bromination of the (*E*)-isomer **33** produced a single diastereoisomer **35**, which underwent base induced decarboxylative debromination, to yield a mixture of vinyl bromides **36** in 18:82 (*E*:*Z*) ratio.

The vinylstannanes **13** and **14** were obtained as a 7:93 (*E*:*Z*) mixture by the reaction of 1-(*o*-methoxyphenyl)propyne **10** with tributyltin hydride, whereas similar treatment of 4-phenylbut-1-yne **27** gave a 81:19 (*E*:*Z*) mixture of the vinylstannanes **25** and **28**. Equilibration of both isomeric mixtures by UV irradiation resulted in mixtures in which the ratio of **13**:**14** was 9:10.

## Experimental

For the general experimental procedures see our earlier paper.<sup>6</sup> Analytical GLC was carried out on a Hewlett-Packard 5890 chromatograph equipped with either an SGE BPI capillary column (0.33 mm i.d. × 25 m) with a 0.5 μm film thickness (column 1), or an SGE BP20 capillary column (0.22 mm i.d. × 25 m) with a 0.33 μm film thickness (column 2). For NMR spectroscopic data, coupling constants (*J*) are given in Hz. Light petroleum refers to the fraction with b.p. 60–80 °C.

*Synthesis of a Mixture of (E)-1-Bromo-2-(o-methoxyphenyl)propene E-29 and Its (Z)-Isomer Z-29.*—Freshly sublimed potassium *tert*-butoxide (2.55 g, 23 mmol) was added under nitrogen to a stirred suspension of bromomethyl(triphenyl)phosphonium bromide (9.91 g, 23 mmol) in dry tetrahydrofuran (THF) (50 cm<sup>3</sup>) at –78 °C. The mixture was stirred at –78 °C for 1 h and *o*-methoxyacetophenone<sup>7</sup> (3.41 g, 23 mmol) in dry THF (5 cm<sup>3</sup>) was added. After the mixture had been stirred at –78 °C for a further 30 min, it was warmed to room temperature and evaporated. The residue was partitioned between ether (200 cm<sup>3</sup>) and hydrochloric acid (3 mol dm<sup>–3</sup>; 150 cm<sup>3</sup>), and the ether extract was washed in turn with hydrochloric acid (3 mol dm<sup>–3</sup>; 150 cm<sup>3</sup>), aqueous sodium carbonate (10%; 100 cm<sup>3</sup>), and brine (100 cm<sup>3</sup>), and then dried (Na<sub>2</sub>SO<sub>4</sub>). The residue obtained on evaporation was fractionated by radial chromatography (ethyl acetate–light petroleum, 1:999) and preparative HPLC (ethyl acetate–light petroleum, 1:999) to give a 35:65 mixture of isomers *E*-**29** and *Z*-**29** (1.96 g, 38%) as an oil, b.p. 115 °C at 1.3 mmHg (Found: C, 52.9; H, 4.8. C<sub>10</sub>H<sub>11</sub>BrO requires C, 52.9; H, 4.9%); δ<sub>H</sub>(CDCl<sub>3</sub>) [(*Z*)-isomer] 2.06 (3 H, d, <sup>4</sup>*J* 1.60, Me), 3.08 (3 H, s, OMe), 6.21 (1 H, q, <sup>4</sup>*J* 1.60, vinyl H), 6.85 (1 H, br d, <sup>3</sup>*J* 8.10, 3-H), 6.88 (1 H, ddd, <sup>3</sup>*J* 7.32 and 7.32, <sup>4</sup>*J* 1.08, 5-H), 7.09 (1 H, dd, <sup>3</sup>*J* 7.32, <sup>4</sup>*J* 1.68, 6-H) and 7.25 (1 H, ddd, <sup>3</sup>*J* 8.10 and 7.32, <sup>4</sup>*J* 1.68, 4-H); stereochemistry confirmed by NOE difference spectroscopy as follows: irradiation at δ 2.06 produced a 4% NOE at δ 6.21 and a 1% NOE at δ 7.09, while irradiation at δ 6.21 produced a 5% NOE at δ 2.06 and a 1% NOE at δ 7.09; δ<sub>C</sub>(CDCl<sub>3</sub>) [(*Z*)-isomer] 23.80 (Me), 55.55 (OMe), 102.86 (vinyl CH), 111.11 (Ar, C-3), 120.49 (ArCH), 128.92 (ArCH), 129.48 (ArCH), 129.59 (vinyl C or Ar, C-1), 140.61 (vinyl C or Ar, C-1) and 155.88 (Ar, C-2); δ<sub>H</sub>(CDCl<sub>3</sub>) [(*E*)-isomer] 2.13 (3 H, d, <sup>4</sup>*J* 1.36, Me), 3.78 (3 H, s, OMe), 6.24 (1 H, q, <sup>4</sup>*J* 1.36, vinyl H) and 6.9–7.5 (4 H, m, ArH); stereochemistry confirmed by NOE difference spectroscopy as follows: irradiation at δ 2.13 produced no NOE at δ 6.24, while irradiation at δ 6.24 had no effect at δ 2.13, but it produced a 3% NOE at δ 7.11; δ<sub>C</sub>(CDCl<sub>3</sub>) [(*E*)-isomer] 20.43 (Me), 55.36 (OMe), 106.13 (vinyl CH), 110.83 (Ar, C-3), 120.52 (ArCH), 129.04 (ArCH), 129.33 (ArCH), 130.89 (vinyl C or Ar, C-1), 140.90 (vinyl C or Ar, C-1) and 156.44 (Ar, C-2).

*Synthesis of Mixtures of Tributyl[(E)-2-(o-methoxyphenyl)prop-1-enyl]stannane 5 and Its (Z)-Isomer 6.*—The Grignard solution prepared from the mixture of vinyl bromides *E*-**31** and *Z*-**31** (0.91 g, 4.0 mmol) and magnesium turnings (0.11 g, 4.4 mmol) in dry THF (15 cm<sup>3</sup>) was decanted (cannula) from excess of magnesium. Tributylchlorostannane was added dropwise until the Grignard solution was just decolourised, and the mixture was then heated at reflux for 1 h. It was then cooled to room temperature, evaporated, and the residue was partitioned between diethyl ether (30 cm<sup>3</sup>) and water (30 cm<sup>3</sup>). The ether phase was washed with brine (50 cm<sup>3</sup>), dried, and evaporated, and the crude product was distilled (Kugelrohr). The 40:60 (*E*:*Z*) mixture of isomers **5** and **6** was obtained as an oil (1.50 g, 86%), b.p. 190 °C at 0.4 mmHg [Found: C, 59.4; H, 9.1; M<sup>+</sup> (<sup>120</sup>Sn) – 1, 437.1870; M<sup>+</sup> (<sup>120</sup>Sn) – Bu, 381.1237. C<sub>22</sub>H<sub>38</sub>OSn requires C, 60.4; H, 8.8%; M (<sup>120</sup>Sn) – 1, 437.1866; M (<sup>120</sup>Sn) – Bu, 381.1240]; λ<sub>max</sub>(EtOH)/nm 278 (ε 2931); δ<sub>H</sub>(CDCl<sub>3</sub>) [(*Z*)-isomer] 0.55 (6 H, t, <sup>3</sup>*J* 8.13, <sup>119</sup>Sn and <sup>117</sup>Sn gave a satellite average of 52 Hz, 3 × SnCH<sub>2</sub>), 0.83 (9 H, t, <sup>3</sup>*J* 7.31, 3 × Me), 1.09–1.44 (12 H, m, 6 × CH<sub>2</sub>), 2.21 (3 H, d, <sup>4</sup>*J* 1.47, vinyl Me), 3.80 (3 H, s, OMe), 5.97 (1 H, q, <sup>4</sup>*J* 1.47, <sup>119</sup>Sn and <sup>117</sup>Sn gave satellites of 71.58 and 67.98 Hz respectively, vinyl H), 6.82 (1 H, dd, <sup>3</sup>*J* 8.22, <sup>4</sup>*J* 1.12, Ar 3-H), 6.88 (1 H, ddd, <sup>3</sup>*J* 7.40 and 7.40, <sup>4</sup>*J* 1.12, Ar 5-H), 7.03 (1 H, dd, <sup>3</sup>*J* 7.40, <sup>4</sup>*J* 2.0, Ar 6-H) and 7.22 (1 H, ddd, <sup>3</sup>*J* 8.22, <sup>3</sup>*J* 7.40, <sup>4</sup>*J* 2.0, Ar 4-H), irradiation at δ 2.21 produced a 4% NOE at δ 5.97, while irradiation at δ 5.97 gave rise to a 9% NOE at δ 2.21; [(*E*)-isomer] (*inter alia*) 2.14 (3 H, d, <sup>4</sup>*J* 0.80, Me), 3.78 (3 H, s, OMe), 5.83 (1 H, q, <sup>4</sup>*J* 0.80, <sup>119</sup>Sn and <sup>117</sup>Sn gave a satellite average of 69.98 Hz, vinyl H), irradiation at δ 2.14 did not produce a NOE at δ 5.83, while irradiation at δ 5.83 had no effect on the signal at δ 2.14.

Irradiation of the above mixture (0.013 g) in deuteriochloroform (0.4 cm<sup>3</sup>) with light from a 125 W medium pressure Hg arc for 72 h produced a mixture of stannanes **5** and **6** in a 1:9 (*E*:*Z*) ratio.

*Synthesis of a Mixture of (E)-2-Bromo-1-biphenyl-2-ylethene E-30 and Its (Z)-Isomer Z-30.*—The mixture of the title compounds, prepared from *o*-phenylcinnamic acid as previously described,<sup>4</sup> was obtained in 75% overall yield as an oil, b.p. 130 °C at 0.19 mmHg (lit.,<sup>4</sup> 157 °C at 0.5 mmHg), shown by <sup>1</sup>H NMR spectroscopy to be a 28:72 (*E*:*Z*) mixture; δ<sub>H</sub>(CDCl<sub>3</sub>) [(*Z*)-isomer] 6.23 (1 H, d, <sup>3</sup>*J* 7.8, 1-H), 6.76 (1 H, d, <sup>3</sup>*J* 7.8, 2-H), 7.10–7.60 (8 H, m, ArH) and 7.76 (1 H, m, ArH); [(*E*)-isomer] (*inter alia*) 6.51 (1 H, d, <sup>3</sup>*J* 13.8, 1-H) and 6.98 (1 H, d, <sup>3</sup>*J* 13.8, 2-H).

[(*E*)-2-Biphenyl-2-ylvinyltributylstannane **19**.—The mixture of vinyl bromides *E*-**30** and *Z*-**30** was treated in turn with magnesium and tributylchlorostannane, as in the preparation of the stannanes **5** and **6**, to yield the title compound **19** as an oil (68%), b.p. 200 °C at 0.2 mmHg [Found: C, 66.7; H, 8.4%; M<sup>+</sup> (<sup>120</sup>Sn) – 1, 469.1912. C<sub>26</sub>H<sub>38</sub>Sn requires C, 66.6; H, 8.2%; M (<sup>120</sup>Sn) – 1, 469.1917]; λ<sub>max</sub>(EtOH)/nm 237 and 262sh (ε 18 171, 13 742); δ<sub>H</sub>(CDCl<sub>3</sub>) 0.75–0.98 (15 H, m, 3 × SnCH<sub>2</sub>, 3 × Me), 1.23–1.39 (6 H, m, 3 × CH<sub>2</sub>), 1.39–1.50 (6 H, m, 3 × CH<sub>2</sub>), 6.81 (1 H, d, <sup>3</sup>*J* 19.41, <sup>119</sup>Sn and <sup>117</sup>Sn gave satellites of 72.36 and 68.83 respectively, ArCH=), 6.89 (1 H, d, <sup>3</sup>*J* 19.41, <sup>119</sup>Sn and <sup>117</sup>Sn gave satellites of 66.48 and 64.12 Hz, respectively, =CHSn), 7.22–7.50 (8 H, m, ArH) and 7.65 (1 H, d, <sup>3</sup>*J* 7.33, ArH).

*Synthesis of a Mixture of Ethyl (E)-5-Phenylpent-2-enoate 31 and Its (Z)-Isomer 32.*—To a solution of ethoxycarbonylmethylene(triphenyl)phosphorane (12.98 g, 37.3 mmol) in dry benzene (50 cm<sup>3</sup>) was added β-phenylpropionaldehyde (5 g, 37.3 mmol). The mixture was heated at reflux for 16 h after which it was

\* The low carbon analysis is attributed to the high moisture sensitivity of this compound.

evaporated, and the residue was separated by flash chromatography (ethyl acetate–light petroleum, 1:9) to yield two fractions. The less polar material was distilled to give the (*Z*)-isomer **32** as an oil (0.75 g, 10%), b.p. 110 °C at 1.5 mmHg (Kugelrohr) (Found: C, 76.5; H, 8.3. C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> requires C, 76.4; H, 7.9%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1719 and 1645;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.23 (3 H, t, <sup>3</sup>J 7.2, Me), 2.50–3.13 (4 H, m, 2 × CH<sub>2</sub>), 4.09 (2 H, q, <sup>3</sup>J 7.2, CH<sub>2</sub>), 5.66 (1 H, dt, <sup>3</sup>J 11.4, <sup>4</sup>J 1.2, vinyl H), 6.12 (1 H, dt, <sup>3</sup>J 11.4, <sup>3</sup>J 6.9, vinyl H) and 6.92–7.32 (5 H, m, ArH).

The more polar material was distilled to yield the (*E*)-isomer **31** as an oil (5.85 g, 77%), b.p. 113 °C at 1.5 mmHg (Found: C, 76.2; H, 8.1. C<sub>13</sub>H<sub>16</sub>O<sub>2</sub> requires C, 76.4; H, 7.9%);  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1722 and 1655;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.23 (3 H, t, <sup>3</sup>J 7.3, Me), 2.25–2.88 (4 H, m, 2 × CH<sub>2</sub>), 4.11 (2 H, q, <sup>3</sup>J 7.3, CH<sub>2</sub>), 5.74 (1 H, dt, <sup>3</sup>J 15.3, <sup>4</sup>J 1.6, vinyl H), 6.91 (1 H, dt, <sup>3</sup>J 15.3, <sup>3</sup>J 6.3, vinyl H) and 6.96–7.32 (5 H, m, ArH).

(*E*)-5-Phenylpent-2-enoic Acid **33** and Its (*Z*)-Isomer **34**.—The above esters **31** and **32** were heated at reflux with sodium hydroxide in methanol–water for 3 h, and the acidic products were isolated by means of diethyl ether in the usual way.

The title compound **33** was obtained as a colourless powder (93%), m.p. 92–94 °C (Found: C, 74.8; H, 7.2. C<sub>11</sub>H<sub>12</sub>O<sub>2</sub> requires C, 75.0; H, 6.9%);  $\nu_{\max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3400–2900, 1699 and 1654;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.33–2.93 (4 H, m, 2 × CH<sub>2</sub>), 5.76 (1 H, dt, <sup>3</sup>J 15.5, <sup>4</sup>J 1.4, vinyl H), 6.79–7.39 (6 H, m, ArH and vinyl H) and 9.80 (1 H, br s, CO<sub>2</sub>H).

(*Z*)-5-Phenylpent-2-enoic acid **34** was produced as a low melting solid, b.p. 103 °C at 0.05 mmHg (Kugelrohr), m.p. 40–41 °C (Found: C, 75.3; H, 7.0. C<sub>11</sub>H<sub>12</sub>O<sub>2</sub> requires C, 75.0; H, 6.9%);  $\nu_{\max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3400–2800, 1695 and 1641;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 2.43–3.17 (4 H, m, 2 × CH<sub>2</sub>), 5.72 (1 H, dt, <sup>3</sup>J 11.4, <sup>4</sup>J 1.2, vinyl H), 6.27 (1 H, dt, <sup>3</sup>J 11.4, <sup>3</sup>J 6.9, vinyl H), 6.88–7.37 (5 H, m, ArH) and 10.70 (1 H, br s, CO<sub>2</sub>H).

Synthesis of a Mixture of (*E*)-Vinylstannane **25** and Its (*Z*)-Isomer **28** via the Mixture of Vinyl Bromides **36**.—A solution of bromine (0.8 cm<sup>3</sup>, 15.6 mmol) in dry chloroform (10 cm<sup>3</sup>) was added dropwise with stirring to a solution of the (*E*)- $\alpha,\beta$ -unsaturated acid **33** at room temperature. The mixture was stirred for 6 h, and then evaporated to yield 2,3-dibromo-5-phenylpentanoic acid **35** (4.01 g, 99%) as a pale yellow solid, m.p. 117–119 °C (from carbon tetrachloride–light petroleum) (Found: C, 39.6; H, 3.8. C<sub>11</sub>H<sub>12</sub>Br<sub>2</sub>O<sub>2</sub> requires C, 39.3; H, 3.6%);  $\nu_{\max}$ (CHCl<sub>3</sub>)/cm<sup>-1</sup> 3300–2900 and 1732;  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 1.88–3.16 (4 H, m, 2 × CH<sub>2</sub>), 4.06–4.54 (2 H, m, 2 × CHBr), 7.03–7.29 (5 H, m, ArH) and 8.49 (1 H, br s, CO<sub>2</sub>H).

The dibromo acid **35** (1.5 g, 4.5 mmol) was heated at reflux in acetone (40 cm<sup>3</sup>) with potassium carbonate (4 g, 28 mmol) for 3 h with protection from light. It was then evaporated and the residue was partitioned between diethyl ether (50 cm<sup>3</sup>) and water (50 cm<sup>3</sup>). The ether layer was washed with brine (50 cm<sup>3</sup>), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated, and the residue distilled (Kugelrohr) to give a 18:82 (*E*:*Z*) mixture (0.8 g, 85%) of (*E*)-1-bromo-4-phenylbut-1-ene *E*-**36** and its (*Z*)-isomer *Z*-**36** as an oil, b.p. 90 °C at 1 mmHg (Found: M<sup>+</sup>, 210.0070; M<sup>+</sup> – Br, 131.0854. C<sub>10</sub>H<sub>11</sub>Br requires M, 210.0044; M – Br, 131.0861);  $\delta_{\text{H}}$ (C<sub>6</sub>D<sub>6</sub>) [(*Z*)-isomer] 2.31–2.37 (2 H, m, allylic CH<sub>2</sub>), 2.43 (2 H, br t, <sup>3</sup>J 7.20, benzylic CH<sub>2</sub>), 5.63 (1 H, dt, <sup>3</sup>J 7.17, <sup>3</sup>J 7.20, vinyl H), 5.80 (1 H, dt, <sup>3</sup>J 7.17, <sup>4</sup>J 1.37, vinyl H), 6.96–7.18 (5 H, m, ArH), irradiation at  $\delta$  2.35 produced a 5% NOE at  $\delta$  5.63, but there was no effect on the signal at  $\delta$  5.80, irradiation at  $\delta$  5.80 produced a 6% NOE at  $\delta$  5.63, while there was no effect on the signal at  $\delta$  2.35; [(*E*)-isomer] 1.86 (2 H, ddt, <sup>3</sup>J 7.25, <sup>4</sup>J 1.68, <sup>3</sup>J 7.75, allylic CH<sub>2</sub>), 2.26 (2 H, br t, <sup>3</sup>J 7.75, benzylic CH<sub>2</sub>),

5.63 (1 H, dt, <sup>3</sup>J 13.75, <sup>4</sup>J 1.68, vinyl H), 5.92 (1 H, dt, <sup>3</sup>J 13.75, <sup>3</sup>J 7.25, vinyl H) and 6.96–7.18 (5 H, m, ArH), irradiation at  $\delta$  1.86 produced a 3% NOE at  $\delta$  5.63, while irradiation at  $\delta$  5.63 gave rise to a 2% effect at  $\delta$  1.86.

The mixture of vinyl bromides *E*-**36** and *Z*-**36** was treated in turn with magnesium and tributylchlorostannane, as in the preparation of the stannanes **5** and **6**, to yield a 1:9 (*E*:*Z*) mixture of the title compounds **25** and **28** reported below.

Synthesis of Mixtures of Tributyl[(*E*)-(o-methoxyphenyl)propen-2-yl]stannane **13** and Its (*Z*)-Isomer **14**.—To freshly distilled 1-(o-methoxyphenyl)propyne (0.90 g, 6.2 mmol) was added tributyltin hydride (1.6 cm<sup>3</sup>, 5.9 mmol). The mixture was stirred at 100 °C for 16 h and then cooled and distilled to yield a 7:93 (*E*:*Z*) mixture of the title compounds **13** and **14** as an oil (2.01 g, 75%), b.p. 195 °C at 0.4 mmHg [Found: C, 59.4; H, 9.2; M<sup>+</sup>(<sup>120</sup>Sn) – Bu, 381.1239. C<sub>22</sub>H<sub>38</sub>OSn requires C, 60.4; H, 8.8%; M(<sup>120</sup>Sn) – Bu, 381.1240];  $\lambda_{\max}$ (EtOH)/nm 245 and 283 ( $\epsilon$  8719, 3713);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) [(*Z*)-isomer] 0.69 (6 H, t, <sup>3</sup>J 8.06, <sup>119</sup>Sn and <sup>117</sup>Sn gave a satellite average of 52.39 Hz, 3 × SnCH<sub>2</sub>), 0.83 (9 H, t, <sup>3</sup>J 7.0, 3 × Me), 1.06–1.70 (12 H, m, 6 × CH<sub>2</sub>), 2.12 (3 H, d, <sup>4</sup>J 1.70, <sup>119</sup>Sn and <sup>117</sup>Sn gave satellites of 43.09 and 39.95 Hz respectively, vinyl Me), 3.81 (3 H, s, OMe), 6.80 (1 H, br d, <sup>3</sup>J 8.40, Ar 3-H), 6.87 (1 H, dd, <sup>3</sup>J 7.44 and 7.44, Ar 5-H), 6.95 (1 H, dd, <sup>3</sup>J 7.44, <sup>4</sup>J 1.60, Ar 6-H), 7.21 (1 H, ddd, <sup>3</sup>J 8.40 and 7.44, <sup>4</sup>J 1.60, Ar 4-H) and 7.23 (1 H, q, <sup>4</sup>J 1.70, vinyl H), irradiation at  $\delta$  2.12 produced a 7% NOE at  $\delta$  7.23, while irradiation at  $\delta$  7.23 produced a 6% NOE at  $\delta$  2.12. [(*E*)-isomer] (*inter alia*) 2.04 (3 H, d, <sup>4</sup>J 1.90, <sup>119</sup>Sn and <sup>117</sup>Sn gave a satellite average of 48.3 Hz, vinyl methyl) and 3.72 (3 H, s, OMe).

Irradiation of the above mixture (0.10 g) in deuteriochloroform (0.4 cm<sup>3</sup>) with light from a 125 W medium pressure Hg arc for 72 h gave a mixture of the stannanes **13** and **14** in a 9:10 (*E*:*Z*) ratio.

Synthesis of Mixtures of Tributyl [(*E*)-4-phenylbut-1-enyl]stannane **25** and Its (*Z*)-Isomer **28**.—(a) Tributyltin hydride (4.10 cm<sup>3</sup>, 15.2 mmol) was added dropwise to 4-phenylbut-1-yne (2.00 g, 15.4 mmol). The mixture was stirred at 90 °C for 5 h, and then distilled to yield a 81:19 (*E*:*Z*) mixture of the title compounds **25** and **28** as an oil (5.83 g, 91%), b.p. 200 °C at 0.8 mmHg [Found: M<sup>+</sup>(<sup>120</sup>Sn) – Bu, 365.1259; M<sup>+</sup>(<sup>118</sup>Sn) – Bu, 363.1246; M<sup>+</sup>(<sup>116</sup>Sn) – Bu, 361.1276. C<sub>22</sub>H<sub>38</sub>Sn requires M(<sup>120</sup>Sn) – Bu, 365.1291; M(<sup>118</sup>Sn) – Bu, 363.1285; M(<sup>116</sup>Sn) – Bu, 361.1287];  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) [(*E*)-isomer] 0.84–0.96 (15 H, m, 3 × SnCH<sub>2</sub> and 3 × Me), 1.31 (6 H, tq, <sup>3</sup>J 7.20 and 7.36, 3 × CH<sub>2</sub>), 1.42–1.54 (6 H, m, 3 × CH<sub>2</sub>), 2.44 (2 H, m, allylic CH<sub>2</sub>), 2.71 (2 H, m, benzylic CH<sub>2</sub>), 5.91 (1 H, dt, <sup>3</sup>J 18.75, <sup>4</sup>J 1.00, <sup>119</sup>Sn and <sup>117</sup>Sn gave satellites of 79.02 and 76.02 Hz respectively, =CHSn), 6.01 (1 H, dt, <sup>3</sup>J 18.75 and 5.75, <sup>119</sup>Sn and <sup>117</sup>Sn gave satellites of 66.51 and 63.51 respectively, vinyl H) and 7.13–7.29 (5 H, m, ArH); [(*Z*)-isomer] (*inter alia*) 2.34 (2 H, ddt, <sup>3</sup>J 7.20 and 8.08, <sup>4</sup>J 1.15, allylic CH<sub>2</sub>), 5.84 (1 H, dt, <sup>3</sup>J 12.38, <sup>4</sup>J 1.15, =CHSn) and 6.55 (1 H, dt, <sup>3</sup>J 12.38 and 7.20, vinyl H).

Tin–Lead Exchange Reactions.—All reactions were monitored initially by <sup>1</sup>H NMR spectroscopy as outlined in Part 1.<sup>1</sup> Preparative scale reactions were then performed, and the presence of all products was verified by comparison of the reaction mixtures with authentic samples by analytical GLC. The following tin–lead exchange reactions were carried out using these procedures:

(a) Tributyl[(*E*)-2-(o-methoxyphenyl)prop-1-enyl]stannane **5** and the (*Z*)-isomer **6** (*E*:*Z*, 2:3) (0.753 g, 1.72 mmol) in dry chloroform (5 cm<sup>3</sup>) were added to LTA (0.7636 g, 1.72 mmol). The mixture was stirred overnight at room temperature, filtered, and the volume was made up to 10 cm<sup>3</sup> with chloroform. The

\* The low carbon analysis is attributed to a high moisture sensitivity.

mixture was then analysed by GLC (column 2) and found to contain 1-(*o*-methoxyphenyl)propyne **10** (25% yield) and 3-methylbenzofuran **9** (31% yield). No 2-methylbenzofuran was present.

A highfield <sup>1</sup>NMR spectroscopic analysis of the reaction of the above mixture of stannanes **5** and **6** with LTA as previously described<sup>1</sup> showed the presence of (*E*)-2-(*o*-methoxyphenyl)prop-1-enyllead triacetate **7** with a vinyl hydrogen resonance at  $\delta$  7.03 with <sup>207</sup>Pb satellites of 900.00 Hz.

(b) (*E*)-Stannane **5** and the (*Z*)-isomer **6** (*E*:*Z*, 1:9) (0.013 g,  $2.97 \times 10^{-5}$  mmol) in dry deuteriochloroform (0.4 cm<sup>3</sup>) were added to a solution of LTA (0.014 g,  $3.16 \times 10^{-5}$  mmol) in dry deuteriochloroform (0.3 cm<sup>3</sup>). The mixture was shaken and the reaction was followed by <sup>1</sup>H NMR spectroscopy. After 3 h, the mixture was filtered and GLC analysis was carried out as in (a) above to show the presence of the acetylene **10** (72% yield) and 3-methylbenzofuran (4% yield).

(c) Tributyl[(*E*)-1-(*o*-methoxyphenyl)prop-1-en-2-yl]stannane **13** and the (*Z*)-isomer **14** (*E*:*Z*, 7:93) (0.458 g, 1.05 mmol) in dry chloroform (0.5 cm<sup>3</sup>) were added to a stirred solution of LTA (0.464 g, 1.05 mmol) in dry chloroform (2.0 cm<sup>3</sup>). The mixture was stirred overnight and analysed by GLC on column 2 as in (a) above to show the presence of the acetylene **10** (65% yield) and 2-methylbenzofuran **18** (7% yield).

(d) (*E*)-Stannane **13** and (*Z*)-stannane **14** (*E*:*Z*, 9:10) (0.100 g, 0.23 mmol) in dry deuteriochloroform were shaken with LTA (0.102 g, 0.23 mmol) in dry deuteriochloroform (2.0 cm<sup>3</sup>). The reaction was followed by <sup>1</sup>H NMR spectroscopy, and shown to give 2-methylbenzofuran (20% yield) and 1-(*o*-methoxyphenyl)propyne (27% yield).

(c) Tributyl[(*E*)-biphenyl-2-ylvinyl]stannane **19** (0.7464 g, 1.59 mmol) in dry chloroform (1 cm<sup>3</sup>) was added to a stirred solution of LTA (0.7052 g, 1.59 mmol) in dry chloroform (8 cm<sup>3</sup>). The mixture was stirred at room temperature for 5 d, filtered, and analysed by GLC on column 1 as in (a) above. This showed the presence of phenanthrene (23% yield), while <sup>1</sup>H NMR spectroscopy indicated the formation of biphenyl-2-ylacetylene **23** (36% yield) and butyl acetate (4% yield).

A highfield <sup>1</sup>H NMR analysis of the reaction of stannane **19** with LTA as previously described<sup>1</sup> showed the presence (*E*)-2-biphenyl-2-ylvinyllead triacetate **20** with vinyl hydrogen resonances at  $\delta$  7.27 and 7.42 with <sup>3</sup>*J* couplings of 14.79 and <sup>207</sup>Pb satellites 704.0 (*J*<sub>cis</sub>) and 860.0 (*J*<sub>gem</sub>), respectively.

(d) Stannane **19** (0.1289 g, 0.27 mmol) and lead tetrabenzoate (0.190 g, 0.27 mmol) were allowed to react in chloroform (3 cm<sup>3</sup>) as in (c) above, and analysis in the same way indicated the formation of phenanthrene (46% yield), the acetylene **23** (20% yield) and butyl benzoate (5% yield).

(e) Tributyl[(*E*)-4-phenylbut-1-enyl]stannane **25** and the (*Z*)-isomer **28** (*E*:*Z*, 81:19) (1.063 g, 2.5 mmol) were treated with LTA (1.119 g, 2.5 mmol) in dry chloroform (6 cm<sup>3</sup>) for 24 h as in (a) above and GLC analysis was carried out on column 1. This showed the presence of 4-phenylbut-1-yne **27** (62% yield) and 1,2-dihydronaphthalene **26** (19% yield).

(f) The stannanes **25** and **28** (*E*:*Z*, 81:19) (0.24 g, 0.57 mmol) were treated with lead tetrabenzoate (0.40 g, 0.58 mmol) in dry chloroform (3 cm<sup>3</sup>) for 24 h as in (a) above. GLC analyses were carried out on column 1, indicating the formation of the acetylene **27** (43% yield) and 1,2-dihydronaphthalene **26** (36% yield).

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