# Mechanism of Arylation of Nucleophiles by Aryllead Triacetates. Part 2. Support for a Ligand Coupling Process and X-Ray Molecular Structure of (*p*-Methoxyphenyl)-α-methylphenacyllead(IV) Diacetate

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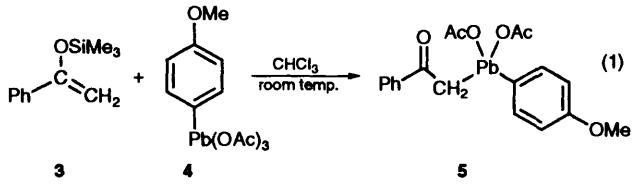
In the presence of boron trifluoride–diethyl ether complex *p*-methoxyphenyllead triacetate **4** and the propiophenone silyl enol ether **6** were found to undergo a rapid reaction to give (*p*-methoxyphenyl)-α-methylphenacyllead diacetate **9** in high yield. Analogous products, **5**, **10** and **11** respectively, were formed when the silyl enol ethers of acetophenone, butyrophenone and isobutyrophenone were treated under the same conditions with aryllead compound **4**. The diorganolead diacetates **9**, **10** and **11** were relatively unstable, giving a number of products when heated at 60 °C in chloroform. In each case there was significant elimination of $Pb(OAc)_2$, with formation of the product of ligand coupling, the deoxybenzoin. α-Methylphenacyl(*o*-prop-2-enyloxy)phenyllead diacetate **21**, which was produced to probe the mechanism of the coupling reaction, behaved similarly to compound **9**, giving no dihydrobenzofuran derivatives. Therefore, it would appear that aryl free radicals are most probably not produced in these thermal reactions, and a ligand-coupling mechanism is proposed.

In the preceding paper,[1] it was firmly established that the non-catalysed arylation reactions of aryllead(IV) triacetates do not proceed by a mechanism involving aryl free radicals. Although it has been suggested that these arylations involve ligand coupling,[2–4] no intermediates similar to those isolated by Barton[5] in the arylation of phenols by arylbismuth(V) reagents have been detected. For the general example of a β-dicarbonyl arylation by an aryllead triacetate depicted in Scheme 1, two intermediates, **1** and **2**, could be involved in a ligand-coupling process, and in this paper we explore this possiblity.

## Results and Discussion

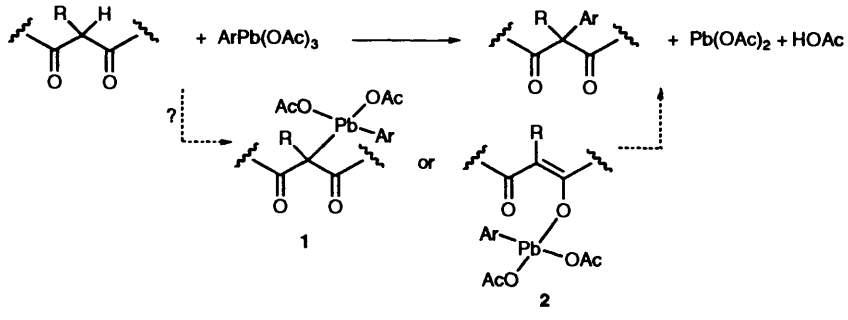
Early in our study of the reactions of aryllead triacetates, we found that the silyl enol ether of acetophenone, compound **3**, reacted with *p*-methoxyphenyllead triacetate **4** to give (*p*-methoxyphenyl)phenacyllead diacetate **5** in high yield[6] [equation (1)]. Analogous diorganolead(IV) diacetates were obtained on treating propiophenone and butyrophenone silyl enol ethers with the aryllead compound **4**, and the reaction was extended to other aryllead triacetates and ring-substituted acetophenones. In our early work, the investigation of the chemistry of the (aryl)phenacyllead diacetates (*e.g.*, **5**) was confined to a study of their behaviour in acid, and we demonstrated that in trifluoroacetic acid they were a source of phenacyl and substituted phenacyl cations.[6]

In the present re-examination of the chemistry of the phenacyllead compound **5** and its analogues, we found that the propiophenone silyl enol ether **6** did not react with *p*-methoxyphenyllead triacetate **4** under the conditions of equation (1), as we previously reported.[6] None of the diorganolead diacetate **9** was produced even after 3 days. The higher reactivity of the *p*-methoxyphenyllead triacetate **4** used in the earlier work was traced to the presence of a small amount of dichloroacetic acid employed in its synthesis.[7] Addition of dichloroacetic acid to the reaction mixture did produce the α-methylphenacyllead compound **9**; however, we have now developed a faster and more reliable method for producing these compounds in high yield. This involves the reaction of the silyl enol ether with an aryllead triacetate in chloroform containing boron trifluoride–diethyl ether complex [equation (2)]. With this procedure the keto lead compound **9** was isolated in 84% yield, while reaction of the silyl enol ethers **3**, **7** and **8** with *p*-methoxyphenyllead triacetate **4**, in the same way, produced the (aryl)phenacyllead diacetates **5**, **10** and **11**,† respectively, in excellent yield.

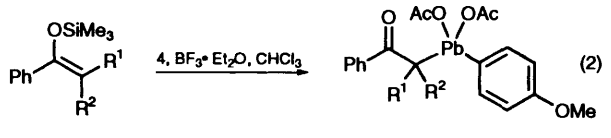



**3** **4** **5**

† Compound **11** was unstable, producing the α-arylated ketone **14** even at room temperature; the yield (approximately 70%) was established by NMR spectroscopy. The reaction also yielded 2-methyl-1-phenylpropenone in 6% yield.




Scheme 1

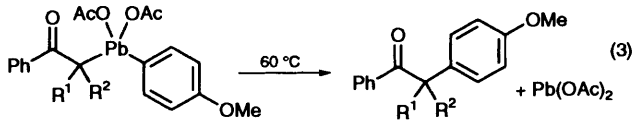



(2)

**3** $R^1 = R^2 = H$
**6** $R^1 = H$, $R^2 = Me$
**7** $R^1 = H$, $R^2 = Et$
**8** $R^1 = R^2 = Me$

**5** $R^1 = R^2 = H$
**9** $R^1 = H$, $R^2 = Me$
**10** $R^1 = H$, $R^2 = Et$
**11** $R^1 = R^2 = Me$

In support of the hypothesis that the mechanism of arylation of β-dicarbonyl compounds by aryllead triacetates may involve ligand coupling in intermediates of type **1**, we found that the phenacyllead(IV) compounds **9–11** produced modest yields of the α-aryl ketones **12–14**, respectively, and $Pb(OAc)_2$ when heated in chloroform at relatively low temperature [equation (3)]. For the keto lead diacetates **5** and **9–11** the ease with which thermal collapse to the α-aryl ketone occurred appeared to depend on the degree of substitution at the carbon attached to lead. For example, with the acetophenone derivative, (*p*-methoxyphenyl)phenacyllead diacetate **5**, none of the expected α-aryl ketone, 4′-methoxybenzoin, was produced after 3 days in refluxing chloroform, whereas the propiophenone- and butyrophenone-derived compounds, **9** and **10** respectively, yielded the α-(*p*-methoxyphenyl) ketones **12** and **13** in 37 and 18% yield, respectively. The keto lead diacetate derived from isobutyrophenone, compound **11**, was even more thermally labile; it had completely decomposed after 14 h at 60 °C, producing the α-arylated ketone **14** in 32% yield.

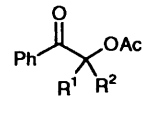



(3)

**9, 10** or **11**

**12** $R^1 = H$, $R^2 = Me$
**13** $R^1 = H$, $R^2 = Et$
**14** $R^1 = R^2 = Me$

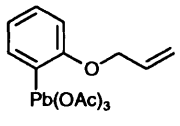
The only other products of significance formed in the above thermal decompositions were the corresponding α-acetoxy ketones, compounds for which the mechanism of formation could also be ligand coupling. The keto lead compound **9** produced α-acetoxypropiophenone **16** in 10% yield, and α-acetoxyisobutyrophenone **18** (2% yield) was obtained in the decomposition of lead compound **11**; however, none of the α-acetoxy ketones **15** and **17** could be detected in the reactions of the acetophenone and butyrophenone derivatives **5** and **10**, respectively. Some hydrolysis of the keto lead compounds **5** and **9–11** to the corresponding ketone was observed in these reactions due to our inability to exclude moisture completely. Also produced in the thermal reactions of the keto lead compounds **5**, **9** and **11** was bis(*p*-methoxyphenyl)lead diacetate **19**, which we believe also results from the presence of moisture.




**15** $R^1 = R^2 = H$
**16** $R^1 = H$, $R^2 = Me$
**17** $R^1 = H$, $R^2 = Et$
**18** $R^1 = R^2 = Me$

$(p\text{-}MeOC_6H_4)_2Pb(OAc)_2$

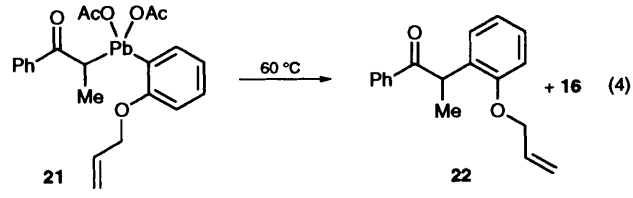
**19**




**20**

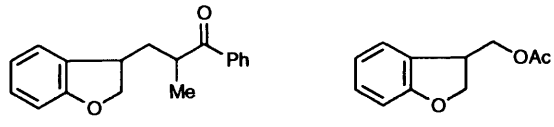
We regard it as significant that no symmetrical products resulting from intermolecular carbon–carbon coupling could be detected in the three thermolyses depicted in equation (3); both GLC and NMR spectroscopic analysis of reaction mixtures showed that none of the possible 1,4-diketones or biaryls was produced.

To further probe the nature of the thermal decompositions of the keto lead compounds, we again used *o*-allyloxyphenyllead triacetate **20**, which was employed in the preceding paper[1] to exclude free-radical mechanisms. The propiophenone silyl enol ether **6** reacted with aryllead compound **20** in the presence of boron trifluoride as in equation (2) to give the (aryl)phenacyllead diacetate **21** in 80% yield (determined by NMR spectroscopy). Like the isobutyrophenone derivative **11**, compound **21** was not sufficiently stable to obtain a satisfactory elemental analysis; however, it was readily characterised by spectroscopy, and shown to yield α-(*o*-allyloxyphenyl)propiophenone **22** (18%) and α-acetoxypropiophenone **16** (21%) when heated at 60 °C in chloroform until the lead(IV) compound could no longer be detected (28 h) [equation (4)]. Here again, intermolecular coupling to give a diketone and/or a biaryl did not occur and, more significantly, the dihydrobenzofurans **23** and **24** were clearly not formed. This result would appear to exclude the intermediacy of aryl free radicals in the thermal collapse of the keto lead compounds, and is in keeping with a ligand-coupling process.




(4)

**21** **22**




**23** **24**

A single-crystal X-ray analysis (see Experimental section) of (*p*-methoxyphenyl)-α-methylphenacyllead diacetate **9** showed it to be dimeric, and an ORTEP diagram for one half (for clarity) of the dimer is reproduced in Fig. 1. The second half of the dimer was produced by a $(1 - x, 1 - y, -z)$ operation. In the dimeric unit each lead atom has pentagonal bipyramidal geometry with the *p*-methoxyphenyl and α-methylphenacyl groups occupying axial positions. Each lead atom is bonded unsymmetrically to both oxygens of the two acetate units, and one oxygen in each monomer unit is bonded to both lead atoms [O(5) and O(5′) (from the other unit) in the ORTEP diagram]. The Pb–O distances range from 2.29 to 2.63 Å. The geometry of lead in compound **9** is similar to that found for both lead atoms in diphenyllead diacetate, which also forms a dimer where oxygen of a water molecule occupies the 7th coordination site in one of the monomer units.[8]

The diaxial arrangement of the two carbon-bound groups in keto lead compound **9** does not favour a direct collapse to the deoxybenzoin derivative **12** and $Pb(OAc)_2$, and, thus, for the necessary orbital overlap in a ligand-coupling process, a thermal rearrangement to an intermediate with one of the groups in an equatorial position would be necessary. This is, in fact, the proposed pathway for a number of reactions of hypervalent species now believed to proceed by ligand coupling.[9]

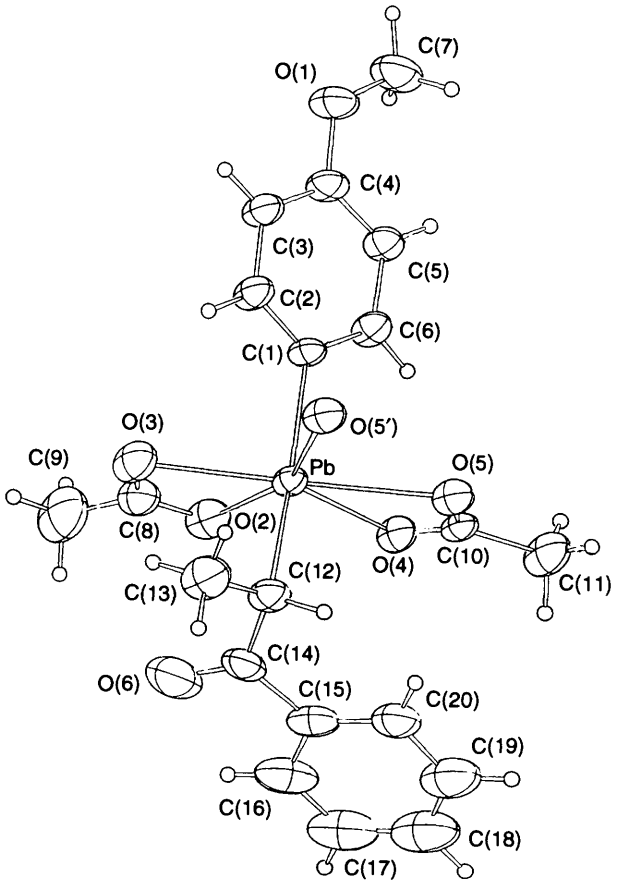



**Fig. 1** X-Ray molecular structure of compound **9** (with atomic numbering used in the crystallographic data)

## Experimental

For general experimental procedures see our earlier paper.[10] Propiophenone trimethylsilyl enol ether **6** was from Aldrich Chemical Co. GLC was performed on a Hewlett-Packard 5890A instrument fitted with an SGE 25QC2/BP1 capillary column (25 m × 0.22 mm; 0.25 μm film thickness) programmed from 50 °C to 300 °C at 15 °C $min^{-1}$. Analytical HPLC was carried out on a Whatman Partisil-5 column (25 cm × 4.6 mm; 5 μm particle size at a flow rate of 1.5 $cm^3$ $min^{-1}$). Preparative HPLC was performed on a Whatman Partisil-10 column (50 cm × 22 mm; 10 μm particle size) at a flow rate of 13.5 $cm^3$ $min^{-1}$.

*Synthesis of Trimethylsilyl Enol Ethers.*—The ketone (40 mmol) was added dropwise during 5 min to a mixture of potassium hydride (2.40 g, 60 mmol) in dry tetrahydrofuran (THF) (150 $cm^3$) and the mixture was stirred for 1 h under nitrogen. Unchanged potassium hydride was allowed to settle and the supernatant solution was transferred by cannula to a stirred solution of trimethylsilyl chloride (5.43 g, 50 mmol) in dry THF (40 $cm^3$). The resultant mixture was stirred for 1 h under nitrogen and then poured into pentane (400 $cm^3$). The mixture was shaken with cold, saturated aq. sodium hydrogen carbonate (2 × 150 $cm^3$), dried ($Na_2SO_4$), filtered, and evaporated. The following compounds were prepared by the above general procedure:

(a) Propiophenone trimethylsilyl enol ether **6** (85%), as an oil, b.p. (Kugelrohr) 100 °C at 0.6 mmHg (lit.,[6] 223 °C at 760 mmHg), identified by $^1H$ NMR spectroscopy.[6]

(b) Butyrophenone trimethylsilyl enol ether **7** (88%), as an oil, b.p. (Kugelrohr) 125 °C at 1.0 mmHg (lit.,[6] 108 °C at 1.0 mmHg), identified by $^1H$ NMR spectroscopy.[6]

(c) Isobutyrophenone trimethylsilyl enol ether **8** (85%), as an oil, b.p. (Kugelrohr) 105 °C at 1.0 mmHg (lit.,[11] 70 °C at 0.01 mmHg); $\delta_H(CDCl_3)$ 0.03 (9 H, s, $SiMe_3$), 1.69 (3 H, s, Me), 1.81 (3 H, s, Me) and 7.35 (5 H, m, Ph).

*Synthesis of the* (p-*Methoxyphenyl*)*phenacyllead Diacetates* **5**, **9** and **10**.—*p*-Methoxyphenyllead triacetate[7] **4** (1.25 g, 2.54 mmol) and the trimethylsilyl enol ether **3**, **6** or **7** (2.79 mmol) were dissolved in dry chloroform (3.0 $cm^3$), and then boron trifluoride–diethyl ether complex (0.134 g, 0.94 mmol) was added by syringe and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with chloroform (12 $cm^3$), then shaken briefly with water (7.5 $cm^3$), and the chloroform layer was filtered. The solvent was evaporated off at 30 °C, and the crude product was triturated with pentane (10 $cm^3$ and 2 × 5 $cm^3$) and dried by pumping at 0.5 mmHg for 1 h. The above general procedure was employed for the preparation of the following compounds:

(a) (*p*-Methoxyphenyl)phenacyllead diacetate **5** (1.227 g, 99%) was obtained as a crystalline solid, m.p. 150–152 °C (decomp.) [lit.,[6] 146 °C (decomp.)]; $\delta_H(CDCl_3)$ 1.84 (6 H, s, 2 × OAc), 3.82 (3 H, s, OMe), 4.40 (2 H, s, $CH_2$), AA'BB' system 7.01 (2 H, m, $^3J$ 9.0, 2 × ArH *meta* to Pb) and 7.64 (2 H, m, $^3J$ 9.0, 2 × ArH *ortho* to Pb), 7.44–7.68 (3 H, m, phenyl 3-, 4- and 5-H) and 8.00 (2 H, m, phenyl 2- and 6-H); $^{207}Pb$ satellites gave $^2J_{H.Pb}$ 192 Hz, $J_{ortho.Pb}$ 192 Hz, and $J_{meta.Pb}$ 67 Hz.

(b) (*p*-Methoxyphenyl)-α-methylphenacyllead diacetate **9** (1.20 g, 84%) was produced as pale yellow crystals, m.p. 138–140 °C* [lit.,[6] 198–202 °C (decomp.)]; $\delta_H(CDCl_3)$ 2.00 (6 H, s, 2 × OAc), 2.19 (3 H, d, $^3J$ 7.2, Me), 3.78 (3 H, s, OMe), 5.18 (1 H, q, $^3J$ 7.2, CH), AA'BB' system 6.99 (2 H, m, $^3J$ 9.0, 2 × ArH *meta* to Pb) and 7.46 (2 H, m, $^3J$ 9.0, 2 × ArH, *ortho* to Pb), 7.42–7.64 (3 H, m, phenyl 3-, 4- and 5-H) and 8.01 (2 H, m, phenyl 2- and 6-H); $^{207}Pb$ satellites gave $J_{Me.Pb}$ 292 Hz, $J_{CH.Pb}$ 186 Hz, $J_{ortho.Pb}$ 163 Hz and $J_{meta.Pb}$ 58 Hz.

(c) (α-*Ethylphenacyl*)-p-*methoxyphenyllead diacetate* **10** (1.34 g, 91%) was obtained as a very moisture-sensitive, pale yellow solid, m.p. 112–114 °C (Found: C, 42.2; H, 4.2. $C_{21}H_{24}O_6Pb$ requires C, 43.5; H, 4.2%); $\delta_H(CDCl_3)$ 1.19 (3 H, t, $^3J$ 7.4, Me), 2.00 (6 H, s, 2 × OAc), 2.48–2.72 (1 H, m, methylene H), 2.81–3.05 (1 H, m, methylene H), 3.74 (3 H, s, OMe), 5.12 (1 H, t, $^3J$ 7.4, CH), AA'BB' system 6.99 (2 H, m, $^3J$ 9.5, 2 × ArH *meta* to Pb) and 7.49 (2 H, m, $^3J$ 9.5, 2 × ArH *ortho* to Pb), 7.41–7.62 (3 H, m, phenyl 3-, 4- and 5-H) and 7.99 (2 H, m, phenyl 2- and 6-H); $^{207}Pb$ satellites gave $J_{CH.Pb}$ 176 Hz, $J_{ortho.Pb}$ 153 Hz, and $J_{meta.Pb}$ 57 Hz.

*Synthesis of* (p-*Methoxyphenyl*)-α,α-*dimethylphenacyllead Diacetate* **11**.—*p*-Methoxyphenyllead triacetate **4** (1.25 g, 2.54 mmol), from which excess of acetic acid had been removed under reduced pressure, and isobutyrophenone trimethylsilyl enol ether **8** (0.615 g, 2.79 mmol) were dissolved in dry deuteriochloroform (3.0 $cm^3$), and boron trifluoride–diethyl ether complex (0.397 g, 2.79 mmol) was added by syringe during 10 min to the stirred mixture. After 25 min, $^1H$ NMR monitoring indicated the presence of some unchanged aryllead triacetate, and further silyl enol ether **8** (0.1 mmol) and boron trifluoride–diethyl ether complex (0.1 mmol) were added, and the mixture was stirred for a further 10 min.

The reaction mixture was diluted with chloroform (15 $cm^3$), and washed successively and briefly with water (10 $cm^3$) and saturated aq. sodium hydrogen carbonate (10 $cm^3$). The chloroform layer was filtered at the pump through Celite and

* This m.p. was obtained by raising the temperature rapidly. When heated slowly from room temperature, decomposition produced the diaryllead diacetate, m.p. ~200 °C.

the solvent was evaporated off under reduced pressure at 30 °C. The crude product was shown by $^1$H NMR spectroscopy to contain the unstable title compound **11** (~55% yield), $\delta_H(CDCl_3)$ 2.5 (6 H, s, 2 × Me), and an AA'BB' system 6.9 (2 H, 2 × ArH *meta* to Pb) and 7.6 (2 H, 2 × ArH *ortho* to Pb); $^{207}$Pb satellites gave $J_{Me.Pb}$ 335 Hz, $J_{ortho.Pb}$ 180 Hz and $J_{meta.Pb}$ 60 Hz.* This analysis also showed the presence of trimethylsilyl fluoride, isobutyrophenone, 2-methyl-1-phenylpropen-1-one[12] (~6% yield), and 2-(*p*-methoxyphenyl)-2-methyl-1-phenylpropan-1-one **14** (~13%).

*Synthesis of α-Methylphenacyl-[o-(prop-2-enyloxy)phenyl]-lead Diacetate* **21**.—*o*-Allyloxyphenyllead triacetate[1] **20** (1.294 g, 2.50 mmol) and propiophenone trimethylsilyl enol ether **6** (0.515 g, 2.50 mmol) were dissolved in dry chloroform (3.0 cm$^3$) and boron trifluoride–diethyl ether complex (0.1183 g, 0.833 mmol) was added by syringe. The mixture was stirred at room temperature for 30 min, and volatile components were evaporated off (Kugelrohr) at 25 °C and 1 mmHg. The resultant viscous oil was found by $^1$H NMR spectroscopy to contain mainly the title compound **21**, $\delta_H(CDCl_3)$ 2.00 (6 H, s, 2 × OAc), 2.24 (3 H, d, $^3J$ 7.2, Me), 5.2–5.5 (3 H, m, PbC*H* and 2 × *gem* vinyl CH), 5.6–6.1 (1 H, m, vinyl CH), 6.9–7.8 (7 H, m, phenyl 3-, 4- and 5-H, and 4 × aryl H), 8.10 (2 H, m, phenyl 2- and 6-H); $^{207}$Pb satellites gave $J_{Me.Pb}$ 336 Hz.

Also present in the above viscous oil was a small amount of propiophenone and ~5% of a diaryllead compound, which showed a signal at $\delta$ 4.7 for an $OCH_2$ group, and is believed to be bis-(*o*-allyloxyphenyl)lead diacetate. Attempts to eliminate the formation of this by-product were unsuccessful, as were attempts to remove it by fractional crystallisation.

*Thermolysis of* (p-*Methoxyphenyl*)*phenacyllead Diacetate* **5**.—The diorganolead compound **5** (0.92 g, 1.67 mmol) was heated at reflux in dry deuteriochloroform (2.5 cm$^3$) for 3 days. $^1$H NMR spectroscopic analysis and GC analysis of the soluble components of the mixture showed the presence of acetophenone (~80% of volatile components by GLC, 40% yield by $^1$H NMR spectroscopy), bis-(*p*-methoxyphenyl)lead diacetate **19** (~33% by $^1$H NMR spectroscopy) and a small amount of anisole. 4'-Methoxydeoxybenzoin, α-acetoxyacetophenone, 4,4'-dimethoxybiphenyl and 1,4-diphenylbutane-1,4-dione could not be detected in the reaction mixture.

*Thermolysis of* (p-*Methoxyphenyl*)-α-*methylphenacyllead Diacetate* **9**.—The lead compound **9** (0.575 g, 1.0 mmol) was stirred in dry deuteriochloroform (1.5 cm$^3$) at 60 °C for 3 days. The precipitate was allowed to settle and analysis of the supernatant solution by $^1$H NMR spectroscopy showed it to contain 2-(*p*-methoxyphenyl)-1-phenylpropan-1-one **12** (37%), α-acetoxypropiophenone **16** (10%), propiophenone (34%), bis-(*p*-methoxyphenyl)lead diacetate **19** (24%), and unchanged starting material (14% recovery). The reaction mixture was treated with dry light petroleum (10 cm$^3$) to precipitate the organolead compounds, and was then filtered through silica gel (2.5 g). Analysis of the filtrate by GLC confirmed the presence of arylated ketone **12**, acetoxy ketone **16**, and propiophenone in approximately the same yields as above. This analysis also showed the presence of anisole (7%), and established that 4,4'-dimethoxybiphenyl, and *meso* and (±)-2,3-dimethyl-1,4-diphenylbutane-1,4-dione were absent from the reaction mixture.

The crude product, obtained on evaporation of the solvent at 30 °C, was fractionated by preparative HPLC in ethyl acetate–light petroleum (7.5:92.5) to yield propiophenone (40 mg, 30%), the arylated ketone **12** (74 mg, 31%) (identical by $^1$H NMR spectroscopy with authentic material[6]) and α-acetoxypropiophenone **16** (19 mg, 10%) ($^1$H NMR and IR spectra identical with those reported previously[13]).

*Thermolysis of* (α-*Ethylphenacyl*)-p-*methoxyphenyllead Diacetate* **10**.—The α-ethylphenacyllead compound **10** (1.160 g, 2.0 mmol) was stirred in dry deuteriochloroform (3.0 cm$^3$) at 60 °C for 3 days. The precipitate was allowed to settle and the supernatant solution was shown by $^1$H NMR spectroscopy to contain none of the starting material. Careful analysis of the spectrum indicated that the solution contained mainly 2-(*p*-methoxyphenyl)-1-phenylbutan-1-one **13**, butyrophenone and bis-(*p*-methoxyphenyl)lead diacetate **19**. Analysis by GLC confirmed the presence of the arylated ketone **13** and butyrophenone, and showed the presence of a small amount of anisole as the only other volatile component of significance. 4,4'-Dimethoxybiphenyl could not be detected.

The crude product obtained on evaporation of the solvent was fractionated by HPLC in ethyl acetate–light petroleum (1:99) to yield 2-(*p*-methoxyphenyl)-1-phenylbutan-1-one **13** (90 mg, 18%) as an oil (lit.,[14] m.p. 38–39 °C); $\delta_H(CDCl_3)$ 0.92 (3 H, t, $^3J$ 7.4, Me), 1.88 (1 H, m, methylene H), 2.20 (1 H, m, methylene H), 3.78 (3 H, s, OMe), 4.42 (1 H, t, $^3J$ 7.4, CH), 6.85 and 7.25 (4 H, AA'BB', 3'-, 5'-H and 2'-, 6'-H, respectively), 7.37–7.54 (3 H, m, phenyl 3-, 4- and 5-H) and 7.97 (2 H, m, phenyl 2- and 6-H).

*Thermolysis of* (p-*Methoxyphenyl*)-α,α-*dimethylphenacyllead Diacetate* **11**.—The total amount of the phenacyllead compound **11** obtained in its synthesis above (~2.54 mmol) was stirred in dry deuteriochloroform (3.0 cm$^3$) at 60 °C for 13.5 h. The precipitate was allowed to settle and the supernatant solution was shown by $^1$H NMR spectroscopy to contain principally the α-arylated ketone **14**, isobutyrophenone and isopropenyl phenyl ketone in the approximate molar proportions 5:3:1. No residual keto lead compound was present. The crude product was filtered through silica gel (5 g) in ethyl acetate–light petroleum (5:95) (100 cm$^3$) and the resulting oil (0.406 g) was fractionated by preparative HPLC. Elution with ethyl acetate–light petroleum (2.5:97.5) afforded three significant fractions, the first of which was isobutyrophenone (70 mg, 18%).

The second fraction eluted yielded 2-(p-*methoxyphenyl*)-2-*methyl*-1-*phenylpropan*-1-*one* **14** (203 mg, 31.5%) as an oil (Found: C, 80.2; H, 7.1. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%); $\lambda_{max}$(MeOH)/nm 230, 243sh, 277 and 285sh (ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 15 000, 10 000, 3400 and 2700); $\nu_{max}(CDCl_3)$/cm$^{-1}$ 1670; $\delta_H(CDCl_3)$ 1.57 (6 H, s, 2 × Me), 3.80 (3 H, s, OMe), 6.88 and 7.24 (4 H, AA'BB', 3'-, 5'-H and 2'-, 6'-H, respectively), 7.1–7.4 (3 H, m, phenyl 3-, 4- and 5-H) and 7.4–7.6 (2 H, m, phenyl 2- and 6-H); *m/z* 254 (M, 0.5%) and 149 (M − PhCO, 100).

The last compound eluted was α-acetoxyisobutyrophenone **18** (12 mg, 2%) (identical $^1$H NMR spectrum with that previously reported[13]).

Analysis of the crude reaction mixture by GLC confirmed the yields of isobutyrophenone and compounds **14** and **18**, and showed that 4,4'-dimethoxybiphenyl was not present. In addition, none of the symmetrical diketone, 2,2,3,3-tetramethyl-1,4-diphenylbutane-1,4-dione,[15] could be detected by $^1$H NMR spectroscopy.

*Thermolysis of* (o-*Allyloxyphenyl*)-α-*methylphenacyllead Diacetate* **21**.—The total amount of the keto lead compound **21** obtained in the above synthesis (~2.50 mmol) was stirred in dry deuteriochloroform (3.0 cm$^3$) at 60 °C for 28 h. The reaction was monitored by $^1$H NMR spectroscopy, which showed that the reaction was complete after *ca.* 20 h, and that the principal products were propiophenone and two compounds displaying methyl doublets at $\delta$ ~1.5.

* Its thermal instability and the complexity of the mixture, prevented further characterisation of compound **11**.

The solvent was evaporated off under reduced pressure at room temperature and the residue was filtered in diethyl ether (10 $cm^3$) through silica gel (2.5 g). Evaporation of the solvent yielded a yellow oil (0.75 g), which was subjected to HPLC in ethyl acetate–light petroleum (1:19) to afford propiophenone (70 mg, 21%) and two other fractions.

The second fraction gave 2-(o-*allyloxyphenyl*)-1-*phenylpropan*-1-*one* **22** (117 mg, 18%) as an oil (Found: $M^+$, 266.1307. $C_{18}H_{18}O_2$ requires M, 266.1307); $\lambda_{max}$(EtOH)/nm 243 and 274sh ($\varepsilon$ 12 170 and 3195); $\nu_{max}$($CHCl_3$)/$cm^{-1}$ 1683 and 1599; $\delta_H$($CDCl_3$) 1.50 (3 H, d, $^3J$ 7.2, Me), 4.60 (2 H, m, $^3J$ 4.8, $OCH_2$), 5.13 (1 H, q, $^3J$ 6.8, C*H*Me), 5.29 (1 H, m, $J_{cis}$ 10.6, *gem* vinyl H), 5.41 (1 H, m, $J_{trans}$ 17.4, *gem* vinyl H), 5.94–6.16 (1 H, m, vinyl H), 6.81–6.92 (2 H, m, aryl 3- and 5-H), 7.11–7.20 (2 H, m, aryl 4- and 6-H), 7.29–7.50 (3 H, m, phenyl 3-, 4- and 5-H) and 7.98 (2 H, m, phenyl 2- and 6-H); *m/z* 266 (M, 12%), 162 (12), 161 (M − PhCO, 91), 133 (13), 119 (12), 107 (34) and 105 (PhCO, 100).

The third fraction afforded α-acetoxypropiophenone **16** (99 mg, 21%) (identical by $^1$H NMR spectroscopy with material obtained above). Analysis, by $^1$H NMR spectroscopy, of the crude mixture from the silica gel filtration column showed that no other significant compounds were present.

*Crystal Structure Analysis of* (p-*Methoxyphenyl*)-α-*methylphenacyllead Diacetate* **9**.—*Crystal data.* $C_{20}H_{22}O_6Pb$, M = 565.6, monoclinic, space group $P2_1/a$, $a$ = 12.862(2), $b$ = 12.505(2), $c$ = 14.016(1) Å, $\beta$ = 116.45(2), $V$ = 2 018.4 $Å^3$, $D_c$ ($Z$ = 4) = 1.86 g $cm^{-3}$. $F$(000) = 1088, $\mu$ = 84.27 $cm^{-1}$, $\lambda$(Mo-Kα) = 0.710 69 Å, Specimen: prisms, 0.03 × 0.175 × 0.275 mm, $N$ = 3510, $N_o$ = 2477, $T_{min}$ = 0.250, $T_{max}$ = 0.781, $I > 2.5\sigma(I)$, $h,k,l$ $-15 \longrightarrow 15$, $0 \longrightarrow 14$, $0 \longrightarrow 16$, $R$ = 0.033, $R'$ = 0.034, $w = 2.42/[\sigma^2(F_o) + 5 \times 10^{-5} F_o^2]$. Residual extrema, 1.0 and −1.3 e $Å^{-3}$.

*Data collection and processing.* Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections. Data were measured on an Enraf–Nonius CAD4 diffractometer within the limits $1.0 \leqslant \theta \leqslant 25°$, with Mo-Kα radiation, graphite monochromator and operating in $\omega$–$\theta$ mode. Lorentz and polarisation effects were corrected for by using the Enraf–Nonius SDP System.[16]

*Structure analysis and refinement.* The structure was solved by direct methods using SHELXS-86.[17] Refinement was by blocked-matrix least squares using SHELX-76.[18] Scattering factors were those supplied in SHELX-76. An ORTEP[19] plot of the molecule is shown in Fig. 1. Additional material, which is available from the Cambridge Crystallographic Data Centre, comprises fractional coordinates, bond lengths and angles, thermal parameters, hydrogen atom coordinates and torsion angles.*

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