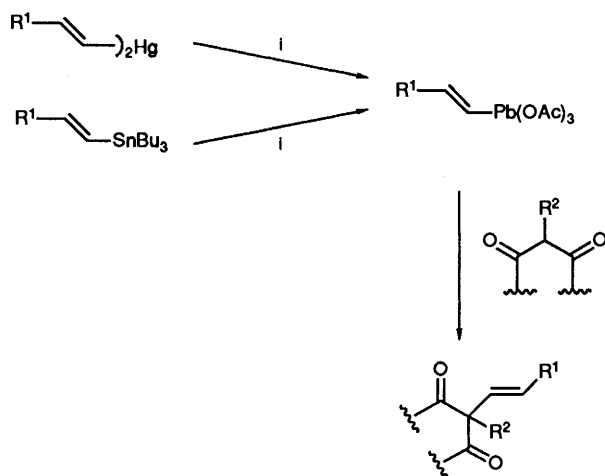


Vinyl Cation Formation by Decomposition of Vinyl-lead Triacetates. The Reactions of Vinylmercury and Vinyltin Compounds with Lead Tetra-acetate

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Vinylmercury compounds and vinylstannanes undergo rapid metal-metal exchange with lead tetra-acetate in chloroform to generate vinyl-lead triacetates, unstable compounds which undergo a thermodynamically favourable reductive elimination of lead(II) acetate. In the presence of mercury(II) salts, vinyl-lead triacetates collapse to the corresponding enol acetate, but in the absence of mercury(II) they yield either the enol acetate or an acetylene depending on the substitution at the double bond. Evidence for the formation of vinyl cations in the collapse of a number of vinyl-lead triacetates has been obtained. Strong support for such intermediates comes from the decomposition of (*E*)-*o*-methoxystyryl-lead triacetate, where the nature of the participation by the neighbouring methoxy group excluded the possibility of involvement of an alkylidenecarbene. Attempted trapping of an alkylidenecarbene by cyclohexane in the decomposition of 2-methylprop-1-enyl-lead triacetate was also unsuccessful, indicating the absence of such an intermediate.

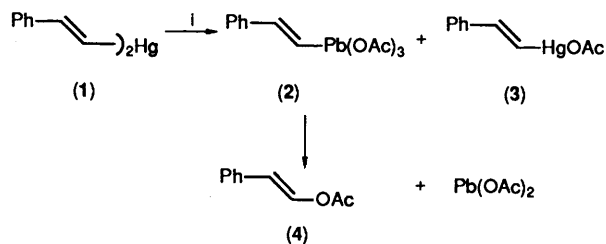
Our successful *C*-vinylation of β -dicarbonyl compounds by vinyl-lead triacetates, generated *in situ* from the reaction of divinylmercury and vinyltin compounds with lead tetra-acetate (LTA)¹ (see Scheme 1), prompted a detailed study of the fate of these unstable lead(IV) compounds in the absence of a soft carbon nucleophile. In this work we had shown that (*E,E*)-distyrylmercury (1) with LTA gave rise initially to (*E*)-styrylmercury acetate (3) and a compound which could not be isolated, but was presumably (*E*)-styryl-lead triacetate (2). When a deuteriochloroform solution of this reaction mixture was kept at room temperature, ¹H NMR signals due to compound (2) gradually decreased with time, while signals due to (*E*)-styryl acetate (4) appeared. After 24 hours only signals due to compounds (3) and (4) were present in the spectrum, indicating a high yielding decomposition of lead compound (2) to the enol acetate (4).



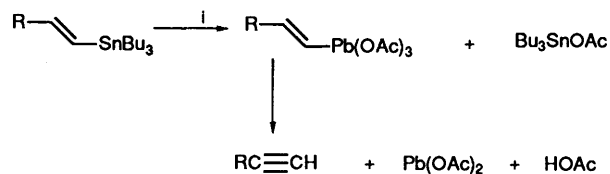
Scheme 1. Reagent: i, LTA.

To our knowledge, Corey and Wollenberg² were the first to propose vinyl-lead triacetates as transient intermediates in a useful synthesis of terminal acetylenes. In their work, reaction of a tributyl(vinyl)stannane with LTA in acetonitrile was employed to generate the vinyl-lead triacetate, which then underwent elimination to produce the acetylene (see Scheme 3).

Further use has been made of this method more recently, but again only for the preparation of alk-1-yne.³ Also relevant to the present work is the brief report of Larock *et al.*⁴ that treatment of vinylmercury chlorides with LTA afforded a stereospecific route to enol acetates; however, of the three mercury compounds examined, only (*E*)-styrylmercury chloride gave a reasonable yield of enol acetate.



Scheme 2. Reagent: i, LTA.



Scheme 3. Reagent: i, LTA.

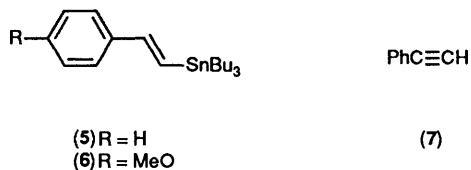
It appeared from this early work that the fate of the vinyl-lead triacetate was dependent on its method of generation; when a vinylstannane was the precursor, elimination occurred to yield an acetylene, while formation from a vinylmercury compound led to displacement of lead by acetate to yield the corresponding enol acetate. To establish conclusively that the same vinyl-lead species was produced by both routes, we examined the reactions of (*E,E*)-distyrylmercury (1) and tributyl[*E*]-styryl]stannane (5) with LTA in deuteriochloroform by ¹H NMR spectroscopy at high resolution. In both reactions a β -substituted (*E*)-styryl compound was produced, and that this was the lead compound (2) in each case was evident from the vinylic proton chemical shifts and couplings (δ 7.32 and 7.50, both doublets, J 15.21 Hz), and the presence of lead satellites due to coupling between ²⁰⁷Pb and the two vinylic protons (J 691.7 and 821.3 Hz, respectively) (see Table). As reported earlier, in the reaction of

Table. NMR spectroscopic data for the vinylic protons of vinyl-lead triacetates^a

Compound	H <i>gem</i> to Pb	H <i>cis</i> to Pb	H <i>trans</i> to Pb
(2)	δ 7.50, $J_{H,H}$ 15.2 $J_{H,Pb}$ 821.3	δ 7.32, $J_{H,H}$ 15.2 $J_{H,Pb}$ 691.7	
(8)	δ 7.37, $J_{H,H}$ 15.0 $J_{H,Pb}$ 831.3	δ 7.25, $J_{H,H}$ 15.0 $J_{H,Pb}$ 692.5	
(14)		δ 6.17, $J_{H,Pb}$ 729.8	
(18)		δ 6.37, $J_{H,Pb}$ 293.9	
(33)	δ 6.89, $J_{H,Pb}$ 864.8		
(48)	δ 7.84, $J_{H,H}$ 14.2 $J_{H,Pb}$ 931.0	δ 7.50 $J_{H,H}$ 14.2 $J_{H,Pb}$ 689.5	
(49)	δ 7.74, $J_{H,H}$ 6.1 $J_{H,Pb}$ 924.0		δ 7.77, $J_{H,H}$ 6.1 $J_{H,Pb}$ 1 667.5
(60)	δ 7.33, $J_{H,Pb}$ 819.0		
(65)	δ 6.37, $J_{H,Pb}$ 924.1		
(72)	δ 7.72, $J_{H,H}$ 14.0 $J_{H,Pb}$ 926.5	δ 7.44, $J_{H,H}$ 14.0 $J_{H,Pb}$ 761.0	

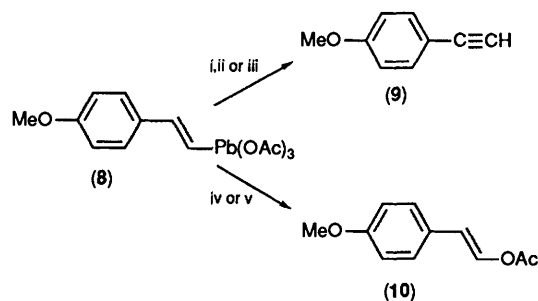
^a The vinyl-lead compounds were generated in CDCl₃ (see Experimental section), and chemical shifts are downfield from SiMe₄ (TMS) as internal standard. Couplings are in Hz and are for ²⁰⁷Pb.

compound (1) only (*E*)-styrylmercury acetate (3) and (*E*)-styryl acetate (4) were present after complete decomposition of the lead compound (24 h), whereas in the reaction of the stannane (5) the lead compound underwent a slower decomposition (48 h) to yield phenylacetylene (7). The decompositions of compound (2) were product specific; none of the enol acetate (4) was produced in the latter reaction, and phenylacetylene could not be detected in the reaction of the mercury compound (1).



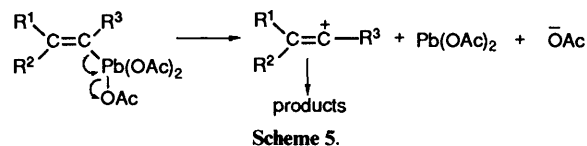
It seemed likely that the different behaviour of the lead compound (2) generated from the divinylmercury compound (1) as in Scheme 2, from that produced from the stannane (5), was due to the presence of the mercury(II) compound (3). This was confirmed by treatment of tributyl[(*E*)-styryl]stannane (5) with LTA, followed by the addition of (*E*)-styrylmercury acetate (3) after 5 min. Here the only product was (*E*)-styryl acetate (4). Further proof that mercury(II) compounds could influence the mode of decomposition of vinyl-lead triacetates came from a series of reactions of (*E*)-*p*-methoxystyryl-lead triacetate (8) (see Scheme 4). The latter compound (8), which was produced in a very rapid tin-lead exchange reaction of tributyl[(*E*)-*p*-methoxystyryl]stannane (6), proved to be unusually stable, and only after 1 h could *p*-methoxyphenylacetylene (9) be detected in the chloroform solution. Thus, by treatment of the reaction mixture with light petroleum 10 min after the addition of LTA to a chloroform solution of substrate (6), it was possible to precipitate the lead compound (8) as an unstable brown powder. The material had the expected ¹H NMR spectrum (see Table and Experimental section); however, attempted further purification by crystallisation from chloroform–light petroleum resulted in decomposition to the acetylene (9), which was the only product detected (NMR spectroscopy) when lead compound (8) was kept at room temperature for 21 h in

deuteriochloroform. The addition of either mercury(II) acetate or (*E*)-styrylmercury acetate (3) to a deuteriochloroform solution of compound (8) had a marked effect on its breakdown, with (*E*)-*p*-methoxystyryl acetate (10) being the only detectable product. Since none of the enol acetate (10) was produced when either acetic acid or tetrabutylammonium acetate was added in place of the mercury(II) compounds, there appeared little doubt that mercury(II) was intimately involved in enol acetate formation.*



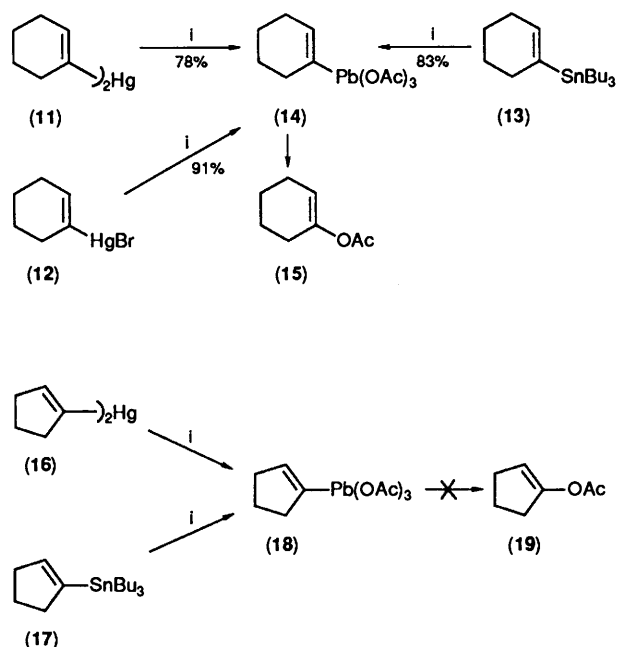
Scheme 4. Reagents and conditions: i, CDCl₃; ii, HOAc, CDCl₃; iii, Bu₄N⁺ OAc⁻, CDCl₃; iv, Hg(OAc)₂, CDCl₃; v, PhCH=CHHgOAc, CDCl₃.

The above elimination and substitution reactions of the vinyl-lead compounds (2) and (8) indicated that the thermodynamically favourable reduction of Pb^{IV} to Pb^{II} made the triacetoxylplumbyl group an exceptionally good leaving group. Thus, although we do not suggest mechanisms at this stage for the reactions of compounds (2) and (8), it appeared to us that the decomposition of vinyl-lead triacetates and related esters may provide a new and convenient route to vinyl cations^{5a} (see Scheme 5). Such a method was of interest, since it would allow the generation of vinyl cations in the absence of nucleophilic solvents, which are required in their solvolytic formation from vinyl triflates and nonaflates.^{5b}

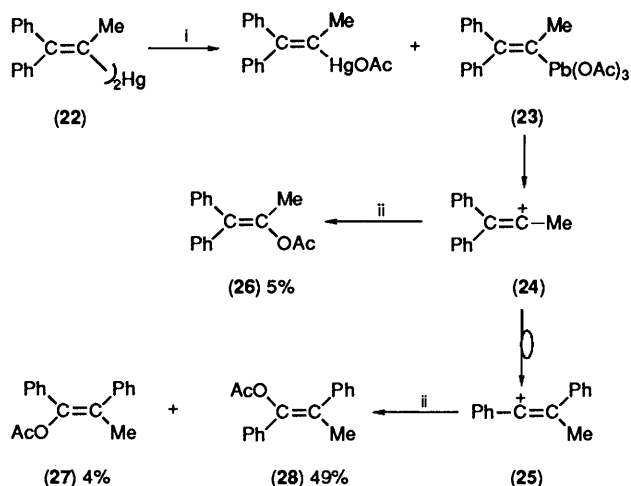
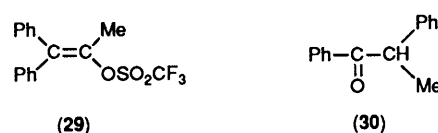


A study of the reactions of di(cyclohex-1-enyl)mercury (11), cyclohex-1-enylmercury bromide (12), tributyl(cyclohex-1-enyl)stannane (13), di(cyclopent-1-enyl)mercury (16), and tributyl(cyclopent-1-enyl)stannane (17) with LTA gave the first indication that vinyl cations are most likely involved in the decompositions of vinyl-lead triacetates in chloroform solution (see Scheme 6). All the cyclohex-1-enyl derivatives gave cyclohex-1-enyl acetate (15) in high yield, while none of the corresponding enol acetate (19) was produced from the cyclopent-1-enyl derivatives (16) and (17), even after 48 h. The five reactions were monitored by NMR spectroscopy, and evidence for the presence of the respective lead(IV) intermediates (14) and (18) was obtained in each case (see Table and Experimental section). In fact, cyclopent-1-enyl-lead triacetate (18) could be isolated from the reaction of the stannane (17) as an unstable solid.¹ The different behaviour of the cyclohex-1-enyl and cyclopent-1-enyl compounds (14) and (18) is exactly analogous to that of cyclohex-1-enyl triflate and cyclopent-1-enyl triflate; the former compound readily undergoes solvolysis in ethanol whereas the cyclopentene derivative does not, reacting preferentially by sulphur–oxygen cleavage.^{5c,6} This has been rationalised in terms of the stabilities of the cyclohex-1-enyl cation (20) and cyclopent-1-enyl cation (21), the latter being of particularly high energy.

* A similar conclusion has been reached by Larock⁴ regarding the palladium(II) acetate-catalysed conversion of vinylmercury(II) compounds into enol acetates.

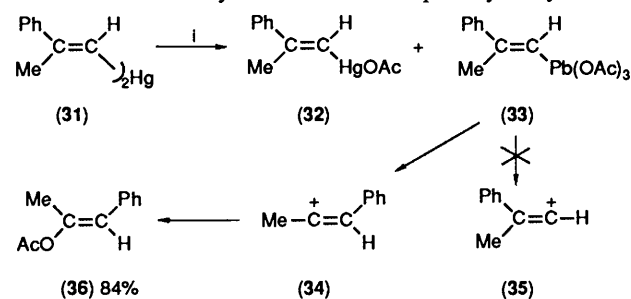
Scheme 6. Reagents and conditions: i, LTA, CHCl₃.

Further strong evidence for the formation of vinyl cations in the decomposition of vinyl-lead triacetates was obtained in the reactions of the divinylmercury compounds (22) and (31), and the stannanes (37), (39), and (42) with LTA in chloroform. As shown in Scheme 7 the mercury compound (22) gave the enol acetates (26), (27), and (28) in yields of 5, 4, and 49%, respectively. Although the vinyl-lead intermediate (23) could not be detected in this case due to the absence of vinylic protons, it is presumably the precursor of the enol acetates, the formation of which is most readily rationalised as shown; collapse of the lead compound (23) would produce the cation (24), which could be captured by acetate ion to give enol acetate (26), or rearrange by phenyl migration to the more stable cation (25). Attack by acetate on this ion would then yield the acetates (27) and (28). Similar behaviour has been noted in the solvolysis of the triflate

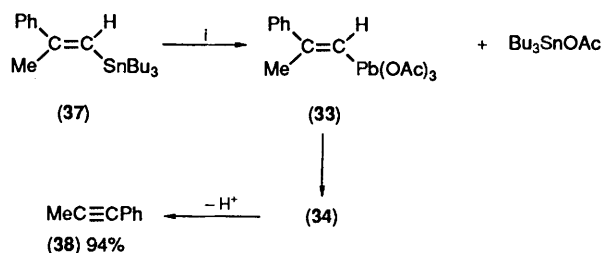
Scheme 7. Reagents: i, LTA, CHCl₃; ii, AcO⁻ (in situ).

(29) in aqueous ethanol, where the ketone (30) is formed in almost quantitative yield.⁶

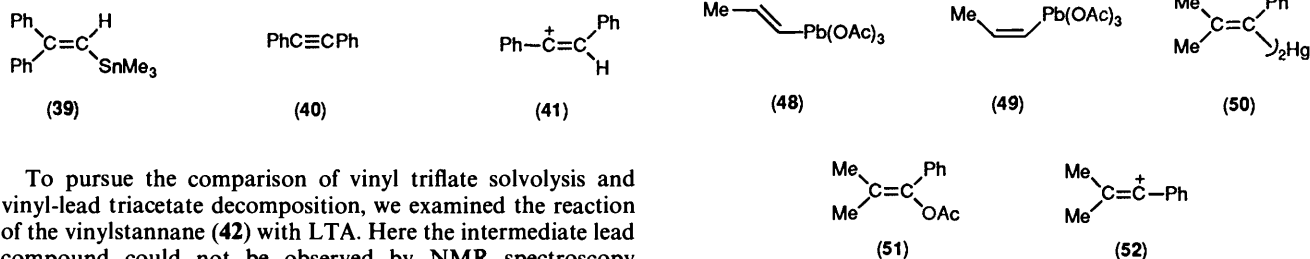
The divinylmercury compound (31) reacted with LTA to give the enol acetate (36) in 84% yield (see Scheme 8). The formation of the vinylmercury acetate (32) and vinyl-lead triacetate (33) were indicated by vinylic proton resonances in the NMR spectrum at δ 5.97 and 6.89, respectively, and as the reaction progressed the latter signal decreased while those due to the enol acetate (36) increased. Confirmation that the signal at δ 6.89 was due to lead compound (33) was obtained from the presence of ²⁰⁷Pb satellites (see Table). Neither of the two enol acetates which could result from attack of acetate on the cation (35) was produced, which would suggest that this ion is not formed. This is consistent with the high energy of vinyl cations having only hydrogen attached to the sp²-hybridised carbon,^{5d} and thus we propose that the rearranged cation (34) is formed by a pathway involving concerted loss of Pb^{II} and phenyl migration. Attack by acetate on cation (34) from the less hindered side would then result in formation of enol acetate (36). The proposed 1,2-phenyl shift is consistent with the higher migratory aptitude of the phenyl group than the methyl group in such systems;^{5e} in fact the migration of an alkyl group across the double bond of a vinyl cation is rare except in cyclic systems.^{5f}

Scheme 8. Reagent: i, LTA, CHCl₃.

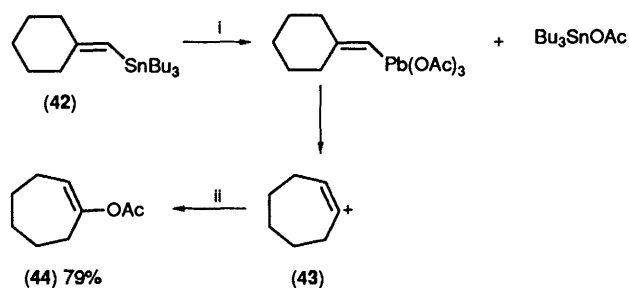
To explore further the 'mercury(II) effect' noted above, we examined the tin analogue (37) of the mercury compound (31). When the stannane (37) was treated in the same way with LTA a rapid reaction occurred (<10 min) to give tributyltin acetate and the vinyl-lead compound (33) (identical by NMR spectroscopy with that obtained above). Further monitoring of the reaction by NMR spectroscopy showed the slow disappearance of this intermediate with the appearance of signals due to 1-phenylpropyne (38), which was present in 94% yield after 22 h (see Scheme 9). None of the enol acetate (36) could be detected by NMR spectroscopy; however, GLC analysis did indicate its possible presence (<5%). It would therefore appear that in the absence of the mercury compound (32), the vinyl cation (34) loses a proton to give the acetylene (38).

Scheme 9. Reagent: i, LTA, CHCl₃.

A result similar to that outlined in Scheme 9 was obtained when trimethyl(β -phenylstyryl)stannane (**39**) was treated with LTA in chloroform; diphenylacetylene (**40**) (90% yield) was the only product, and we believe that it is formed in a similar manner to the acetylene (**38**), *i.e.* via the rearranged vinyl cation (**41**).



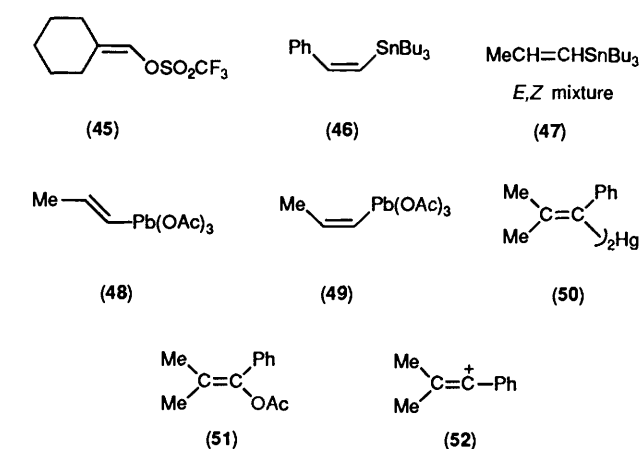
To pursue the comparison of vinyl triflate solvolysis and vinyl-lead triacetate decomposition, we examined the reaction of the vinylstannane (**42**) with LTA. Here the intermediate lead compound could not be observed by NMR spectroscopy because of a slow tin-lead exchange compared with the collapse of the vinyl-lead compound, which produced cyclohept-1-enyl acetate (**44**) in 79% yield (see Scheme 10). This parallels almost exactly the solvolysis of the vinyl triflate (**45**) in aqueous trifluoroethanol to give cycloheptanone in quantitative yield.^{5g} Just as in that case, the reaction is most readily rationalised as proceeding through the cyclohept-1-enyl cation (**43**), which, as in the reaction of the divinylmercury compound (**31**), is probably formed by a concerted loss of Pb^{II} and methylene migration. Here, just as with the reaction of the stannane (**13**), where acetylene formation is blocked, the enol acetate results.



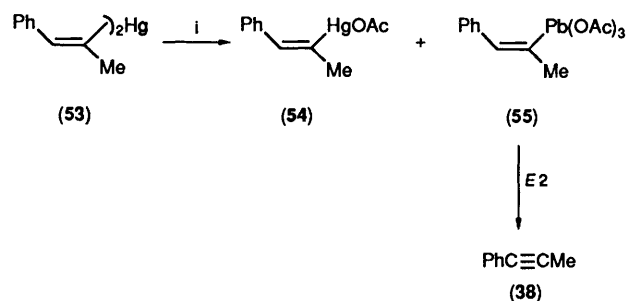
Scheme 10. Reagents: i, LTA, CHCl₃; ii, AcO⁻ (*in situ*).

A number of other substrates were treated with LTA to allow us to examine further the generality of the finding that vinylstannanes with a β -hydrogen yield acetylenes, while vinylmercury compounds give enol acetates. The (*Z*)-isomer (**46**) was found to behave in the same way as the (*E*)-isomer (**5**). Although compound (**46**) could not be obtained free of its isomer (**5**), a 35:65 mixture of isomers (**5**) and (**46**) reacted with LTA to give phenylacetylene (**7**) in 95% yield. The only difference in behaviour of the two compounds was the much slower tin-lead exchange of the (*Z*)-isomer (**46**) than that of the (*E*)-isomer (**5**). A similar result was obtained with a mixture of the (*E*)- and (*Z*)-vinylstannane (**47**); the (*Z*)-isomer was also slower to react in the metal-metal exchange; however, only propyne (**55**) was produced in the reaction. Interestingly, although both (*E*)- and (*Z*)-vinyl-lead triacetates, (**48**) and (**49**), respectively, could be observed in the NMR spectrum (see Table), the (*Z*)-isomer (**49**) was considerably less stable. We suggest that this could be due to an *E2*-type elimination operating in this case, although a stepwise process involving an intermediate vinyl cation, followed by abstraction of a proton, cannot be excluded.

The vinylmercury compound (**50**) reacted with LTA to give the enol acetate (**51**) in 80% yield. No other products were observed, as would be expected on the grounds of the stability of the vinyl cation (**52**). The divinylmercury compounds (**53**) and (**58**) were the only compounds in this study which did not follow



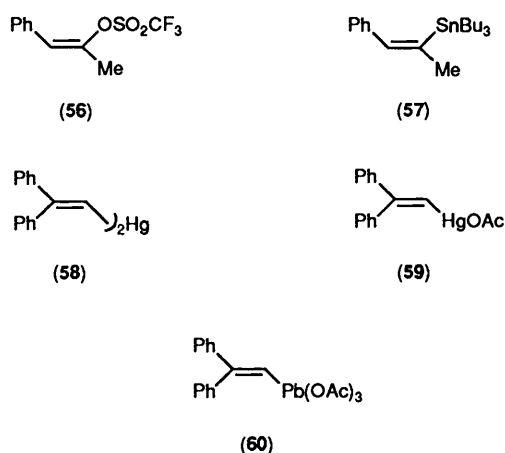
the general pattern of reactivity noted above. Treatment of compound (**53**) with LTA gave 1-phenylpropyne (**38**) as the only isolable product in 88% yield (see Scheme 11). Although the formation of the vinylmercury acetate (**54**) was indicated by a vinyl proton resonance at δ 7.13 in the ¹H NMR spectrum, the presence of the intermediate vinyl-lead triacetate (**55**) could not be confirmed due to the masking of the signal due to the vinyl proton by those due to the aromatic protons. The *trans*



Scheme 11. Reagent: i, LTA, CHCl₃.

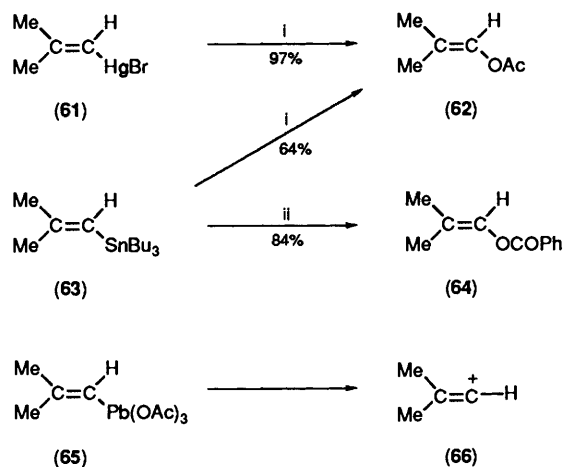
arrangement of the proton and the leaving group in the vinyl-lead triacetate (**55**), a situation not present in any of the other mercury-derived vinyl-lead compounds, could then result in direct formation of the acetylene (**38**) by an *E2*-type elimination; however, a stepwise reaction proceeding through a vinyl cation is not excluded. A similar *E2*-type mechanism has been proposed for the solvolysis of the analogous vinyl triflate (**56**), which also gives the acetylene (**38**) in 77–95% yield in aqueous trifluoroethanol.⁷ Here, unlike our reaction outlined in Scheme 11, some vinyl cation formation, with a hydride shift to produce a more stable vinyl cation, was indicated by the isolation of small amounts of benzyl methyl ketone and ethyl phenyl ketone. As expected, the analogous stannane (**57**) also gave a high yield (94%) of the acetylene (**38**) on treatment with LTA, and again we tentatively propose the operation of an *E2*-type elimination of the vinyl-lead intermediate (**55**).

The divinylmercury compound (**58**), the other compound which behaved anomalously, reacted with LTA to give diphenylacetylene (**40**) in 70% yield. It thus reacted similarly to the analogous stannane (**39**), and a mechanism involving the rearranged vinyl cation (**41**) is presumably operating in this case. Thus, even though the initial metal-metal exchange proceeded in the usual way, as indicated by the presence in the NMR spectrum of a vinyl proton resonance at δ 6.25 due to the vinylmercury acetate (**59**) and one at δ 7.33 due to the lead compound (**60**) (see Table for ²⁰⁷Pb satellite data), the nature of the product did not appear to be influenced by the presence of Hg^{II}, as in the case of the closely related divinylmercury



compound (31). The difference in behaviour of the two compounds may lie in the different stabilities of the two vinyl cations (41) and (34).

The reactions of the vinylmercury compound (61) and the

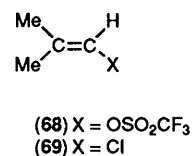
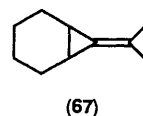


Scheme 12. Reagents and conditions: i, LTA, CHCl_3 ; ii, $\text{Pb}(\text{OCOPh})_4$, CHCl_3 .

corresponding vinylstannane (63) with LTA are of significance with regard to the mechanism of substitution of lead by acetate in some of the above compounds. Both reactions (see Scheme 12) yielded the enol acetate (62) *via* an unstable intermediate with a vinyl proton resonance in the NMR spectrum at δ 6.37; this would appear to be the vinyl-lead compound (65), since ^{207}Pb satellites are present in the spectrum (see Table). In a further experiment the vinylstannane (63) reacted with lead tetrabenzoate to give the enol benzoate (64) in high yield. These results, especially of the stannane (63), are consistent with a mechanism involving collapse of the vinyl-lead intermediate to the vinyl cation (66), which is then captured by the nucleophile. Although primary vinyl cations are of high energy, thermodynamic data for the stabilising effect of β -methyl groups^{5d} would suggest that such an ion may be accessible with a 'super' leaving group. In fact the vinyl cation (66) has been proposed as an intermediate in a reaction in $\text{FSO}_3\text{H}-\text{SbF}_5$ solution.^{8*} In seeking alternative ways of rationalising the results obtained with the stannane (63), the reactions of the stannanes (37), (39), and (42) should be kept in mind. All involve migrations which

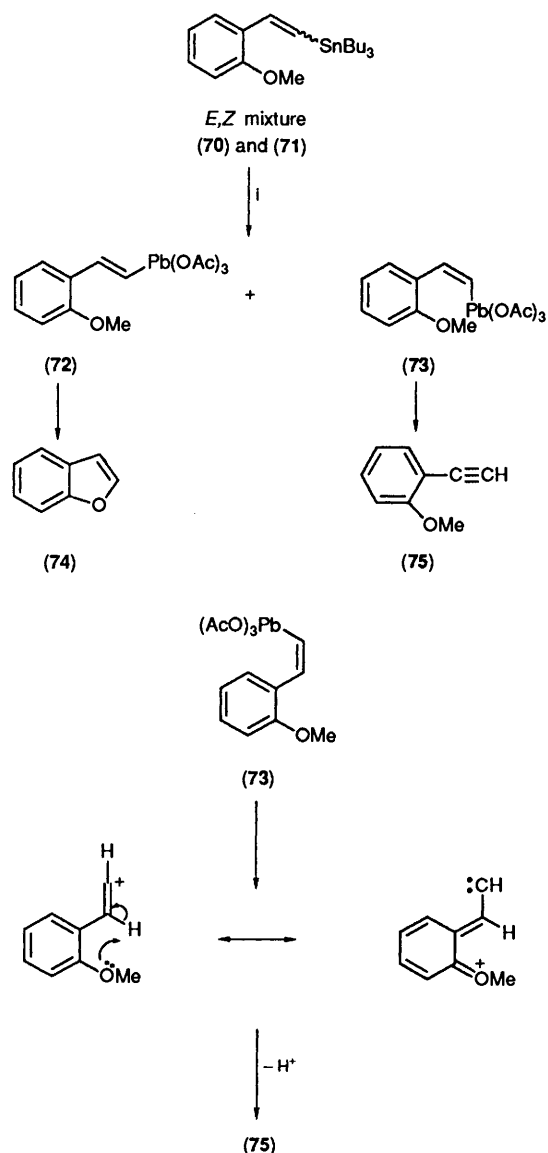
are probably concomitant with departure of Pb^{II} , and for which analogous migrations have been noted in solvolyses of vinyl triflates.^{5e} In the case of compound (63), the only shift possible is that of a methyl group, a migration which is regarded as highly unlikely with vinyl cations in non-cyclic systems. We have rejected the possibility of an $\text{Ad}_N\text{-E}$ mechanism on the grounds of the reaction conditions and the nature of the substrate, while an internal collapse of the intermediate vinyl-lead compound would leave unexplained the stability of cyclopent-1-enyl-lead triacetate and its failure to yield any of the corresponding enol acetate.

Experiments which implicate Vinyl Cations rather than Alkylidenecarbenes in Vinyl-lead Tricarboxylate Decompositions.—Since the possibility existed that the decompositions of a number of the above vinyl-lead compounds could have been proceeding *via* alkylidenecarbene intermediates⁹ rather than vinyl cations, two experiments were conducted to resolve this point. In the first of these, 2-methylprop-1-enyl-lead triacetate (65) was generated in chloroform from the corresponding vinylstannane (63) as outlined above, and the mixture was then stirred for 24 h with a large excess of cyclohexene. Analysis of the product by FTIR and ^1H NMR spectroscopy showed that the enol acetate (62) was produced in similar yield to that obtained in the absence of cyclohexene, and that none of the product of carbene trapping, the isopropylidencyclopropane (67),^{10,11} had been formed. Similar experiments had been carried out in order to trap the intermediate in the base-induced elimination reactions of the vinyl triflate (68)¹⁰ and the vinyl chloride (69),¹¹ and in both cases the cyclopropane derivative (67) was produced.



Our second approach to this problem involved a study of the decomposition products of (*E*)-*o*-methoxystyryl-lead triacetate (72) and its (*Z*)-isomer (73), which were generated by reaction of the corresponding tributyl(vinyl)stannanes (70) and (71), respectively, with LTA in chloroform. Although neither of the stannanes (70) and (71) could be obtained free of the other isomer, we were able to outline the reaction pathways for each compound (see Scheme 13) by the use of mixtures containing different ratios of (70) and (71) (see later). An ^1H NMR spectroscopic study of the tin-lead exchange reaction of the mixture of stannanes (70) and (71) showed that the (*E*)-compound (70) reacted rapidly with LTA to give the (*E*)-vinyl-lead compound (72) (see Table and Experimental section), while the (*Z*)-isomer underwent a slower reaction. The product in the latter case was presumably the (*Z*)-vinyl-lead triacetate (73), but its NMR spectrum could not be recorded. Within 0.5 h the lead compound (72) could no longer be detected, and the spectrum contained signals due to benzofuran (74) and *o*-methoxyphenylacetylene (75). Proof of the identity and the yields of compounds (74) and (75) were further established by GC analysis. For a mixture containing 81% of the (*E*)-isomer

* A mechanism involving ion (66) has been queried on the grounds of the high energy of primary vinyl cations.^{5f}



Scheme 13. Reagent: i, LTA, CHCl₃.

(70) and 19% of the (*Z*)-isomer (71), an analysis after 0.5 h showed the product to contain benzofuran (74) (83% yield), *o*-methoxyphenylacetylene (75) (9% yield), and unchanged (*Z*)-stannane (7%); however, when the (*E*):(*Z*) ratio of stannanes (70) and (71) was 60:40 the yields of benzofuran (74) and *o*-methoxyphenylacetylene (75) after 24 h were 61 and 30% respectively. Thus, it would appear that the benzofuran (74) arises from the (*E*)-vinyl-lead triacetate (72), while the (*Z*)-vinyl-lead compound is the precursor of *o*-methoxyphenylacetylene (75).

The above results for the reactions of the lead compounds (72) and (73) would appear to exclude alkylidenecarbene formation, since insertion into a C–H bond of the methoxy group by such an intermediate would have been expected.⁹ The formation of benzofuran (74) from the (*E*)-isomer (72) indicates that this isomer collapses to a vinyl cation, which then undergoes intramolecular attack by the neighbouring oxygen. Although it is apparent that the (*Z*)-isomer (73) is the precursor of the acetylene (75), the possibility that it also gives rise to a

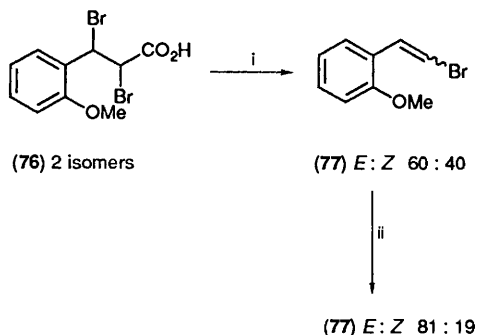
small amount of benzofuran cannot be excluded. The formation of the acetylene (75) could be rationalised in terms of an *E2*-type elimination, or it may involve formation of a cation in a conformation which cannot undergo cyclisation, followed by proton loss as indicated.*

We believe that the above results provide strong evidence that the decomposition of certain vinyl-lead triacetates provides a new and useful route to vinyl cations. The way in which Hg^{II} affects the fate of these ions in certain cases remains unknown and is being investigated further by us.

Characterisation of Vinyl-lead Triacetates by ¹H NMR Spectroscopy.—The ²⁰⁷Pb-vinyl proton coupling constants for many of the vinyl-lead triacetates generated in this work are recorded in the Table. It can be seen that the relative sizes of the couplings by ²⁰⁷Pb to the *geminal*, *cis*, and *trans* vinylic protons are $J_{\text{Pb,H}(\text{trans})} > J_{\text{Pb,H}(\text{gem})} > J_{\text{Pb,H}(\text{cis})}$ which is consistent with the values reported for tetravinyl-lead.¹² The considerably larger values for the couplings in the vinyl-lead triacetates, compared with those for tetravinyl-lead, are consistent with the finding that attachment of electron-withdrawing groups to Pb results in an increase in the magnitude of the ²⁰⁷Pb–H coupling constant.¹³

Synthesis of Vinylmercury Acetates, Stannanes, and Enol Acetates.—The previously unreported vinylmercury acetates (3), (32), and (54) were prepared by reaction of the corresponding vinylmercury bromides¹ with silver acetate in chloroform or tetrahydrofuran (THF).

The synthesis of the stannanes was also carried out by formation of the Grignard reagent from the corresponding vinyl bromide, followed by reaction with either tributylchlorostannane or chlorotrimethylstannane. Compounds (6), (13), (37), (46), (57), (70), and (71) are reported here for the first time. As noted earlier, neither of the isomeric stannanes (70) and (71) could be obtained free of the other isomer. They were obtained by the above general method as a 60:40 (*E*):(*Z*) mixture from a similar mixture of the corresponding vinyl bromides (77); this mixture was in turn produced from a base-catalysed decarboxylative debromination of a diastereoisomeric mixture of dibromides (76)¹⁴ (see Scheme 14). When the mixture of isomeric vinyl bromides (77) was irradiated with a tungsten lamp in the presence of iodine, the *E*:*Z* ratio at equilibrium was 81:19. This latter material was used to produce a corresponding isomer mixture of the stannanes (70) and (71).



Scheme 14. Reagents and conditions: i, K₂CO₃; ii, I₂, hv.

The enol acetates, which were required for identification, were prepared by standard procedures from the corresponding aldehyde or ketone; of these, compounds (26), (27), (28), and (51) have not been reported previously. The enol acetates (10) and (36) were prepared as previously described, and have been shown (see Experimental section) to be a mixture of *E* and *Z* isomers.

* We thank a referee for suggesting the latter possibility.

Experimental

For the general experimental procedures see our earlier paper.¹⁵ Analytical GLC was carried out on either a Pye Series 104 chromatograph or a Hewlett Packard 5890 instrument, and one of the following columns: column 1, 10% Carbowax 20M on Gas Chrom Q (80–100 mesh), 2 mm i.d. \times 1.5 m; column 2, 3% OV-17 on Gas Chrom Q (100–120 mesh), 2 mm i.d. \times 1.5 m; column 3, SGE capillary column BPI, 0.33 mm i.d. \times 25 m.

Synthesis of Vinylmercury Acetates.—To a solution of the vinylmercury bromide¹ (3 mmol) in THF (40 ml) or chloroform (100 ml) was added silver acetate (3 mmol), and the mixture was stirred overnight in the dark. The mixture was filtered through Celite, the solvent was evaporated off, and the residue was purified by crystallisation.

The following compounds were prepared by the above general method.

(a) (E)-Styrylmercury acetate (**3**) (89%), m.p. 146–148 °C (from heptane) (Found: C, 33.0; H, 3.1. C₁₀H₁₀HgO₂ requires C, 33.1; H, 2.8%); λ_{\max} (EtOH) 259 nm (ϵ 15 100); ν_{\max} (Nujol) 1 610 cm⁻¹; δ_{H} (CDCl₃) 2.07 (3 H, s, OAc), 6.52 (1 H, d, *J* 18.4 Hz, ¹⁹⁹Hg satellites gave *J*_{H,Hg} 239 Hz, α -H), 6.79 (1 H, d, *J* 18.4 Hz, ¹⁹⁹Hg satellites gave *J*_{H,Hg} 294 Hz, β -H), and 7.34 (5 H, m, Ph).

(b) (E)-2-Phenylprop-1-enylmercury acetate (**32**) (80%), m.p. 125–128 °C (from chloroform–cyclohexane) (Found: C, 34.7; H, 3.3. C₁₁H₁₂HgO₂ requires C, 35.1; H, 3.2%); λ_{\max} (MeCN) 263 nm (16 500); ν_{\max} (Nujol) 1 600 and 1 580 cm⁻¹; δ_{H} (CDCl₃) 2.07 (3 H, s, OAc), 2.42 (3 H, d, *J* 1.1 Hz, ¹⁹⁹Hg satellites gave *J*_{Me,Hg} 36 Hz, Me), 6.00 (1 H, m, ¹⁹⁹Hg satellites gave *J*_{H,Hg} 242 Hz, vinyl H), and 7.20–7.52 (5 H, m, Ph).

(c) (Z)- α -Methylstyrylmercury acetate (**54**) (50%), m.p. 56–58 °C (from light petroleum) (Found: C, 36.3; H, 3.3. C₁₁H₁₂HgO₂ requires C, 35.1; H, 3.2%); λ_{\max} (cyclohexane) 229 and 261 nm (8 200 and 7 800); ν_{\max} (Nujol) 1 590 cm⁻¹; δ_{H} (CDCl₃) 2.00 (3 H, s, OAc), 2.21 (3 H, d, *J* 1.8 Hz, ¹⁹⁹Hg satellites gave *J*_{Me,Hg} 189 Hz, Me), 7.15 (1 H, q, *J* 1.8 Hz, ¹⁹⁹Hg satellites gave *J*_{H,Hg} 550 Hz, vinyl H), and 7.20–7.56 (5 H, m, Ph).

(d) β -Phenylstyrylmercury acetate (**59**) (22%), m.p. 131–132 °C (from cyclohexane) (lit.,¹⁶ 130 °C); λ_{\max} (dioxane) 242 and 274 nm (12 800 and 12 500); δ_{H} (CDCl₃) 2.00 (3 H, s, OAc), 6.25 (1 H, s, ¹⁹⁹Hg satellites gave *J*_{H,Hg} 239.8 Hz, vinyl H), 7.32 (5 H, br s, Ph), and 7.42 (5 H, br s, Ph).

Synthesis of Trialkyl(vinyl)stannanes.—The vinyl bromide (10 drops) and ethylene dibromide (3 drops) were added to magnesium turnings (1.5–2.0 mol equiv.) in THF (10 ml) under nitrogen. Once initiation had occurred, a solution of the remainder of the vinyl bromide (3–10 mmol) in THF (30 ml) was added during 1 h at reflux. The mixture was refluxed for a further 1 h, and the dark solution was then decanted (cannula) from the excess of magnesium. The trialkylchlorostannane was added dropwise until the Grignard solution was just decolourised, and the mixture was heated at reflux for 1 h, then cooled to room temperature, the solvent was evaporated off, and the residue was partitioned between diethyl ether and water. The ether phase was washed with water, then dried, the solvent was evaporated off, and the crude product was distilled (Kugelrohr).

The following compounds were prepared according to the above general method.

(a) Tributyl[(E)-*p*-methoxystyryl]stannane (**6**) (68%), b.p. 215 °C at 0.2 mmHg (Kugelrohr) (Found: C, 59.5; H, 8.4. C₂₁H₃₆OSn requires C, 59.6; H, 8.6%); λ_{\max} (hexane) 275 nm (21 540); ν_{\max} (film) 1 600 cm⁻¹; δ_{H} (CDCl₃) 0.64–1.08 and 1.12–2.4 (27 H, m, 3 \times Bu), 3.79 (3 H, s, OMe), 6.67 (1 H, d, *J* 19.2 Hz, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ²*J*_{Sn,H} average of 67 Hz, vinyl H), 6.82 (1 H, d, *J* 19.2 Hz, vinyl H), and 6.85 and 7.35 (4 H, AA'BB', ArH).

(b) Tributyl(cyclohex-1-enyl)stannane (**13**), purified by semi-

preparative GLC (3% OV-17 on Chromosorb G at 185 °C) (Found: C, 58.7; H, 10.1. C₁₈H₃₆Sn requires C, 58.2; H, 9.8%); λ_{\max} (hexane) 230 nm (1 280); ν_{\max} (film) 1 610 cm⁻¹; δ_{H} (CDCl₃) 0.70–1.78 and 1.92–2.40 (35 H, m, 3 \times Bu and 4 \times CH₂, and 5.79 (1 H, m, vinyl H).

(c) (E)-Tributyl(2-phenylprop-1-enyl)stannane (**37**) (64%), b.p. 150 °C at 0.05 mmHg (Kugelrohr) (Found: C, 62.0; H, 9.3. C₂₁H₃₆Sn requires C, 61.9; H, 8.9%); λ_{\max} (EtOH) 254 nm (12 900); ν_{\max} (film) 1 600 cm⁻¹; δ_{H} (CDCl₃) 0.90 (9 H, t, *J* 7.2 Hz, 3 \times Me), 0.98 (6 H, t, *J* 9.0 Hz, 3 \times CH₂Sn), 1.33 (6 H, m, 3 \times CH₂), 1.37–1.59 (6 H, m, 3 \times CH₂), 2.21 (3 H, d, ⁴*J*_{H,Me} 0.67 Hz, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ⁴*J*_{Sn,Me} average of 10 Hz, Me), 6.28 (1 H, q, ⁴*J*_{H,Me} 0.67 Hz, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ²*J*_{Sn,H} 63 and 66 Hz, respectively), and 7.20–7.48 (5 H, m, Ph).

(d) Tributyl(cyclohexylenemethyl)stannane (**42**) (75%), b.p. 200 °C at 0.2 mmHg (Kugelrohr); δ_{H} (CDCl₃) 0.88–1.72 (33 H, m, 3 \times Bu and 3 \times CH₂), 2.21 (2 H, m, CH₂), 2.35 (2 H, m, CH₂), and 5.37 (1 H, m, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ²*J*_{Sn,H} average of 76 Hz, vinyl H). Other spectral data corresponded with reported values.¹⁷

(e) Tributyl[(Z)-styryl]stannane (**46**) and the (E)-isomer (**5**)¹ (ratio 87:13, respectively) (19%) was obtained by distillation [b.p. 165 °C at 0.3 mmHg (Kugelrohr)] followed by chromatography in hexane on a column of silica gel; λ_{\max} (hexane) 257 nm (9 970); δ_{H} for (Z)-isomer (CDCl₃) 0.7–1.9 (27 H, m, 3 \times Bu), 6.21 (1 H, d, *J* 13.6 Hz, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ²*J*_{Sn,H} values of 56.0 and 56.6 Hz, respectively, vinyl H), 7.29 (5 H, br s, Ph), and 7.65 (1 H, d, *J* 13.6 Hz, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ³*J*_{Sn,H} values of 130.4 and 136.8 Hz, respectively, vinyl H).

(f) Tributyl[(Z)- α -methylstyryl]stannane (**57**) (72%), b.p. 180 °C at 0.1 mmHg (Kugelrohr) (Found: C, 62.0; H, 8.8. C₂₁H₃₆Sn requires C, 61.9; H, 8.9%); λ_{\max} (EtOH) 249 nm (8 060); δ_{H} (CDCl₃) 0.72 (6 H, t, *J* 8 Hz, 3 \times CH₂Sn), 0.83 (9 H, t, *J* 6 Hz, 3 \times Me), 1.23 (6 H, m, 3 \times CH₂), 1.34 (6 H, m, 3 \times CH₂), 2.10 (3 H, d, ⁴*J*_{Me,H} 1.8 Hz, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ³*J*_{Me,Sn} values of 39.1 and 42.8 Hz, respectively, Me), 7.26 (1 H, m, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ³*J*_{Sn,H} average of 125 Hz, vinyl H), and 7.04–7.50 (5 H, m, Ph).

(g) Tributyl(2-methylprop-1-enyl)stannane (**63**) (46%), b.p. 115–120 °C at 1.5 mmHg (lit.,¹⁸ 104–105 °C at 0.4 mmHg); δ_{H} (CDCl₃) 0.70–1.69 (27 H, m, 3 \times Bu), 1.78 (3 H, s, Me), 1.89 (3 H, d, *J* 1.4 Hz, Me), and 5.45 (1 H, m, ¹¹⁷Sn and ¹¹⁹Sn satellites gave an average *J*_{H,Sn} 73.8 Hz, 1-H).

Trimethyl- β (phenylstyryl)stannane (39).—Butyl-lithium in hexane (2.5M; 7.8 ml, 20 mmol) was added dropwise to a stirred solution of 2,2-diphenylvinyl bromide (5 g, 19 mmol) in dry diethyl ether (40 ml) at –78 °C under nitrogen. The solution was stirred at –78 °C for 1 h, warmed to –20 °C for 0.5 h, and then cooled again to –78 °C. A solution of chlorotrimethylstannane (3.85 g, 19 mmol) in dry diethyl ether (20 ml) was added dropwise and the mixture was stirred at –78 °C for 1 h, and then allowed to warm to room temperature overnight. The solution was filtered through Celite and the solvent was evaporated off. The residue was distilled to give the title compound (**39**) as an oil (4.13 g, 62%), b.p. 130 °C at 0.2 mmHg (Kugelrohr) (lit.,¹⁹ 116–118 °C at 0.2 mmHg); δ_{H} (CDCl₃) –0.08 (9 H, s, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ²*J*_{Me,Sn} values of 53.2 and 55.8 Hz, respectively, 3 \times Me), 6.67 (1 H, s, ¹¹⁷Sn and ¹¹⁹Sn satellites gave ²*J*_{Sn,H} values of 65.8 and 68.9 Hz, respectively, vinyl H), 7.21–7.40 (8 H, m, ArH), and 7.54 (2 H, m, ArH).

Synthesis of the Mixtures of Tributyl[(E)-*o*-methoxystyryl]stannane (70) and its (Z)-Isomer (71).—2,3-Dibromo-3-(*o*-methoxyphenyl)propionic acid (**76**) (9.48 g, 28 mmol), prepared by the method of Reimer and Howard¹⁴ as a mixture of diastereoisomers, was dissolved in acetone (50 ml) and the

solution was heated at reflux with potassium carbonate for 5 h. The solvent was then evaporated off and the residue was partitioned between diethyl ether (100 ml) and water (100 ml). The ether phase was washed with brine (50 ml), dried (Na_2SO_4), and the solvent was evaporated off to yield 1-bromo-2-(*o*-methoxyphenyl)ethylene (**77**) (4.51 g, 75%) as a 60:40 mixture of *E* and *Z* isomers, b.p. 100 °C at 0.7 mmHg (lit.,²⁰ 139 °C at 16 mmHg); $\delta_{\text{H}}(\text{CDCl}_3)$ [(*E*)-isomer] 3.84 (3 H, s, OMe), 6.82–6.95 (2 H, m, ArH), 6.90 (1 H, d, *J* 14.0 Hz, 1-H), 7.21–7.27 (2 H, m, ArH), and 7.31 (1 H, d, *J* 14.0 Hz, 2-H); [(*Z*)-isomer] (*inter alia*) 3.82 (3 H, s, OMe), 6.44 (1 H, d, *J* 8.0 Hz, 1-H), and 7.25 (1 H, d, *J* 8.0 Hz, 2-H).

Irradiation of the above 60:40 mixture (**77**) (0.3 g) in carbon tetrachloride (5 ml) containing iodine (30 mg) for 3 h produced compound (**77**) in an *E:Z* isomer ratio of 81:19 (by NMR spectroscopy).

The above mixtures of isomeric vinyl bromides (**77**) were each converted into corresponding mixtures (81:19, *E:Z* ratio and 60:40, *E:Z* ratio) of vinylstannanes (**70**) and (**71**) by the above general method for the synthesis of trialkyl(vinyl)stannanes. The mixture containing 81% of the (*E*)-isomer (**70**) was obtained as an oil, b.p. 220 °C at 22 mmHg (Kugelrohr) (Found: C, 59.7; H, 8.5. $\text{C}_{21}\text{H}_{36}\text{OSn}$ requires C, 59.6; H, 8.6%); λ_{max} 255, 301, and 349 nm (10 340, 5 522, and 1 964); $\nu_{\text{max}}(\text{film})$ 1 599 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ (**70**) 0.86–1.00 (15 H, m, 3 \times SnCH_2 and 3 \times Me), 1.35 (6 H, m, 3 \times CH_2), 1.56 (6 H, m, 3 \times CH_2), 3.85 (3 H, s, OMe), 6.81 (1 H, d, *J* 19.6 Hz, ^{117}Sn and ^{119}Sn satellites gave $J_{\text{H,Sn}}$ 70.0 and 73.2 Hz, vinyl H), 6.85 (1 H, d, *J* 8.4 Hz, ArH *ortho* to OMe), 6.93 (1 H, dd, *J* 7.6, 7.6 Hz, ArH *para* to OMe), 7.19 (1 H, ddd, *J* 8.4, 7.6, 1.6 Hz, ArH *para* to vinyl), 7.27 (1 H, d, *J* 19.6 Hz, ^{117}Sn and ^{119}Sn satellites gave $J_{\text{H,Sn}}$ average of 64 Hz, vinyl H), and 7.51 (1 H, dd, *J* 7.6, 1.6 Hz, ArH *ortho* to vinyl).

From the mixture containing 40% of (*Z*)-isomer (**71**) the following NMR data could be obtained: $\delta_{\text{H}}(\text{CDCl}_3)$ (**71**) 3.82 (3 H, s, OMe), 6.24 (1 H, d, *J* 13.5 Hz, ^{117}Sn and ^{119}Sn satellites gave $J_{\text{H,Sn}}$ 62.0 and 64.0 Hz, vinyl H), and 7.69 (1 H, d, *J* 13.5 Hz, vinyl H).

Synthesis of Enol Acetates.—The aldehyde or ketone (5 g) was heated at reflux overnight with isopropenyl acetate (10 g) containing toluene-*p*-sulphonic acid (0.1 g). Acetone and excess of isopropenyl acetate were removed from the reaction mixture by distillation, and the residue was poured into a cold mixture of saturated aq. sodium carbonate and pentane. The organic phase was dried (Na_2SO_4), the solvent was evaporated off, and the residue was distilled.

The following compounds were prepared by the above procedure.

(a) Cyclohex-1-enyl acetate (**15**) (63%), b.p. 88 °C at 28 mmHg (lit.,²¹ 78 °C at 20 mmHg); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.30–1.85 (4 H, m, 2 \times CH_2), 1.85–2.2 (7 H, m, 2 \times CH_2 and OAc), and 5.30 (1 H, m, vinyl H).

(b) Cyclopent-1-enyl acetate (**19**) (36%), b.p. 158–160 °C at 760 mmHg (lit.,²² 84–87 °C at 69 mmHg); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.65–2.00 (2 H, m, CH_2), 2.10 (3 H, s, OAc), 2.12–2.51 (4 H, m, 2 \times CH_2), and 5.33 (1 H, m, vinyl H).

(c) α -Methyl- β -phenylstyryl acetate (**26**) (54%), b.p. 140 °C at 1 mmHg (Kugelrohr), which was purified for analysis by HPLC (Whatman Partisil 10 M20 column; 2.5% ethyl acetate in light petroleum) (Found: C, 81.0; H, 6.0. $\text{C}_{17}\text{H}_{16}\text{O}_2$ requires C, 80.9; H, 6.4%); $\lambda_{\text{max}}(\text{MeOH})$ 240 nm (12 300); $\nu_{\text{max}}(\text{film})$ 1 750 and 1 660 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.90 (3 H, s, Me), 2.00 (3 H, s, OAc), 7.10 (5 H, br s, Ph), and 7.17 (5 H, br s, Ph); *m/z* 252 (M^+ , <5%, 211 (23), and 210 (100)).

(d) Cyclohept-1-enyl acetate (**44**) (30%), b.p. 50 °C at 1 mmHg (Kugelrohr) (lit.,²³ 64 °C at 4 mmHg); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.35–1.85 (6 H, m, 3 \times CH_2), 1.85–2.41 (4 H, m, 2 \times CH_2), 2.06 (3 H, s, OAc), and 5.37 (1 H, t, *J* 7.2 Hz, vinyl H).

(e) 2-Methyl-1-phenylprop-1-enyl acetate (**51**) (30%), 100 °C at 1 mmHg (Kugelrohr), which was purified for analysis by HPLC (Whatman Partisil 10 M20 column; 1.5% ethyl acetate in light petroleum) (Found: C, 76.0; H, 7.6. $\text{C}_{12}\text{H}_{14}\text{O}_2$ requires C, 75.8; H, 7.4%); $\lambda_{\text{max}}(\text{hexane})$ 241 nm (9 100); $\nu_{\text{max}}(\text{film})$ 1 750 and 1 600 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.75 (3 H, s, Me), 1.79 (3 H, s, Me), 2.14 (3 H, s, OAc), and 7.30–7.46 (5 H, m, Ph); *m/z* 190 (M^+ , 6%), 149 (11), 148 (100), and 147 (30).

Synthesis of the Isomeric Enol Acetates (27) and (28).—1,2-Diphenylpropan-1-one²⁴ (**30**) (10 g), acetic anhydride (20 g), and sodium acetate (1.4 g) were heated at reflux overnight, and the mixture was cooled, then diluted with diethyl ether. The organic phase was washed successively with water and 5% aq. sodium carbonate, dried (Na_2SO_4), and the solvent was evaporated off. The residue was distilled to give a mixture of the isomers (**27**) and (**28**), b.p. 150–160 °C at 1 mmHg (Kugelrohr). Fractionation by HPLC, using the conditions employed for purification of compound (**26**) above, afforded two fractions. The material of shorter retention time (44 min) (20% yield) was crystallised from pentane to give (*E*)-1,2-diphenylprop-1-enyl acetate (**27**), m.p. 86–88 °C (Found: C, 81.4; H, 6.5. $\text{C}_{17}\text{H}_{16}\text{O}_2$ requires C, 80.9; H, 6.4%); $\lambda_{\text{max}}(\text{hexane})$ 251 nm (9 500); $\nu_{\text{max}}(\text{Nujol})$ 1 760, 1 660, and 1 600 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 1.85 (3 H, s, Me), 2.12 (3 H, s, OAc), 7.23–7.43 (8 H, m, ArH), and 7.48–7.55 (2 H, m, ArH); *m/z* 252 (M^+ , 5%), 211 (19), and 210 (100).

The material of longer retention time (56 min) was distilled to yield (*Z*)-1,2-diphenylprop-1-enyl acetate (**28**) (73%), b.p. 150 °C at 1 mmHg (Kugelrohr) (Found: C, 80.5; H, 6.9%); $\lambda_{\text{max}}(\text{hexane})$ 260 nm (10 100); $\nu_{\text{max}}(\text{film})$ 1 760, 1 670, and 1 610 cm^{-1} ; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.08 (3 H, s, OAc), 2.22 (3 H, s, Me), and 7.08–7.25 (10 H, m, Ph); *m/z* 252 (M^+ , 8%), 211 (19), and 210 (100).

Synthesis of 2-Methylprop-1-enyl Acetate (62).—The title compound (**62**) was obtained from isobutyraldehyde by the method used to obtain enol acetates (**27**) and (**28**). It was obtained as a liquid, b.p. 124–126 °C at 760 mmHg (lit.,²⁵ 122–128 °C at 760 mmHg); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.60–1.71 (6 H, m, 2 \times Me), 2.11 (3 H, s, OAc), and 6.80 (1 H, m, vinyl H).

(*E*)-*p*-Methoxystyryl Acetate (**10**).—The preparation of enol acetate (**10**) was carried out by the method of Criegee *et al.*,²⁶ to give a mixture of the *E* and *Z* isomers, b.p. 125–127 °C at 0.5 mmHg (lit.,²⁶ 118–120 °C at 0.9 mmHg); (*E*)-isomer (**10**): $\delta_{\text{H}}(\text{CDCl}_3)$ 2.10 (3 H, s, OAc), 3.77 (3 H, s, OMe), 6.25 (1 H, d, *J* 12.6 Hz, β -H), 6.81 and 7.21 (4 H, AA'BB', ArH), and 7.62 (1 H, d, *J* 12.6 Hz, α -H); (*Z*)-isomer: $\delta_{\text{H}}(\text{CDCl}_3)$ 2.19 (3 H, s, OAc), 3.80 (3 H, s, OMe), 5.58 (1 H, d, *J* 7.2 Hz, β -H), 6.88 and 7.49 (4 H, AA'BB', ArH), and 7.13 (1 H, d, *J* 7.2 Hz, α -H).

(*E*)- α -Methylstyryl Acetate (**36**).—The title compound (**36**), as prepared by the method of Smith,²⁷ was a mixture of *E* and *Z* isomers in the ratio of 1:2.7, respectively, which could not be separated by preparative GLC. (*E*)-Isomer: $\delta_{\text{H}}(\text{CDCl}_3)$ 2.11 (3 H, s, Me), 2.17 (3 H, s, OAc), 6.25 (1 H, s, vinyl H), and 7.14–7.26 (5 H, m, Ph). Irradiation at δ 6.25 did not result in the observation of an NOE at δ 2.11. (*Z*)-isomer: $\delta_{\text{H}}(\text{CDCl}_3)$ 2.08 (3 H, s, Me), 2.18 (3 H, s, OAc), 5.95 (1 H, s, vinyl H), and 7.24–7.44 (5 H, m, Ph). Irradiation at δ 5.95 produced a 7% NOE at δ 2.08, and irradiation at δ 2.08 produced a 6% NOE at δ 5.95.

(*E*)-*p*-Methoxystyryl-lead Triacetate (**8**).—LTA (0.6 g) was added to a solution of the stannane (**6**) (0.5 g) in dry chloroform (4 ml) and the solution was stirred in a dry atmosphere for 10 min. Dry light petroleum (15 ml) was added, and the solution was kept at 0 °C for 2 days. The precipitated material was collected under dry nitrogen to afford the title compound (**8**) as a brown solid, which was used without further purification;

δ_{H} (CDCl₃) 2.08 (9 H, s, 3 × OAc), 3.83 (3 H, s, OMe), 6.90 and 7.40 (4 H, AA'BB', *meta* protons to Pb and *ortho* protons to Pb, respectively), 7.25 (1 H, d, *J* 15.0 Hz, ²⁰⁷Pb satellites gave ²*J*_{H,Pb} 692.5, α -H), and 7.37 (1 H, d, *J* 15.0 Hz, ²⁰⁷Pb satellites gave ³*J*_{H,Pb} 831.3 Hz, β -H).

Reactions of (E)-p-Methoxystyryl-lead Triacetate (8).—In separate experiments the reagents listed in Scheme 4 (10 mg) were added to a solution of the lead compound (8) (20 mg) in deuteriochloroform (0.3 ml) and the solution was kept at room temperature for 24 h. A quantitative NMR spectroscopic analysis of the reaction mixture was then carried out by the use of methylene dibromide as an internal standard. The results were as follows: (a) addition of mercury(II) acetate produced the enol acetate (10) (84%); (b) addition of (*E*)-styrylmercury acetate (3) produced the enol acetate (10) (65%); (c) addition of tetrabutylammonium acetate produced the acetylene (9) (100%); (d) addition of acetic acid produced the acetylene (9) (43%).

Mercury-Lead and Tin-Lead Exchange Reactions.—(Method A). The exchange reactions were studied by following the disappearance of the starting material and the formation of product by ¹H NMR spectroscopy. The presence of all products was verified by comparison of the reaction mixture with authentic samples by analytical GLC.

The vinylmercury compound or vinylstannane (30–70 mg) was dissolved in CDCl₃ (0.4 ml) and 1 drop of an accurately weighed reference compound (CHCl₃, CH₂Cl₂, or CH₂Br₂) was added. An initial spectrum was obtained, and the ratio of starting material to reference compound was determined by careful integration of the respective resonances. A solution of LTA (1.0–1.1 mol equiv.) in CDCl₃ (0.3 ml) was added (with shaking), and the course of the reaction at room temperature was followed by recording of spectra at intervals of 2–3 min. A final spectrum was recorded at 24 h.

Spectra were obtained on a Varian EM-390 instrument with TMS lock, and on Bruker WM400 and AC200F instruments, with deuterium lock, for the high-resolution exchange experiments. In most cases a spectrum with sweep width 10 ppm was obtained, followed by expansion of the vinyl proton region (δ 4.0–7.0), with careful integration. All integrals were expressed relative to that of the reference compound. In cases where the vinylic signals were completely hidden by the aromatic signals, and it could not be determined if Pb satellites were equidistant from the central vinylic peak, spin-tickling experiments were performed to confirm that the two satellite wings were electronically connected.

(Method B). The exchange reaction was conducted as in (A) above, except that a known volume of the internal standard solution was added to the reaction mixture. After the reaction had proceeded for the desired time, the mixture was diluted to a known volume, and the concentration of the product was determined by GLC or HPLC. All integrals were referenced to the internal standard, and duplicate or triplicate injections were made, so that a reproducibility of at least 5% was achieved.

The following metal–metal exchange experiments were conducted by use of the above procedures.

(a) Di(cyclohex-1-enyl)mercury (11) was treated with LTA (Method A) to give, after 1 h, cyclohex-1-enylmercury acetate (100%) (vinyl proton resonance at δ 5.57), and cyclohex-1-enyl-lead triacetate (14) (100%) (vinyl proton resonance at δ 6.17, ²⁰⁷Pb satellites gave ³*J*_{H,Pb} 729.8 Hz). After 24 h the signal at δ 6.17 had been largely replaced by one at δ 5.30 due to enol acetate (15) (78%), while that at δ 5.57 was unchanged (94%). GLC analysis was performed with column 1 at 100 °C.

(b) Cyclohex-1-enylmercury bromide (12) was treated with

LTA (Method A) to give, after 20 min, a solution containing lead compound (14) (resonance at δ 6.17) and the starting material (12) (62%) (vinyl proton resonance at δ 5.66). After 23 h the only vinyl proton signal in the NMR spectrum was that at δ 5.30 due to enol acetate (15) (91%). GLC analysis was conducted with column 1 at 100 °C.

(c) Tributyl(cyclohex-1-enyl)stannane (13) was treated with LTA (Method A) to yield, after 20 min, a solution containing starting stannane (13) (61%) and the lead intermediate (14) (vinyl proton signal at δ 6.17) (23%). After 29 h the only vinyl proton resonance in the NMR spectrum was that at δ 5.30 due to the enol acetate (15) (83%). GLC analysis was carried out with column 1 at 100 °C.

(d) Di(cyclopent-1-enyl)mercury (16) was treated with LTA (Method A) to produce a solution containing cyclopent-1-enylmercury acetate (vinyl proton signal at δ 5.82) and cyclopent-1-enyl-lead triacetate (18) (vinyl proton resonance at δ 6.37, ²⁰⁷Pb satellites gave ³*J*_{H,Pb} 293.9 Hz). After 4 days the signals at δ 5.82 and 6.37 were still present and no other vinyl proton signals had appeared in the spectrum. GLC analysis with column 1 at 90 °C showed that enol acetate (19) was not present.

(e) Tributyl(cyclopent-1-enyl)stannane (17) was treated with LTA (Method A) to give a solution containing the vinyl-lead compound (18) (vinyl proton signal at δ 6.37). NMR and GLC analysis as in (d) above after 70 h failed to detect the enol acetate (19).

(f) Bis(α -methyl- β -phenylstyryl)mercury (22) was treated with LTA (Method B). The mixture was stirred overnight, and analysis by HPLC [Brownlee S1 100 5 μ m column (4.6 × 25 cm) with 0.5% ethyl acetate in light petroleum as eluting solvent and benzophenone as internal standard] showed the presence of enol acetates (26), (27), and (28) in yields of 5, 4, and 49%, respectively.

(g) Bis[(*E*)-2-phenylprop-1-enyl]mercury (31) was treated with LTA (Method A). After 20 min the presence of compound (31) could not be detected in the solution, which contained the vinylmercury acetate (32) (vinyl proton signal at δ 5.97) (94%) and the vinyl-lead triacetate (33) (methyl resonance at δ 2.50 and vinyl proton resonance at δ 6.89) (94%). After 14 h, analysis showed the presence of mercury compound (32) (84%) and the enol acetate (36) (84%), while none of the lead compound (33) could be detected.

(h) Tributyl[(*E*)-2-phenylprop-1-enyl]stannane (37) was treated with LTA (Methods A and B). After 10 min the presence of compound (37) could not be detected in the solution, which contained the vinyl-lead compound (33) (methyl resonance at δ 2.50 and vinyl proton signal at δ 6.89, ²⁰⁷Pb satellites gave ²*J*_{H,Pb} 864.8 Hz) (100%). After 22 h the solution contained 1-phenylpropyne (38) (94%) and a small amount (<5%) of the enol acetate (36) (analysis by GLC on column 1 at 115 and 150 °C), while the intermediate lead compound (33) was not present (NMR spectroscopy).

(i) Trimethyl-(β -phenylstyryl)stannane (39) was treated with LTA (Method B). The mixture was stirred for 16 h and analysis by GLC (column 2 at 160 °C; phenanthrene as internal standard) showed the presence of diphenylacetylene (40) (90%). (*E*)-1,2-Diphenylvinyl acetate and its (*Z*)-isomer, and β -phenylstyryl acetate could not be detected.

(j) Tributyl(cyclohexyldienemethyl)stannane (42) was treated with LTA (Method B). The mixture was stirred for 16 h, and analysis by GLC (column 1 at 150 °C) indicated the presence of cyclohept-1-enyl acetate (44) (79%). No other products could be detected.

(k) 2-Methylprop-1-enylmercury bromide (61) was treated with LTA (Method A). Analysis after 5 min showed the absence of compound (61) and appearance of a lead intermediate (65) (vinyl proton resonance at δ 6.37). The concentration of

intermediate (65) decreased, while that of enol acetate (62) (vinyl proton signal at δ 6.80) increased with time. After 15 min the yield of compound (62) was 89% and after 3.3 h this had increased to 97%.

(l) Tributyl-(2-methylprop-1-enyl)stannane (63) was treated with LTA (Method A). Analysis after 0.5 h showed the absence of the stannane (63) and the appearance of the lead intermediate (65) (vinyl proton resonance at δ 6.37, ^{207}Pb satellites gave $^2J_{\text{H,Pb}}$ 924.1 Hz). The concentration of intermediate (65) decreased, while that of enol acetate (62) (vinyl proton signal at δ 6.80) increased with time. After 2 h the yield of compound (62) was 21%, and after 42.3 h this had increased to 64%.

(m) A mixture of tributyl[(*Z*)-styryl]stannane (46) (65%) and the (*E*)-isomer (5) (35%) was treated with LTA (Method A). After 20 min 23% of compound (46) and 77% of its isomer (5) had reacted, and the only other compound detected in the mixture was phenylacetylene (7). The yield of the acetylene (7) after 42.7 h was 95%.

(n) A mixture of tributyl[(*E*)-prop-1-enyl]stannane [(*E*)-(47)] and the (*Z*)-isomer [(*Z*)-(47)] was treated with LTA (Method A). The signals in the NMR spectrum due to the vinyl protons of the (*E*)-isomer (δ 5.9–6.1) were observed to decrease more rapidly than those due to the (*Z*)-isomer at δ 5.8 and 6.6, and after 2 min both isomers had been consumed. After 2 min signals due to the (*E*)-lead compound (48) [δ 2.04 (3 H, dd, $^3J_{\text{H,Me}}$ 6.80, $^4J_{\text{H,Me}}$ 1.48 Hz, Me), 7.50 (1 H, dq, $^3J_{\text{H,H}}$ 14.20, $^3J_{\text{H,Me}}$ 6.80 Hz, ^{207}Pb satellites gave $^3J_{\text{H,Pb}}$ 689.5 Hz, 2-H), and 7.84 (1 H, dq, $^3J_{\text{H,H}}$ 14.20, $^4J_{\text{H,Me}}$ 1.48 Hz, ^{207}Pb satellites gave $^2J_{\text{H,Pb}}$ 931.0 Hz, 1-H)] and the (*Z*)-lead compound (49) [δ 7.74 (1 H, d, $^3J_{\text{H,H}}$ 6.10 Hz, ^{207}Pb satellites gave $^2J_{\text{H,Pb}}$ 924.0 Hz, 1-H) and 7.77 (1 H, dq, $^3J_{\text{H,H}}$ 6.10, $^3J_{\text{H,Me}}$ 5.0 Hz, ^{207}Pb satellites gave $^3J_{\text{H,Pb}}$ 1 667.5 Hz, 2-H)] were both clearly visible. Signals due to the latter compound (49) were no longer observable after 18 min, while those due to the (*E*)-isomer (48) were still present after 1 h. After 21 h the only detectable product was propyne (55%) (acetylenic and methyl proton resonances at δ 1.83).

(o) Bis-(2-methyl-1-phenylprop-1-enyl)mercury (50) was treated with LTA (Method B). The mixture was stirred for 17 h, and analysis by GLC (column 1 at 160 °C; naphthalene as internal standard) showed the presence of the enol acetate (51) (80%).

(p) Bis[(*Z*)- α -methylstyryl]mercury (53) was treated with LTA (Methods A and B). The mixture was stirred for 24 h, and analysis by GLC (column 1 at 115 °C; durene as internal standard) showed the presence of 1-phenylpropyne (38) (88%). Analysis by NMR spectroscopy also showed the presence of the vinylmercury acetate (54) (vinyl proton resonance at δ 7.13). The three enol acetates which could have been produced were not detected.

(q) Tributyl[(*Z*)- α -methylstyryl]stannane (57) was treated with LTA (Methods A and B). Analysis as in (p) above after 24 h showed the presence of the acetylene (38) (94%). No enol acetates could be detected, and because of the distribution of signals in the NMR spectrum it was not possible to obtain evidence for the presence of a vinyl-lead intermediate.

(r) Bis-(β -phenylstyryl)mercury (58) was treated with LTA (Methods A and B). The metal-exchange reaction was shown to be complete after 5 min (NMR spectroscopy) and the spectrum contained signals for β -phenylstyrylmercury acetate (59) (vinyl proton resonance at δ 6.25, ^{199}Hg satellites gave $^2J_{\text{H,Hg}}$ 239.8 Hz) and β -phenylstyryl-lead triacetate (60) (vinyl proton resonance at δ 7.33, ^{207}Pb satellites gave $^2J_{\text{H,Pb}}$ 819.0 Hz). Analysis by GLC (column 2 at 175 °C; phenanthrene as internal standard) showed the presence of diphenylacetylene (40) (70%). The two isomeric α -phenylstyryl acetates and β -phenylstyryl acetate could not be detected.

(s) Tributyl[(*E*)-*o*-methoxystyryl]stannane (70), containing 19% of the (*Z*)-isomer (71), was treated with LTA (Method A).

Analysis of the reaction mixture by NMR spectroscopy after 2 min showed the presence of benzofuran (74) (35% yield) and (*E*)-*o*-methoxystyryl-lead triacetate (72) [δ 7.44 (1 H, d, J 14.0 Hz, ^{207}Pb satellites gave $^3J_{\text{H,Pb}}$ 761.0 Hz, β -H) and 7.74 (1 H, d, J 14.0 Hz, ^{207}Pb satellites gave $^2J_{\text{H,Pb}}$ 926.5 Hz, α -H)], while after 30 min the mixture contained benzofuran (83% yield), *o*-methoxyphenylacetylene (75) (9%), and the (*Z*)-stannane (71).

(t) A mixture of the (*E*)-stannane (70) (60%) and (*Z*)-stannane (71) (40%) was treated with LTA (Method B). Analysis of the reaction mixture by GLC (column 3 at 100 °C) after 24 h showed it to contain benzofuran (74) (61%) and *o*-methoxyphenylacetylene (75) (30%).

Attempted Carbene-trapping Experiments with the Stannane (63).—A solution of tributyl-(2-methylprop-1-enyl)stannane (63) (3.46 g, 10 mmol) in chloroform (10 ml) was added to a solution of LTA (4.45 g, 10 mmol) in chloroform (10 ml), and the mixture was stirred at room temperature for 2 min (metal-metal exchange complete by NMR spectroscopy). Freshly distilled cyclohexene (1.1 ml, 108 mmol) was then added, and the mixture was stirred at room temperature for 24 h. The mixture was filtered, and the filtrate was concentrated at room temperature to 3 ml. Analysis by FTIR showed no absorption at 1 776 cm^{-1} , which is present in the cyclopropane derivative (67);¹⁰ the only carbonyl absorption was at 1 736 cm^{-1} , due to isobutenyl acetate (62). Analysis by ^1H NMR spectroscopy showed the presence of enol acetate (62), tributyltin acetate, and cyclohexene; there were no signals at δ 1.75, which have been assigned to the methyl groups of compound (67).¹¹

Acknowledgements

This work was supported by a grant from the Australian Research Grants Scheme. M. G. M. gratefully acknowledges receipt of a Commonwealth Postgraduate Research Award. We are grateful to Mrs. J. Morgan, for the synthesis of stannanes (5), (6), (13), and (58), and to Drs. J. E. Nemorin and B. A. Rowe for determination of the NMR spectra and for helpful discussions.

References

- M. G. Moloney and J. T. Pinhey, *J. Chem. Soc., Chem. Commun.*, 1984, 965; *J. Chem. Soc., Perkin Trans. 1*, 1988, 2874.
- E. J. Corey and R. H. Wollenberg, *J. Am. Chem. Soc.*, 1974, **96**, 5581.
- M. Shibasaki, Y. Torisawa, and S. Ikegami, *Tetrahedron Lett.*, 1982, **23**, 4607.
- R. C. Larock, K. Oertle, and K. M. Beatty, *J. Am. Chem. Soc.*, 1980, **102**, 1966.
- P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, 'Vinyl Cations,' Academic, New York, 1979; (a) p. 1; (b) p. 212; (c) p. 282; (d) p. 6; (e) p. 448; (f) p. 462; (g) p. 467.
- M. Hanack, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 333.
- K.-P. Jackel and M. Hanack, *Chem. Ber.*, 1977, **110**, 199.
- H. Hogeveen and C. F. Roobeck, *Tetrahedron Lett.*, 1971, 3343.
- H. D. Hartzer in 'Carbenes,' eds. R. A. Moss and M. Jones, Wiley, New York, 1975, vol. 2, ch. 2.
- P. J. Stang, M. G. Mangum, D. P. Fox, and P. Haak, *J. Am. Chem. Soc.*, 1974, **96**, 4562.
- M. Tanabe and R. A. Walsh, *J. Am. Chem. Soc.*, 1963, **85**, 3522.
- S. Cawley and S. S. Danyluk, *J. Phys. Chem.*, 1964, **68**, 1240.
- D. de Vos, H. O. van der Kooij, J. Wolters, and A. van der Gen, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 1465.
- M. Reimer and M. Howard, *J. Am. Chem. Soc.*, 1928, **50**, 196.
- J. T. Pinhey and E. G. Roche, *J. Chem. Soc., Perkin Trans. 1*, 1988, 2415.
- S. Patai, M. Harnik, and E. Hoffman, *J. Am. Chem. Soc.*, 1950, **72**, 923.
- H. Nemoto, X.-M. Wu, H. Kurobe, K. Minemura, M. Ihara, K. Fukumoto, and T. Kametani, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1185.
- M. L. Saihi and M. Pereyre, *Bull. Soc. Chim. Fr.*, 1977, 125.

- 19 A. Alvanipour, C. Eaborn, and D. R. M. Walton, *J. Organomet. Chem.*, 1980, **201**, 233.
- 20 R. Quelet and R. Golsé, *Compt. Rend.*, 1946, **223**, 159 (*Chem. Abstr.*, 1947, **41**, 723a).
- 21 W. M. Quattlebaum and C. A. Noffsinger, USP 2 467 095/Apr. 12, 1949 (*Chem. Abstr.*, 1949, **43**, 5795i).
- 22 L. Goodman, A. Benitez, C. D. Anderson, and B. R. Baker, *J. Am. Chem. Soc.*, 1958, **80**, 6582.
- 23 N. J. Leonard and F. H. Owens, *J. Am. Chem. Soc.*, 1958, **80**, 6039.
- 24 D. J. Cram and F. A. A. Elhafez, *J. Am. Chem. Soc.*, 1952, **74**, 5828.
- 25 P. Bedoukian, *J. Am. Chem. Soc.*, 1944, **66**, 1325.
- 26 R. Criegee, P. Dimroth, K. Noll, R. Simon, and C. Weis, *Chem. Ber.*, 1957, **90**, 1070.
- 27 G. G. Smith, *J. Am. Chem. Soc.*, 1953, **75**, 1134.

Paper 0/00575D
Received 7th February 1990
Accepted 25th April 1990