

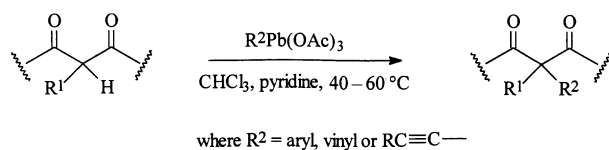
# $\alpha$ -Arylation of ketones by aryllead triacetates. Effect of methyl and phenyl substitution at the $\alpha$ position

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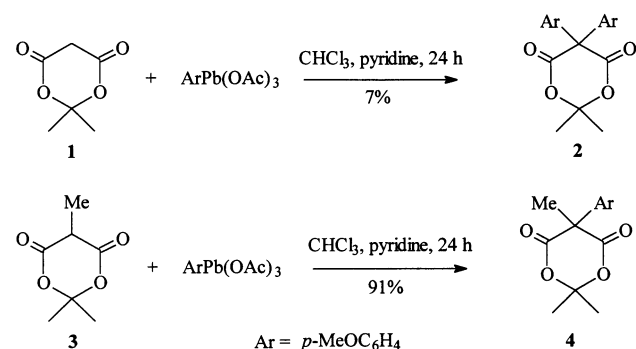
**An examination of the  $\alpha$ -arylation of a number of ketones and their enolate salts by *p*-methoxyphenyllead triacetate provides further evidence for a very marked selectivity in the arylation reaction. It is found that the reaction proceeds well at tertiary  $\alpha$ -carbons and at secondary centres activated by the presence of a phenyl group, but fails where the secondary centre is unactivated and at primary  $\alpha$ -carbons.**

In an examination of the reactions of organolead triacetates extending over a number of years, we have shown that these electrophilic reagents react with a range of soft carbon acids such as  $\beta$ -dicarbonyl compounds.<sup>1–3</sup> With the latter compounds the reactions provide ready access to a wide variety of  $\alpha$ -aryl,  $\alpha$ -vinyl and  $\alpha$ -alk-1-ynyl  $\beta$ -dicarbonyl compounds<sup>4–9</sup> (Scheme 1).



**Scheme 1**

These reactions, which most likely proceed by a ligand exchange followed by ligand coupling,<sup>10</sup> show a number of significant features. Firstly, in most cases reactions proceed fastest and in highest yields with the more acidic  $\beta$ -dicarbonyls, and with such substrates (*e.g.*  $\beta$ -diketones and  $\beta$ -keto esters) the general reaction outlined in Scheme 1 takes place simply on mixing the organolead triacetate and substrate in chloroform–pyridine at 20–60 °C. With the less acidic compounds such as diethyl malonates the reaction is slow, and for a fast, high-yielding reaction it has been found best to employ the diethyl malonate salt.<sup>6</sup> This is consistent with a ligand exchange involving the enolate of the dicarbonyl compound. The other main feature of these reactions is not readily explained; this concerns the preference for the electrophilic substitution to proceed at sites with only one replaceable hydrogen as illustrated with the examples in Scheme 2. Whereas Meldrum's acid **1** reacted slowly with *p*-



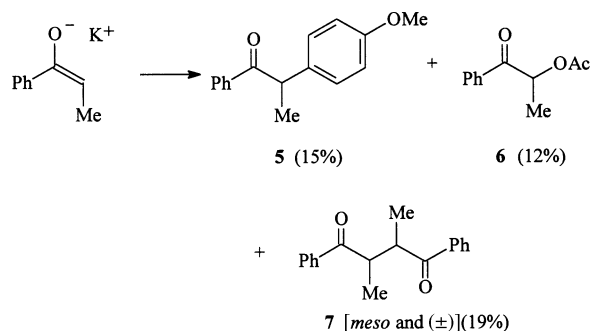
**Scheme 2**

*p*-methoxyphenyllead triacetate (1 equiv.) to give only the diarylated product **2** in very low yield after 24 h, the 5-methyl derivative **3** reacted rapidly with the same lead reagent to give the

arylated compound **4** in >90% yield after 1 h. An important consequence of this reactivity of aryllead triacetates, which applies also to the vinyllead and alkynyllead reagents, is that their reactions provide a ready means of generating highly functionalised quaternary carbon centres around which in some cases there is considerable steric congestion.

Early in this work we found that simple ketones such as cyclohexanone and acetophenone were unreactive towards aryllead triacetates under our standard chloroform–pyridine conditions. Attempts were also made to react the potassium enolates of these two ketones with *p*-methoxyphenyllead triacetate in tetrahydrofuran (THF)–pyridine; however, both reactions resulted only in recovery of the ketones. This was in sharp contrast to the behaviour of the arylbismuth(v) compounds of Barton and co-workers,<sup>11,12</sup> which are thought to react with enolates and other carbon acids by a ligand coupling mechanism similar to that of our aryllead reagents. They reported that triphenylbismuth carbonate reacts with the potassium enolates of cyclohexanone and acetophenone to give 2,2,6,6-tetra-phenylcyclohexanone and 2,2,2-triphenylacetophenone, respectively, in excellent yields.<sup>11</sup>

An increase in reactivity of  $\beta$ -dicarbonyls towards arylation by aryllead triacetates on replacement of one of the  $\alpha$ -hydrogens by a methyl group, as illustrated in Scheme 2, is also displayed in simple ketones. For example, we found that the potassium enolate of propiophenone did react with *p*-methoxyphenyllead triacetate in THF–pyridine to give the deoxybenzoin derivative **5** in modest yield (15%) (Scheme 3). Also pro-

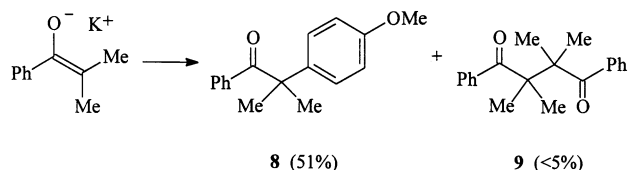


**Scheme 3** Reagents and conditions: *p*-MeOC<sub>6</sub>H<sub>4</sub>Pb(OAc)<sub>3</sub>, THF, pyridine, room temp., N<sub>2</sub>

duced in similar yields were  $\alpha$ -acetoxy ketone **6** and a mixture of the *meso* and ( $\pm$ ) isomers **7**, the product of oxidative dimerisation. Propiophenone (36%) was also recovered from this reaction.

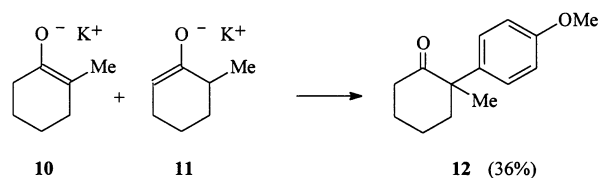
Further confirmation of the effect of substitution at the  $\alpha$ -

carbon on the ease of arylation was found in the reaction of the potassium enolate of isobutyrophenone with *p*-methoxyphenyllead triacetate. The  $\alpha$ -arylated ketone **8** was formed in considerably higher yield (51%) and it was not accompanied by the  $\alpha$ -acetoxy ketone. Analysis of the crude reaction product by GC-MS indicated the presence of a very small amount (<5%) of the dimer **9**, while the remaining starting material was accounted for as recovered isobutyrophenone (Scheme 4).



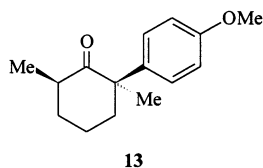
**Scheme 4** Reagents and conditions: *p*-MeOC<sub>6</sub>H<sub>4</sub>Pb(OAc)<sub>3</sub>, THF, pyridine, room temp., N<sub>2</sub>

Further compelling evidence for the effect of  $\alpha$ -substitution on the ease of the arylation reaction was found in the reactions of the enolates of 2-methylcyclohexanone and 2,6-dimethylcyclohexanone. The mixture of the potassium enolates of 2-methylcyclohexanone, **10** and **11**, which are present in the ratio of 67 : 33 when formed with KH in THF,<sup>13</sup> was treated with *p*-methoxyphenyllead triacetate in THF–pyridine to give a single arylated ketone, 2-(*p*-methoxyphenyl)-2-methylcyclohexanone **12** in a yield of 36% (54% from enolate **10**) (Scheme 5). None of



**Scheme 5** Reagents and conditions: *p*-MeOC<sub>6</sub>H<sub>4</sub>Pb(OAc)<sub>3</sub>, THF, pyridine, room temp., N<sub>2</sub>

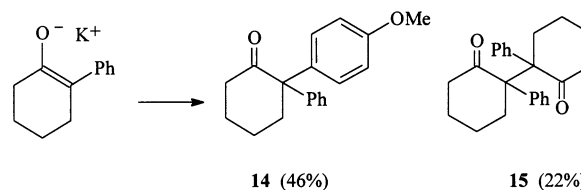
the 6-arylated compound was present and no dimers could be detected. Consistent with this result, the potassium enolate of 2,6-dimethylcyclohexanone reacted with the same aryllead reagent under the same conditions to produce 2,6-dimethyl-2-(*p*-methoxyphenyl)cyclohexanone in good yield (75%) as a mixture of isomers (GC analysis). The only other material present was 2,6-dimethylcyclohexanone. On the basis of the <sup>1</sup>H NMR spectrum of the mixture, the major component (>95%) was the *cis*-isomer **13**. The assignment was based on the chemical shifts



of the 6-methyl signals for the two isomers. In the major component this was a doublet at  $\delta$  0.99, while for the minor component the corresponding doublet was at  $\delta$  1.01. It has been found that for such pairs of cyclohexanone isomers, an equatorial methyl group resonates at higher field than an axial methyl, while the aromatic AA'BB' resonances ( $\delta$  7.06 and 6.87) were consistent with an equatorial configuration for the *p*-methoxyphenyl group.<sup>5</sup>

We have found that the presence of an  $\alpha$ -phenyl group, which can stabilise the enol tautomer by conjugation, can also result in enhanced reactivity of ketones to arylation. The potassium enolate of 2-phenylcyclohexanone reacted in THF–pyridine with *p*-methoxyphenyllead triacetate to give 2-(*p*-methoxy-

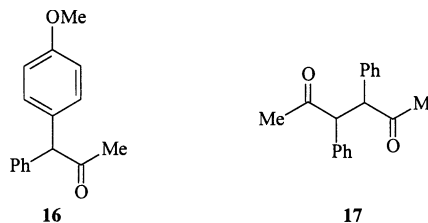
phenyl)-2-phenylcyclohexanone **14** in moderate yield (46%) and a mixture of the *meso* and ( $\pm$ ) isomers of the dimer **15** in 22% yield (Scheme 6). Recovered 2-phenylcyclohexanone accounted for the remaining starting material.



**Scheme 6** Reagents and conditions: *p*-MeOC<sub>6</sub>H<sub>4</sub>Pb(OAc)<sub>3</sub>, THF, pyridine, room temp., N<sub>2</sub>

Unlike 2-methylcyclohexanone and 2,6-dimethylcyclohexanone, 2-phenylcyclohexanone has a sufficiently acidic  $\alpha$ -hydrogen for the arylation to proceed with the ketone itself; thus, when the ketone and the same aryllead triacetate were kept in chloroform–pyridine at 40 °C for 24 h, a similar yield (46%) of the diaryl ketone **14** was obtained. This was unaccompanied by the dimers **15** and is therefore a more useful synthetic route to compound **14**. Moreover, the method could clearly be used to access a wide range of unsymmetrical 2,2-diaryl ketones.

The increase in reactivity of simple ketones due to the presence of an  $\alpha$ -aryl group also extends to compounds in which the  $\alpha$ -carbon is secondary. Benzyl methyl ketone was found to react with *p*-methoxyphenyllead triacetate in chloroform–pyridine at 40 °C to give the arylated ketone **16** in 20% yield after 20 h. As



with the arylation of 2-phenylcyclohexanone, this proved to be a better route to compound **16** than by arylation of the potassium enolate of benzyl methyl ketone. In a reaction conducted with the potassium enolate and *p*-methoxyphenyllead triacetate under the conditions outlined in Scheme 6, a mixture consisting of the *meso* and ( $\pm$ ) dimers **17** (total of 25%) and the arylated ketone **16** (5%) was produced.

The examples of ketone  $\alpha$ -arylation presented here further illustrate the unusual selectivity displayed by aryllead triacetates. The preference for arylation at tertiary carbons leading to quaternary centres, which in many cases are sterically crowded, is a feature which makes them potentially very useful reagents for synthesis, especially in the area of natural products chemistry.

## Experimental

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. IR Spectra were recorded on a Perkin-Elmer 221 spectrophotometer and UV spectra on a Perkin-Elmer 402 instrument. NMR Spectra were determined with SiMe<sub>4</sub> as internal standard on a Varian HA100 instrument; *J* values are given in Hz. Microanalyses were performed by the Australian Microanalytical Service, Melbourne and mass spectra were recorded on an AEI model MS902 double focusing instrument. Thin layer chromatography was carried out on glass plates spread with 1 mm layers of Merck Kieselgel 60. *p*-Methoxyphenyllead triacetate was prepared as previously

reported.<sup>14</sup> Light petroleum refers to the fraction of bp 60–70 °C. Analytical gas chromatography (GC) was carried out on a Hewlett-Packard 402 instrument equipped with a flame ionisation detector and one of the following columns: column 1, 3% OV17 (50 : 50 phenyl-methyl silicone gum) on Gas Chrom Q (100–120 mesh); column 2, 3% OVI (100% methyl silicone gum) on Gas Chrom Q (100–120 mesh). Ether refers to diethyl ether.

#### Reaction of propiophenone potassium enolate with *p*-methoxyphenyllead triacetate

Propiophenone potassium enolate (2 mmol) in dry THF (6 cm<sup>3</sup>) was added dropwise over 2 min to *p*-methoxyphenyllead triacetate (1.08 g, 2.2 mmol) and dry pyridine (1.04 g, 13 mmol) in dry THF (6 cm<sup>3</sup>). The mixture was stirred at room temperature under N<sub>2</sub> for 1 h and then the precipitate was removed by filtration and washed with light petroleum. The solvent was evaporated from the combined filtrate and light petroleum washings, and the residue was fractionated by thin layer chromatography using light petroleum-ether (10 : 1) as the developing solvent. Five fractions were obtained, the least polar being propiophenone.

Fraction 2, the next in order of polarity, afforded 2-(*p*-methoxyphenyl)-1-phenylpropan-1-one **5** as colourless crystals, mp 48–50 °C (from pentane) (lit.,<sup>15</sup> 58–59.5 °C);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.50 (3 H, d, 3-H<sub>3</sub>), 3.71 (3 H, s, OMe), 4.62 (1 H, q, 2-H), 6.80 and 7.19 (4 H, AA'BB', *p*-methoxyphenyl 3-H and 5-H, 2-H and 6-H, respectively), 7.0–7.6 (3 H, m, phenyl 3-H, 4-H and 5-H) and 7.8–8.1 (2 H, m, phenyl 2-H and 6-H).

Fraction 3 yielded *meso*-2,3-dimethyl-1,4-diphenylbutane-1,4-dione **7** as colourless crystals, mp 101–102 °C [lit.,<sup>16</sup> 85–86 °C for *meso*, ( $\pm$ ) mixture];  $\delta_{\text{H}}(\text{CDCl}_3)$  1.14 (6 H, d, 2  $\times$  Me), 3.9–4.2 (2 H, m, 2-H and 3-H), 7.3–7.6 (6 H, m, *m*- and *p*-phenyl-H) and 7.9–8.15 (4 H, m, *o*-phenyl-H).

Fraction 4 afforded ( $\pm$ )-2,3-dimethyl-1,4-diphenylbutane-1,4-dione **7** as colourless crystals, mp 86–88 °C (from hexane) (lit.,<sup>17</sup> 86–87 °C);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.29 (6 H, d, 2  $\times$  Me), 3.8–4.2 (2 H, m, 2-H and 3-H), 7.3–7.7 (6 H, m, *m*- and *p*-phenyl-H) and 7.9–8.1 (4 H, m, *o*-phenyl-H).

Fraction 5, the most polar material, yielded 2-acetoxy-1-phenylpropan-1-one **6** as an oil,  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1740 and 1700 (lit.,<sup>18</sup> 1740 and 1700 cm<sup>-1</sup>);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.53 (3 H, d, *J* 7, Me), 2.14 (3 H, s, COMe), 5.98 (1 H, d, *J* 7, 2-H), 7.4–7.7 (3 H, m, *m*- and *p*-phenyl-H) and 7.9–8.0 (2 H, m, *o*-phenyl-H).

Analysis by GC of the crude product using column 1 showed the yields to be: propiophenone (36%), 2-(*p*-methoxyphenyl)-1-phenylpropan-1-one **5** (15%), the *meso* and ( $\pm$ ) dimers **7** (19% in total) and the  $\alpha$ -acetoxy ketone **6** (12%)

#### Reaction of isobutyrophenone potassium enolate with *p*-methoxyphenyllead triacetate

Isobutyrophenone potassium enolate (2 mmol) in THF (6 cm<sup>3</sup>) was added dropwise to a stirred solution of *p*-methoxyphenyllead triacetate (1.08 g, 2.2 mmol) and pyridine (1.04 g, 13 mmol) in THF (6 cm<sup>3</sup>) at room temperature under N<sub>2</sub>. The mixture was stirred for 1 h and then poured into ether (50 cm<sup>3</sup>). The ether solution was filtered, washed with hydrochloric acid (1 M; 20 cm<sup>3</sup>), dried (MgSO<sub>4</sub>) and the solvent was evaporated. The residual oil was fractionated by thin layer chromatography in light petroleum-ether (9 : 1) to yield 2-(*p*-methoxyphenyl)-2-methyl-1-phenylpropan-1-one **8** as a colourless oil (Found: C, 80.2; H, 7.1. C<sub>17</sub>H<sub>18</sub>O<sub>2</sub> requires C, 80.3; H, 7.1%);  $\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  1670;  $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$  230, 243sh, 277 and 285sh ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  15 000, 10 000, 3400 and 2700);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.57 (6 H, s, 2  $\times$  Me), 3.80 (3 H, s, OMe), 6.88 and 7.24 (4 H, AA'BB', 3-H and 5-H, 2-H and 6-H, respectively), 7.1–7.4 (3 H, m, *m*- and *p*-phenyl-H) and 7.4–7.6 (2 H, m, *o*-phenyl-H).

Analysis by GC (column 2) of the product prior to chromatography showed the presence of isobutyrophenone (48%),

arylated ketone **8** (51% yield) and material *M*<sub>w</sub> 294 corresponding to the dimer **9** (<5%).

#### Reaction of 2-methylcyclohexanone potassium enolate with *p*-methoxyphenyllead triacetate

The mixture of potassium enolates **10** and **11** (4 mmol) in THF (20 cm<sup>3</sup>) was added to a solution of *p*-methoxyphenyllead triacetate (2.16 g, 4.4 mmol) and pyridine (2.1 g, 27 mmol) in THF (20 cm<sup>3</sup>) at room temperature under N<sub>2</sub>. The mixture was stirred for 24 h, poured into ether (100 cm<sup>3</sup>) and then worked up as in the previous experiment. The oily product was fractionated by thin layer chromatography in light petroleum-ethyl acetate (49 : 1) to afford 2-(*p*-methoxyphenyl)-2-methylcyclohexanone **12** as colourless crystals, mp 96–98 °C (Found: C, 76.9; H, 8.3. C<sub>14</sub>H<sub>18</sub>O<sub>2</sub> requires C, 77.0; H, 8.3%);  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1700;  $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$  231, 278 and 284 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  8800, 1600 and 1400);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.25 (3 H, s, Me), 1.5–2.8 (8 H, m, 4  $\times$  CH<sub>2</sub>), 3.80 (3 H, s, OMe), 6.87 and 7.10 (4 H, AA'BB', 3-H and 5-H, 2-H and 6-H, respectively); *m/z* 218 (M, 45%), 176 (13), 175 (100), 161 (37), 148 (40), 135 (11), 121 (21), 91 (12) and 77 (10).

The GC analysis (column 2) of the crude product from the above reaction showed the yield of the arylated ketone **12** to be 36%. There were no significant peaks which might correspond to a dimer of 2-methylcyclohexanone or to the acetoxy ketone.

#### Reaction of 2,6-dimethylcyclohexanone potassium enolate with *p*-methoxyphenyllead triacetate

The enolate salt (1 mmol) in THF (5 cm<sup>3</sup>) was added to a stirred solution of *p*-methoxyphenyllead triacetate (540 mg, 1.1 mmol) and pyridine (290 mg, 3.3 mmol) in THF (5 cm<sup>3</sup>) at room temperature under N<sub>2</sub>, and the mixture was stirred for 4 h. The mixture was poured into ether (50 cm<sup>3</sup>) and worked up as for the reaction of isobutyrophenone enolate above. The oily residue was fractionated by thin layer chromatography in light petroleum-ether (17 : 3) to yield *c*-2,6-dimethyl-*r*-2-(*p*-methoxyphenyl)cyclohexanone **13** as a colourless oil (Found: C, 77.8; H, 8.9. C<sub>15</sub>H<sub>20</sub>O<sub>2</sub> requires C, 77.6; H, 8.7%);  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1705;  $\lambda_{\text{max}}(\text{EtOH})/\text{nm}$  227, 276 and 282 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  8800, 1600 and 1300);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.99 (3 H, d, 6-Me), 1.24 (3 H, s, 2-Me), 1.2–2.8 [7 H, m, CH(CH<sub>2</sub>)<sub>3</sub>], 3.79 (3 H, s, OMe) 6.87 and 7.06 (4 H, AA'BB', 3-H and 5-H, 2-H and 6-H, respectively); *m/z* 232 (M, 34%), 204 (16), 189 (23), 162 (10), 161 (66), 149 (11), 148 (100), 147 (15), 135 (37), 133 (14), 121 (14), 91 (17) and 77 (13).

Analysis by GC (column 2) of the crude product from the above reaction showed the yield of arylated ketone **13** to be 75%. No material corresponding to a dimer of 2,6-dimethylcyclohexanone or to the acetoxy ketone could be detected.

#### Reaction of 2-phenylcyclohexanone potassium enolate with *p*-methoxyphenyllead triacetate

The enolate salt (1 mmol) in THF (3 cm<sup>3</sup>) was added to a stirred solution of *p*-methoxyphenyllead triacetate (540 mg, 1.1 mmol) and pyridine (520 mg, 6.6 mmol) in THF (3 cm<sup>3</sup>) at room temperature under N<sub>2</sub>. After 1 h the mixture was poured into ether (50 cm<sup>3</sup>) and worked up as for the reaction of isobutyrophenone enolate above to give a solid residue which was fractionated by thin layer chromatography in light petroleum-ether (4 : 1). Four fractions were obtained, the least polar of which was 2-phenylcyclohexanone.

The next more polar product crystallised from light petroleum to afford either *meso*- or ( $\pm$ )-2,2'-*dioxo*-1,1'-*diphenyl*-1,1'-*bicyclohexyl* **15**, mp 189–190 °C (Found: C, 83.0; H, 7.8. C<sub>24</sub>H<sub>26</sub>O<sub>2</sub> requires C, 83.2; H, 7.6%);  $\nu_{\text{max}}(\text{CHCl}_3)/\text{cm}^{-1}$  1700;  $\lambda_{\text{max}}(\text{MeOH})/\text{nm}$  254, 260, 266 and 290 ( $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  510, 580, 510 and 290);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.0–3.6 [16 H, m, 2  $\times$  (CH<sub>2</sub>)<sub>4</sub>], 6.4–6.7 (2 H, m, ArH) and 6.7–7.7 (8 H, m, ArH); *m/z* 346 (M, 1%), 174 (100), 145 (10) and 91 (30).

The next fraction in order of polarity crystallised from light

petroleum to give either meso- or ( $\pm$ )-2,2'-dioxo-1,1'-diphenyl-1,1-bicyclohexyl **15**, mp 150–151 °C (Found: C, 83.1; H, 7.8.  $C_{24}H_{26}O_2$  requires C, 83.2; H, 7.6%);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1705;  $\lambda_{\max}(\text{MeOH})/\text{nm}$  256, 262, 267, 272 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  530, 580, 530 and 540);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.0–3.3 [16 H, m,  $2 \times (\text{CH}_2)_4$ ], 5.6–6.0 (1 H, m, ArH), 6.4–8.0 (9 H, m, ArH);  $m/z$  346 (M, 1%), 175 (14), 174 (100), 173 (20), 172 (11), 145 (13), 130 (18), 117 (11) and 91 (35).

The most polar fraction crystallised from light petroleum to yield 2-(*p*-methoxyphenyl)-2-phenylcyclohexanone **14** as colourless crystals, mp 113–114 °C (Found: C, 81.1; H, 7.1.  $C_{19}H_{20}O_2$  requires C, 81.4; H, 7.2%);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1705;  $\lambda_{\max}(\text{MeOH})/\text{nm}$  271sh, 277 and 283 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  1500, 1800 and 1600);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.6–2.1 (4 H, m,  $2 \times \text{CH}_2$ ), 2.4–2.7 (4 H, m,  $2 \times \text{CH}_2$ ), 3.79 (3 H, s, OMe), 6.83 and 6.99 (4 H, AA'BB', 3-H and 5-H, 2-H and 6-H, respectively) and 6.8–7.5 (5 H, m,  $5 \times \text{phenyl-H}$ );  $m/z$  281 (M + 1, 18%), 280 (59), 252 (65), 224 (27), 223 (100), 197 (35), 179 (19), 165 (29), 152 (23), 121 (18), 115 (48), 91 (31) and 77 (15).

Analysis of the crude reaction product by GC (column 2) showed the yield of the arylated ketone **14** to be 46%, while the combined yield of *meso* and ( $\pm$ ) dimers **15** was 22%. 2-Phenylcyclohexanone (22%) was recovered from the reaction.

#### Reaction of 2-phenylcyclohexanone with *p*-methoxyphenyllead triacetate in chloroform–pyridine

2-Phenylcyclohexanone (522 mg, 3.0 mmol) was added to a stirred solution of *p*-methoxyphenyllead triacetate (1.62 g, 3.3 mmol) and pyridine (790 mg, 10 mmol) in chloroform (5  $\text{cm}^3$ ) at 40 °C and the reaction was monitored by GC using column 2. These analyses showed that after 1 h the yield of 2-(*p*-methoxyphenyl)-2-phenylcyclohexanone **14** was 5%. This rose to 21% after 7 h, and after 24 h the yield was 46%. The yield of ketone **14** did not increase after 24 h and all of the analyses indicated that none of the dimer **15** had been produced.

#### Reaction of benzyl methyl ketone potassium enolate with *p*-methoxyphenyllead triacetate

Benzyl methyl ketone potassium enolate (2 mmol) was reacted with *p*-methoxyphenyllead triacetate (1.08 g, 2.2 mmol) under the same conditions as outlined above for the potassium enolate of isobutyrophenone, and the reaction was worked up in the same way. The oily product was fractionated by thin layer chromatography in light petroleum–ethyl acetate (9:1) to give benzyl methyl ketone and three more polar fractions.

The least polar of these crystallised from light petroleum to yield ( $\pm$ )-3,4-diphenylhexane-2,5-dione ( $\pm$ )-**17**, mp 110–113 °C (lit.,<sup>19</sup> 98–100 °C);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.13 (6 H, s,  $2 \times \text{Me}$ ), 3.49 (2 H, s, 3-H and 4-H), 6.8–7.5 (10 H, m,  $10 \times \text{phenyl-H}$ ).

The next fraction in order of polarity crystallised from light petroleum to give *meso*-3,4-diphenylhexane-2,5-dione *meso*-**17**, mp 200–202 °C (lit.,<sup>19</sup> 201–202 °C);  $\delta_{\text{H}}(\text{CDCl}_3)$  1.88 (6 H, s,  $2 \times \text{Me}$ ), 4.62 (2 H, s, 3-H and 4-H) and 7.2–7.5 (10 H, m,  $10 \times \text{phenyl-H}$ ).

The most polar fraction afforded 1-(*p*-methoxyphenyl)-1-phenylpropan-2-one **16** as an oil (Found:  $M^+$ , 240.1149.  $C_{16}H_{16}O_2$  requires  $M^+$ , 240.1149);  $\nu_{\max}(\text{CHCl}_3)/\text{cm}^{-1}$  1710;  $\lambda_{\max}(\text{MeOH})/\text{nm}$  231, 270, 278 and 283 ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$  12 500, 2000, 2100, 2100 and 1800);  $\delta_{\text{H}}(\text{CDCl}_3)$  2.22 (3 H, s, COMe), 3.78 (3 H, s, OMe), 6.86 and 7.15 (4 H, AA'BB', 3-H and 5-H, 2-H and 6-H, respectively) and 7.1–7.4 (5 H, m,  $5 \times \text{phenyl-H}$ ).

Analysis by GC (column 2) of the above crude product

showed the yields to be: benzyl methyl ketone (62%), ( $\pm$ )-dimer **17** (12%), *meso*-dimer **17** (13%) and arylated ketone **16** (5%).

#### Reaction of benzyl methyl ketone with *p*-methoxyphenyllead triacetate in chloroform–pyridine

Benzyl methyl ketone (161 mg, 1.2 mmol) was added to a stirred solution of *p*-methoxyphenyllead triacetate (650 mg, 1.32 mmol) and pyridine (310 mg, 4 mmol) in chloroform (1.5  $\text{cm}^3$ ) at 40 °C. After 24 h the reaction was worked up as for the reaction of isobutyrophenone potassium enolate above and the oily product was analysed by GC (column 2). This showed the presence of the arylated ketone **16** (20% yield), but none of the dimers **17**.

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