Mechanism of Arylation of Nucleophiles by Aryllead Triacetates. Part 1. Exclusion of a Pathway involving Aryl Free Radicals

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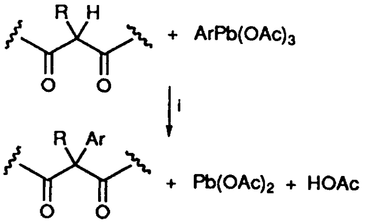
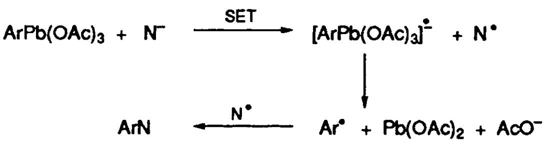
o-(Prop-2-enyloxy)phenyllead triacetate **6**, which was obtained by treatment of the corresponding boronic acid with lead tetraacetate, has been shown to react with iodide and azide ions, 2,4,6-trimethylphenol, ethyl 2-oxocyclopentanecarboxylate, and the sodium salt of 2-nitropropane to give only those products which, in a formal sense, are derived by direct nucleophilic displacement of the $Pb(OAc)_3$ group. The complete absence of 3-substituted dihydrobenzofurans among the products is strong evidence that aryl free radicals are not involved in the arylation reactions of aryllead triacetates.

For some time we have been examining the chemistry of organolead(IV) tricarboxylates, and have developed these compounds as a new class of reagent for use in organic synthesis.[1] In particular, we have shown that aryllead triacetates are useful reagents for the arylation of a variety of anions.[1] In the main, the anions have been 'soft' carbon nucleophiles, such as those from phenols[1,2] and nitroalkanes,[1,3] and from enolisable β-dicarbonyl compounds[1] as depicted in the general example of Scheme 1; however, they will also react with iodide ion[4] and azide ion[5] to give aryl iodides and aryl azides in almost quantitative yield. Reaction at nitrogen in amines or at oxygen, even in systems in which the anion is delocalised, cannot generally be achieved, although Barton[6] has shown that the arylation of amines can be effected with these reagents by the use of copper catalysis.



Scheme 1 *Reagents and conditions:* i, $CHCl_3$, pyridine, 40–60 °C

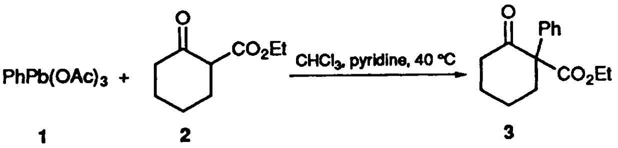
We have now turned our attention to the mechanisms of the above arylation reactions, and initially we examined the possibility of the involvement of free radicals. The ready arylation of iodide and azide ions, and the salts of nitroalkanes, and the failure of aryllead triacetates to react with other non-carbon nucleophiles in the absence of copper catalysis, indicated that a single-electron-transfer mechanism could be operating; a possible pathway is outlined in Scheme 2, although this could equally well be an S_{RN^1} process.



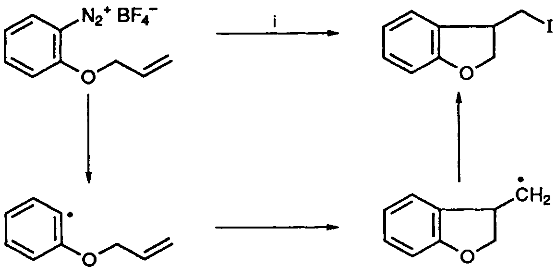
Scheme 2

Results and Discussion

In one reaction, that of phenyllead triacetate **1** with ethyl 2-oxocyclohexanecarboxylate **2** to give the arylated keto ester **3**, the presence of free radicals has been excluded by Barton.[7] In that work the phenylation reactions of several bismuth(V) reagents, phenyllead triacetate, and two diphenyliodine(III) salts were found to be unaffected by the presence of free-radical-trapping agents. More recently the same approach has been used to show that the arylation of 4-hydroxycoumarins by aryllead triacetates does not involve free radicals.[8]



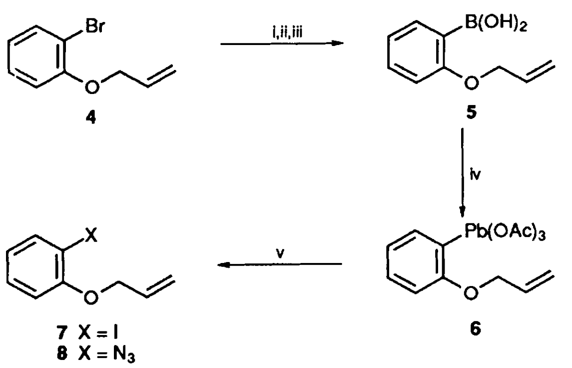
A somewhat different approach has been adopted in a mechanistic study of the reactions of arenediazonium salts with iodide ion, and a number of S_{RN^1} reactions. In that work by Beckwith,[9] an intramolecular trapping method, an example of which is depicted in Scheme 3, was employed to show the intermediacy of aryl free radicals, and we have made use of this elegant approach to study a number of reactions of aryllead triacetates.



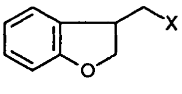
Scheme 3 *Reagents:* i, NaI, Me_2CO

For the synthesis of the required aryllead compound, *o*-(prop-2-enyloxy)phenyllead triacetate **6**, we employed our boron–lead exchange route[10] (Scheme 4), rather than the slower tin–lead exchange procedure,[11] to avoid the possibility of lead tetraacetate reacting with the double bond. The arylboronic acid **5** was obtained from the bromo compound **4** in 48% yield, while the yield of the aryllead compound **6** in the boron–lead exchange was 81%.

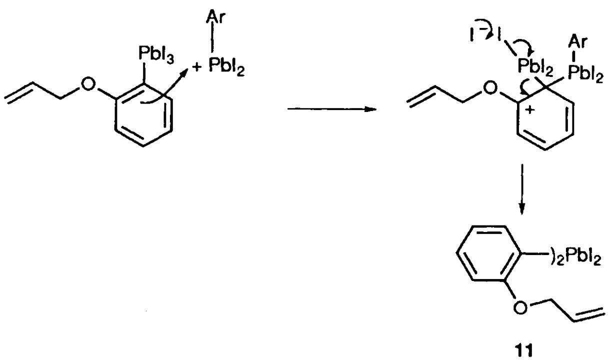
When the *o*-allyloxyphenyllead compound **6** was treated with sodium iodide in acetone there was a rapid reaction and after 30 minutes allyl *o*-iodophenyl ether **7** was obtained in 75% yield, together with the diaryllead diiodide **11** (15% yield), which is presumably formed by an *ipso* electrophilic substitution (Scheme 5); the formation of I_2 and PbI_2 support this proposal. None of the product of free radical cyclisation in the *exo* mode,



Scheme 4 *Reagents and conditions:* i, BuLi, −78 °C; ii, $B(OCHMe_2)_3$, −78 °C; iii, H_3O^+; iv, LTA, 10% $Hg(OAc)_2$, $CHCl_3$; v, NaI, Me_2CO (for **7**) [or NaN_3, DMSO (for **8**)]



9 X = I
10 X = N_3

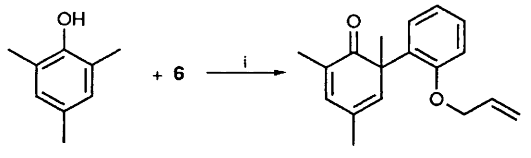


Scheme 5

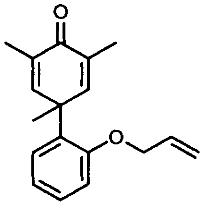
the (iodomethyl)dihydrobenzofuran **9**, was obtained, and the absence of this compound from the reaction mixture was confirmed by careful monitoring of the reaction by high-field ^1H NMR spectroscopy. We can therefore state that iododeplumbation does not proceed by a free-radical pathway. A similar result was obtained when the lead compound **6** was treated with sodium azide in dimethyl sulfoxide (DMSO) at room temperature; only the unstable aryl azide **8** (74% yield) was obtained. Again, signals could not be detected in the region of the ^1H NMR spectrum where the non-aromatic protons of compound **10** would be expected to resonate.

For our examination of *C*-arylation we selected 2,4,6-trimethylphenol **12**, ethyl 2-oxocyclopentanecarboxylate **15**, and 2-nitropropane **17**, three compounds of widely different structural types which have been shown by us to undergo ready arylation with a variety of aryllead triacetates.[1] When the phenol **12** was treated with the aryllead triacetate **6** in the presence of pyridine at 40 °C with chloroform as solvent, the arylated dienone **13** was isolated in 50% yield (70% by ^1H NMR spectroscopy) (Scheme 6); no products resulting from free-radical cyclisation to a dihydrobenzofuran were present in the reaction mixture. Unlike the reaction of mesitol **12** with *p*-methoxyphenyllead triacetate,[2] none of the 2,5-dienone **14** could be detected.

The reaction of the β-keto ester **15** with aryllead compound **6** was carried out in a similar way to that of the phenol **12** above to give the arylated keto ester **16** in 90% yield, while 2-(*o*-allyloxyphenyl)-2-nitropropane **18**, a slightly unstable compound, was isolated in 64% yield from a reaction of the sodium salt of 2-nitropropane **17** and the lead compound **6** in DMSO. As in the three earlier reactions, the reactions of the keto ester **15** and nitro compound **17** failed to produce any compounds incorporating a dihydrobenzofuran moiety.



Scheme 6 *Reagents and conditions:* i, pyridine, $CHCl_3$, 40 °C, 20.5 h



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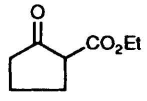

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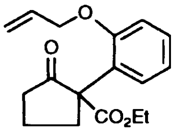

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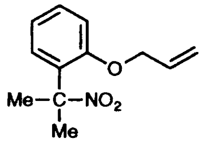
Me_2CHNO_2

17



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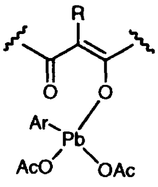
From these results and those of Barton and his collaborators,[7,8] it would appear most likely that none of the arylation reactions of aryllead triacetate, which occur without copper or acid catalysis (reviewed in ref. 1), involves free radicals; thus, they probably proceed by an initial ligand exchange, followed by ligand coupling.[12,13] For those substrates which undergo *C*-arylation, the bonding to lead in the intermediate lead(IV) species could be through oxygen or carbon as depicted in structures **19** and **20**, respectively, for the general reaction of a β-dicarbonyl compound given in Scheme 1.



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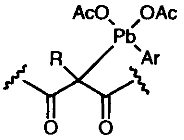

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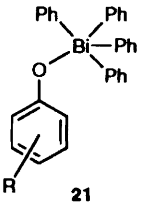

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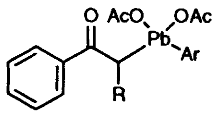

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For the related arylations by arylbismuth(V) reagents,[14] which were introduced by Professor Sir Derek Barton at almost the same time as our aryllead(IV) reagents, intermediates have been isolated in the case of phenols.[15] These are O–Bi bonded intermediates, as in structure **21**, which collapse thermally with ligand coupling to give the *o*-phenylated phenol. Attempts to isolate a similar intermediate from reactions of aryllead triacetates and phenols have not been successful;[16] however, the silyl enol ethers of a group of alkyl phenyl ketones have been shown to react with aryllead triacetates to yield aryl(phenacyl)-lead diacetates,[17] as in structure **22**, and the possibility that similar C–Pb bonded intermediates occur in the arylations of β-dicarbonyl compounds is explored in the following paper.

Experimental

For general experimental procedures see our earlier paper.[18] Allyl *o*-bromophenyl ether **4** was obtained by a previously reported method.[19]

Preparation of o-*(Prop-2-enyloxy)phenylboronic Acid* **5**.—Butyllithium in hexane (2.2 mol dm^{-3}; 103 cm^3, 227 mmol) was added during 10 min to a solution of allyl *o*-bromophenyl ether (44.0 g, 206.6 mmol) in anhydrous tetrahydrofuran (200 cm^3) at −78 °C, and the mixture was stirred for 1 h under dry nitrogen. Triisopropyl borate (38.84 g, 206.6 mmol) was added during 10 min, and the mixture was stirred for 1.5 h at −78 °C, then was allowed to warm overnight to room temperature. Hydrochloric acid (10%; 250 cm^3) and diethyl ether (500 cm^3) were added and the mixture was shaken for 5 min. The organic layer was separated and washed successively with hydrochloric acid (10%; 2 × 250 cm^3) and water (250 cm^3), and the solvent was evaporated off. The residue was stirred with light petroleum (100 cm^3) for 1 h at 0 °C, and the precipitate was collected at the pump and washed with ice-cold light petroleum (2 × 100 cm^3). The solid was crystallised from chloroform–light petroleum to give o-*(prop-2-enyloxy)phenylboronic acid* **5** (17.77 g, 48%) as needles, m.p. 67–68 °C (Found: C, 60.7; H, 6.3. $C_9H_{11}BO_3$ requires C, 60.7; H, 6.2%); λ_{max}(1,4-dioxane)/nm 286 (ε/dm^3 mol^{-1} cm^{-1} 3013); ν_{max}(CHCl$_3$)/cm^{-1} 3514 and 1601; δ_H(CDCl$_3$) 4.59 (2 H, m, OCH$_2$), 5.33 (1 H, m, J_{cis} 11, *gem* vinyl H), 5.40 (1 H, m, J_{trans} 18, *gem* vinyl H), 5.94–6.16 (1 H, m, vinyl H), 6.71 (2 H, s, exch., 2 × OH), 6.86 (1 H, m, ^3J 9.0, 3-H), 6.97–7.05 (1 H, m, 4-H), 7.33–7.41 (1 H, m, 5-H) and 7.84 (1 H, m, ^3J 7.5, 6-H); δ_C(CDCl$_3$) 69.2 (OCH$_2$), 111.2 (aryl CH), 119.1 (vinyl CH$_2$), 121.3 (aryl CH), 132.3 (vinyl CH), 132.7 (aryl CH), 136.9 (aryl CH), 137.5 (C-1) and 163.5 C-2); *m*/*z* 180 (M, 18%), 134 (60), 133 (14), 120 (25), 119 (23), 91 (18), 78 (10), 77 (19), 76 (11), 65 (32), 51 (10), 45 (20) and 41 (100).

Preparation of o-*(Prop-2-enyloxy)phenyllead Triacetate* **6**.—The arylboronic acid **5** (8.90 g, 50 mmol) was added during 15 min to a stirred solution of dry lead tetraacetate (LTA) (22.17 g, 50 mmol) and mercury(II) acetate (1.594 g, 5 mmol) in dry chloroform (75 cm^3) at 40 °C. The mixture was stirred at 40 °C for 1 h, and then overnight at room temperature. The reaction mixture, which gave a negative test for LTA, was filtered through Celite, and washed with chloroform (2 × 150 cm^3). The chloroform solution was washed with water (200 cm^3) and the aqueous layer was re-extracted with chloroform (2 × 400 cm^3). The combined chloroform phases were filtered (Celite) and concentrated to 150 cm^3. Dry light petroleum (750 cm^3) was added and the mixture was kept at 0 °C overnight. The precipitate was collected, and was crystallised from chloroform*–light petroleum to give the *title compound* **6** (20.96 g, 81%) (Found: C, 35.0; H, 3.5. $C_{15}H_{18}O_7Pb$ requires C, 34.8; H, 3.5%); λ_{max}(EtOH)/nm 279 and 313sh (ε 4190 and 1951); ν_{max}(CHCl$_3$)/cm^{-1} 3015, 1590, 1571 and 1469; δ_H(CDCl$_3$) 2.10 (9 H, s, 3 × OAc). 4.65 (2 H, m, OCH$_2$), 5.33 (1 H, m, J_{cis} 9.8, *gem* vinyl H), 5.45 (1 H, m, J_{trans} 17.6, *gem* vinyl H), 6.00–6.10 (1 H, m, vinyl H), 7.04 (1 H, m, ^3J 8.3, Ar 3-H), 7.17–7.21 (1 H, m, Ar 5-H), 7.42–7.46 (1 H, m, Ar 4-H), 7.81 (1 H, m, ^3J 8.1, Ar 6-H); ^{207}Pb satellites gave $J_{3,Pb}$ 231 Hz, $J_{4,Pb}$ ~ 37 Hz, $J_{5,Pb}$ 133 Hz and $J_{6,Pb}$ 422 Hz; δ_C(CDCl$_3$) 21.07 (Me), 70.85 (OCH$_2$), 114.38 (aryl CH), 119.44 (vinyl CH$_2$), 124.02 (aryl CH), 132.58 (aryl or vinyl CH), 132.62 (aryl or vinyl CH), 133.75 (aryl or vinyl CH), 151.71 (C-1), 157.40 (C-2) and 180.53 (C=O).

Reaction of the Aryllead Triacetate **6** *with Sodium Iodide*.—A solution of sodium iodide (0.60 g, 4 mmol) in acetone (10 cm^3) was added to a solution of the *o*-allyloxyphenyllead compound **6** (0.517 g, 1 mmol) in acetone (10 cm^3) and the mixture was stirred for 0.5 h at room temperature. The acetone, from which PbI$_2$ had precipitated, was evaporated off at room temperature and the residue was partitioned between dichloromethane (80 cm^3) and water (40 cm^3). The organic layer, which was coloured by iodine, was separated, and the aqueous layer was washed with dichloromethane (20 cm^3). The dichloromethane phases were combined, and dried (Na$_2$SO$_4$), and the solvent was evaporated off at room temperature. The residue was dissolved in tetrachloromethane, filtered through Celite, and the solvent was evaporated off to give a yellow oil (0.273 g) which was shown by ^{1}H NMR spectroscopy to be predominantly allyl *o*-iodophenyl ether **7**.[20] The crude material was filtered through a column of silica gel (2 g) in light petroleum to yield the pure aryl iodide **7** (0.194 g, 75%) (identified by ^{1}H NMR and mass spectra). Elution of the column with tetrachloromethane afforded a yellow solid, which was crystallised from tetrachloromethane–light petroleum at 0 °C to give *bis-*[o-*(prop-2-enyloxy)phenyl*]*lead diiodide* **11** (0.053 g, 15%) as yellow prisms, m.p. 122–123 °C (Found: C, 29.8; H, 2.4. $C_{18}H_{18}I_2O_2Pb$ requires C, 29.7; H, 2.5%); δ_H(CDCl$_3$) 4.48 (4 H, m, 2 × OCH$_2$), 5.06 (2 H, m, J_{cis} 11.0, 2 × *gem* vinyl H), 5.15 (2 H, m, J_{trans} 17.3, 2 × *gem* vinyl H), 5.63–5.75 (2 H, m, 2 × vinyl H), 6.90 (2 H, m, ^3J 7.7, Ar 3-H), 7.20–7.26 (2 H, m, Ar 5-H), 7.38–7.44 (2 H, m, Ar, 4-H) and 7.90 (2 H, m, ^3J 7.9, Ar 6-H); ^{207}Pb satellites gave $J_{3,Pb}$ 101 Hz, $J_{5,Pb}$ 48 Hz and $J_{6,Pb}$ 188 Hz; δ_C(CDCl$_3$) 69.7 (OCH$_2$), 112.4 (aryl CH), 118.1 (vinyl CH$_2$), 123.1 (aryl CH), 131.9 (vinyl CH), 132.4 (aryl CH), 134.9 (aryl CH), 141.7 (C-1) and 158.7 (C-2).

Reaction of o-*(Prop-2-enyloxy)phenyllead Triacetate* **6** *with Sodium Azide*.—A mixture of sodium azide (0.156 g, 2.4 mmol) and aryllead triacetate **6** (1.034 g, 2.0 mmol) in dry DMSO (6 cm^3) was stirred for 2.5 h in the dark at room temperature. After work-up as previously described,[5] the residual brown oil (0.345 g, 99%) was filtered, with protection from light, through a small column of silica gel (2 g). Elution with light petroleum afforded *o*-(prop-2-enyloxy)phenyl azide **8** (0.267 g, 74%) as a pale yellow oil, which was too unstable for combustion analysis; δ_H(CDCl$_3$) 4.52 (2 H, m, ^3J 5.3, ^4J 1.5, OCH$_2$), 5.28 (1 H, m, J_{cis} 10.5, $^2J \sim {}^4J = 1.4$, *gem* vinyl H), 5.41 (1 H, m, J_{trans} 17.3, $^2J \sim {}^4J = 1.5$, *gem* vinyl H), 5.92–6.14 (1 H, m, J_{trans} 17.2, J_{cis} 10.5, ^3J 5.3, vinyl H) and 6.80–7.08 (4 H, m, 4 × aryl H).

The crude product and the chromatographed material showed no significant differences in their ^{1}H NMR spectra. No other material of significance was recovered when the silica gel column was stripped with chloroform.

Reaction of o-*(Prop-2-enyloxy)phenyllead Triacetate* **6** *with* 2,4,6-*Trimethylphenol* **12**.—The aryllead triacetate **6** (1.034 g, 2.0 mmol) was dissolved in [^{2}H$_5$]pyridine (0.505 g, 6.0 mmol) and dry deuteriochloroform (6.0 cm^3). Mesitol **12** (0.248 g, 1.82 mmol) was added, and the mixture was stirred at 40 °C for 20 h with monitoring by ^{1}H NMR spectroscopy. No signals which could be assigned to a dihydrobenzofuran were observed between δ 2.0 and 4.35.† The mixture was diluted with

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* CHCl$_3$ (2.0 cm^3) contained AcOH (4 drops) and Ac$_2$O (1 drop).

† A reaction carried out on an NMR scale in the same way showed that the product **13** was produced in 70% yield, by the use of 1,2-dichloroethane as an internal standard.

chloroform (30 cm^3), and washed successively with cold, dil. sulfuric acid (3 mol dm^{-3}; 20 cm^3) and water (20 cm^3), and dried (Na_2SO_4). The residual oil, obtained on evaporation of the solvent, was dissolved in ether (50 cm^3) and washed in turn with cold aq. sodium hydroxide (3 mol dm^{-3}; 25 cm^3), water (25 cm^3), and brine (25 cm^3), and dried (Na_2SO_4). The solvent was evaporated off and the residue was filtered in light petroleum–ethyl acetate (9:1) through silica gel (2 g), to give a yellow oil (0.32 g, 66%) on evaporation of the solvent. The product was purified by HPLC [light petroleum–ethyl acetate (9:1)] on a Whatman Partisil 10 M20 column to afford 2,4,6-*trimethyl*-6-[o-(*prop*-2-*enyloxy*)*phenyl*]*cyclohexa*-2,4-*dienone* **13** (0.244 g, 50%) as an oil (Found: C, 80.9; H, 7.8. $C_{18}H_{20}O_2$ requires C, 80.6; H, 7.5%); λ_{max}(EtOH)/nm 277 and 311 (ε 3242 and 4408); ν_{max}($CHCl_3$)/cm^{-1} 1662, 1647, 1587 and 1488; δ_H($CDCl_3$) 1.46 (3 H, s, 6-Me), 1.88 (3 H, d, ^4J 1.6, 4-Me), 1.94 (3 H, d, ^4J 1.5, 2-Me), 4.35 (2 H, m, ^3J 5.4, OCH_2), 5.15 (1 H, m, J_{cis} 9.0, *gem* vinyl H), 5.22 (1 H, m, J_{trans} 15.8, *gem* vinyl H), 5.70 (1 H, narrow m, 5-H), 5.74–5.90 (1 H, m, vinyl H), 6.72 (1 H, narrow m, 3-H), 6.80 (1 H, m, ^3J 8.0, aryl 3-H), 7.00 (1 H, m, aryl H), 7.24 (1 H, m, aryl H) and 7.40 (1 H, m, ^3J 8.0, aryl 6-H); *m/z* 268 (M, 36%), 228 (17), 227 (M – C_3H_5, 100), 212 (227 – Me, 47), 211 (10), 199 (11), 115 (10) and 91 (10). No other material of significance was eluted from the column.

Reaction of o-(*Prop*-2-*enyloxy*)*phenyllead Triacetate* **6** *with Ethyl* 2-*Oxocyclopentanecarboxylate* **15**.—The aryllead triacetate **6** (0.6824 g, 1.32 mmol), β-keto ester **15** (0.1872 g, 1.20 mmol) and dry pyridine (0.316 g, 4.0 mmol) were stirred in dry chloroform (2 cm^3) at 40 °C for 1 h, then overnight at room temperature. The mixture was diluted with chloroform (30 cm^3), then was washed successively with sulfuric acid (3 mol dm^{-3}; 20 cm^3) and water (20 cm^3), and the extract was dried (Na_2SO_4) and evaporated. The crude product (0.33 g, 97%) was purified by flash chromatography [light petroleum–ethyl acetate (7:3)] to yield *ethyl* 2-*oxo*-1-[o-(*prop*-2-*enyloxy*)*phenyl*]*cyclopentanecarboxylate* **16** (0.31 g, 90%) as an oil (Found: C, 70.9; H, 7.2. $C_{17}H_{20}O_4$ requires C, 70.8; H, 7.0%); λ_{max}(EtOH)/nm 272 and 278 (ε 1962 and 1860); ν_{max}($CHCl_3$)/cm^{-1} 1753 and 1721; δ_H($CDCl_3$) 1.23 (3 H, t, *J* 7.4, Me), 1.87 (1 H, m, 4α- or 4β-H), 2.03 (1 H, m, 4β- or 4α-H), 2.35 (1 H, m, 5α- or 5β-H), 2.48 (2 H, m, 3-H_2), 2.94 (1 H, m, 5β- or 5α-H), 4.19 (2 H, m, CH_2Me), 4.51 (2 H, m, allylic CH_2), 5.26 (1 H, m, J_{cis} 10.5, *gem* vinyl H), 5.37 (1 H, m, J_{trans} 17.1, *gem* vinyl H), 5.99 (1 H, m, vinyl H), 6.90 (2 H, m, 2 × aryl H), 6.97 (1 H, m, aryl H) and 7.24 (1 H, m, aryl H); *m/z* 288 (M, 33%), 215 (M – CO_2Et, 21), 202 (15), 201 (100), 187 (11), 173 (30), 159 (85), 147 (15), 146 (14), 145 (12), 133 (16), 131 (22), 118 (15), 115 (12) and 91 (20).

Reaction of o-(*Prop*-2-*enyloxy*)*phenyllead Triacetate* **6** *with the Sodium Salt of* 2-*Nitropropane* **17**.—Sodium hydride (47 mg, 1.95 mmol) and 2-nitropropane (133.5 mg, 1.5 mmol) were stirred in dry DMSO (2.5 cm^3) at room temperature for 4 h under dry nitrogen. A solution of the aryllead triacetate **6** (853 mg, 1.65 mmol) in dry DMSO (4 cm^3) was added by syringe and the mixture was stirred overnight, diluted with water (30 cm^3), and then extracted with diethyl ether (4 × 30 cm^3), and the combined extracts were then washed with water (3 × 100 cm^3), dried (Na_2SO_4), and evaporated. The crude product (0.304 g, 92%) was purified by flash chromatography [light petroleum–ethyl acetate (9:1)] to give 2-*nitro*-2-[o-(*prop*-2-*enyloxy*)*phenyl*]*propane* **18** (0.213 g, 64%) as an unstable oil (Found: M^+, 221.1052; M^+ – NO_2, 175.1123. $C_{12}H_{15}NO_3$ requires M, 221.1052; M – NO_2, 175.1123); ν_{max}($CHCl_3$)/cm^{-1} 1604, 1547 and 1492; δ_H($CDCl_3$) 1.96 (6 H, s, 2 × Me), 4.50 (2 H, m, OCH_2), 5.25 (1 H, m, J_{cis} 10.7, *gem* vinyl H), 5.33 (1 H, m, J_{trans} 17.1, *gem* vinyl H), 5.93 (1 H, m, vinyl CH), 6.93 (1 H, m, ^3J 8.3, aryl 3-H), 7.00 (1 H, m, aryl H) and 7.33 (2 H, m, 2 × aryl H); δ_C($CDCl_3$), 27.5 (C-1), 69.7 (OCH_2), 88.8 (C-2), 113.3 (aryl or vinyl CH), 118.0 (aryl or vinyl CH), 121.1 (aryl or vinyl CH), 126.8 (aryl or vinyl CH), 130.0 (aryl C-1), 130.4 (aryl or vinyl CH), 132.9 (aryl or vinyl CH) and 156.3 (aryl C-2); *m/z* 221 (M, 1.5%), 176 (14), 175 (M – NO_2, 100), 147 (12), 134 (35), 133 (47), 121 (86), 119 (34), 115 (14), 107 (72), 105 (30), 103 (11), 91 (55), 79 (14), 77 (20) and 65 (12).

Acknowledgements

This work was supported by a grant from the Australian Research Council.

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Paper 3/00454F
Received 25*th January* 1993
Accepted 15*th March* 1993