

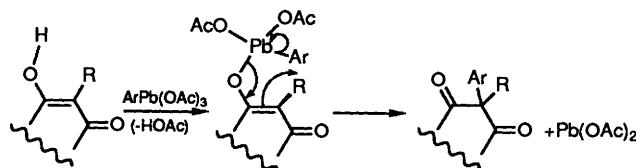
## Reaction of Aryl-lead Triacetates with Sodium Azide in Dimethyl Sulphoxide: A New Route to Aryl Azides

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Aryl-lead triacetates react readily with sodium azide in dimethyl sulphoxide at room temperature to give aryl azides in high yield. By employing aryl-lead triacetates, generated *in situ* from arylboronic acids, this new reaction provides a two-step route from aryl halides to aryl azides.

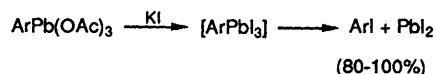
The majority of the reported reactions of aryl-lead triacetates involve the displacement of the triacetoxylead group by a soft carbon nucleophile.<sup>1,2</sup> These reactions, which have been shown in one case not to involve free radicals,<sup>3</sup> are thought to proceed by ligand exchange followed by a collapse of the intermediate as shown in Scheme 1. Under the conditions of these reactions



Scheme 1.

(chloroform, pyridine, 40–60 °C), arylation of nitrogen and oxygen is not generally observed. However, by use of conditions which clearly involve different reaction mechanisms, such reactions can be induced. In trifluoroacetic acid, aryl-lead triacetates undergo a reductive substitution to give the aryl trifluoroacetate and lead(II),<sup>4</sup> while recently it has been shown by Barton and co-workers<sup>5</sup> that aliphatic and aromatic primary and secondary amines undergo N-arylation with these reagents in the presence of a copper catalyst. A reaction which may be mechanistically related to the last reaction is that of aryl-lead triacetates with cuprous cyanide, which we have found<sup>6</sup> to give aryl cyanides in moderate yields (30–40%).

As far as we are aware, the only other non-carbon nucleophile to undergo arylation with aryl-lead triacetates in the absence of a strong acid or a metal catalyst is iodide. As with arenediazonium salts and arylthallium(III) bistrifluoroacetates,<sup>7</sup> aqueous potassium iodide converts these compounds into aryl iodides in high yield,<sup>6,8</sup> and a reaction sequence similar to that proposed for the thallium compounds (see Scheme 2) would

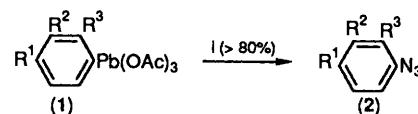


Scheme 2.

appear likely. In view of certain similarities in the behaviour of arenediazonium salts and aryl-lead triacetates, it was of interest to investigate the reaction of the lead compounds with azide ion, which produces aryl azides in high yield with arenediazonium salts.<sup>9</sup>

A <sup>1</sup>H NMR spectroscopic study of the reaction of *p*-methoxyphenyl-lead triacetate (1a) with sodium azide (1.2 mol equiv.) in dry [2H<sub>6</sub>]DMSO showed that *p*-methoxyphenyl azide (2a) was produced at an appreciable rate, with the conversion being complete (90% yield) after 2.5 h at room temperature. The reaction, which gave no other observable

products, proceeded equally well under nitrogen or in the presence of oxygen, while light had no significant effect on the rate of the reaction. Similar <sup>1</sup>H NMR spectroscopic studies were conducted for reactions of the aryl-lead triacetates (1b–g) with sodium azide under the same conditions (see Scheme 3), and in



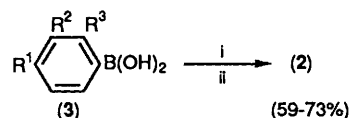
- a; R<sup>1</sup> = MeO, R<sup>2</sup> = R<sup>3</sup> = H
- b; R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = H
- c; R<sup>1</sup> = Me, R<sup>2</sup> = R<sup>3</sup> = H
- d; R<sup>1</sup> = F, R<sup>2</sup> = R<sup>3</sup> = H
- e; R<sup>1</sup> = R<sup>2</sup> = H, R<sup>3</sup> = MeO
- f; R<sup>1</sup> = R<sup>2</sup> = MeO, R<sup>3</sup> = H
- g; R<sup>1</sup> = CF<sub>3</sub>, R<sup>2</sup> = R<sup>3</sup> = H

Scheme 3. Reagents and conditions: i, NaN<sub>3</sub>, DMSO, room temp., 1–3 h.

all cases complete conversion into the corresponding aryl azide, (2b–g) respectively, occurred within 3 h at room temperature. Isolated yields of the azides (2a–e), from preparative scale reactions carried out in the same way, were in the range 75–87%. Since the reaction proceeds readily with aryl-lead triacetates containing both electron-releasing and electron-withdrawing groups, it would appear to be a new general route to aryl azides.

The mechanism of the reaction remains to be determined; however, we have carried out a number of experiments which would appear to eliminate a free radical pathway such as an S<sub>RN1</sub> reaction, a possibility to be considered in view of the potential of azide ion to act as a single electron donor.<sup>10</sup> As noted previously, the rates of reactions of *p*-methoxyphenyl-lead triacetate (1a) with sodium azide carried out with tungsten lamp irradiation or in the dark were not significantly different. Rates and yields were similarly unaffected when this reaction was performed in the presence of 1,1-diphenylethylene, or in an oxygen-saturated atmosphere.

The use of aryl-lead triacetates generated *in situ* from arylboronic acids, as described in the preceding paper,<sup>11</sup> has also been investigated as a more convenient route to aryl azides. The compounds (2a–d) and (2f) were prepared as indicated in Scheme 4 from the corresponding arylboronic acids, (3a–d) and



Scheme 4. Reagents and conditions: i, P6(OAc)<sub>4</sub>, Hg(OAc)<sub>2</sub>, CHCl<sub>3</sub>; ii, NaN<sub>3</sub>, DMSO.

(3f) respectively, in isolated yields of 59–82%. Thus, this provides a convenient two-step procedure for converting an aryl halide into the corresponding azide in good overall yield.

### Experimental

For the general experimental procedures see the preceding paper.<sup>11</sup> <sup>1</sup>H NMR spectroscopic analyses of reactions of the aryl-lead triacetates (1a–g) with sodium azide were carried out in [<sup>2</sup>H<sub>6</sub>]DMSO at a concentration of 0.033M, with a 20% excess of sodium azide, and with dibromomethane as internal reference.

**Preparation of Aryl-lead Triacetates.**—Previously reported methods were used to prepare *p*-methoxyphenyl-lead triacetate (1a),<sup>12</sup> phenyl-lead triacetate (1b),<sup>13</sup> *p*-tolyl-lead triacetate (1c),<sup>14</sup> *p*-fluorophenyl-lead triacetate (1d),<sup>13</sup> *o*-methoxyphenyl-lead triacetate (1e),<sup>13</sup> 3,4-dimethoxyphenyl-lead triacetate (1f),<sup>13</sup> and *p*-trifluoromethylphenyl-lead triacetate (1g).<sup>13</sup>

**Preparation of Arylboronic Acids.**—*p*-Methoxyphenylboronic acid (3a) and 3,4-dimethoxyphenylboronic acid (3f) were obtained from the corresponding aryl-lithium compound as outlined in the preceding paper,<sup>11</sup> while *p*-tolylboronic acid (3c) and *p*-fluorophenylboronic acid (3d) were prepared by the Grignard route.<sup>15</sup>

**Reaction of Aryl-lead Triacetates with Sodium Azide.**—The aryl-lead triacetate (2.0 mmol) and sodium azide (2.4 mmol) were stirred in dry dimethyl sulphoxide (10 ml) in a stoppered flask in the dark at room temperature. After 3 h, ether (200 ml) and water (50 ml) were added and the mixture shaken. The ether extract was washed with water (4 × 50 ml) and saturated brine (50 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated under reduced pressure with a minimum of heating.

The following compounds were synthesised by the above method. (i) *p*-Methoxyphenyl azide (2a) (0.22 g, 75%) was obtained as a crystalline solid, m.p. 35–36 °C (from methanol) (lit.,<sup>16</sup> 34–35 °C);  $\nu_{\max}(\text{CHCl}_3)$  2 120, 1 280, and 1 245 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  3.75 (3 H, s, OCH<sub>3</sub>) and 6.93 (4 H, s, ArH).

(ii) Phenyl azide (2b) (0.19 g, 78%) was obtained as a liquid (lit.,<sup>17</sup> b.p. 44–45 °C at 4 mmHg);  $\nu_{\max}(\text{film})$  2 090, 1 585, 1 485, and 1 285 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  6.8–7.5 (5 H, m, ArH).

(iii) *p*-Tolyl azide (1c) (0.20 g, 75%) was obtained as a liquid (lit.,<sup>17</sup> b.p. 38–40 °C at 1.5 mmHg);  $\nu_{\max}(\text{film})$  2 090, 1 495, and 1 293 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  2.34 (3 H, s, CH<sub>3</sub>), 6.90–7.10, and 7.13–7.40 (4 H, AA'BB', 3-, 5-H and 2-, 6-H respectively).

(iv) *p*-Fluorophenyl azide (1d) (0.21 g, 78%) was obtained as a liquid (lit.,<sup>17</sup> b.p. 56 °C at 9 mmHg);  $\nu_{\max}(\text{film})$  2 090, 1 495, 1 296, and 1 225 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  6.97 and 7.05 (4 H, AA'BB', ArH).

(v) *o*-Methoxyphenyl azide (1e) (0.26 g, 87%) was obtained as a liquid (lit.,<sup>18</sup> b.p. 49 °C at 1 mmHg);  $\nu_{\max}(\text{film})$  2 070, 1 295, and 1 245 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  3.83 (3 H, s, CH<sub>3</sub>) and 6.8–7.27 (4 H, m, ArH).

**Synthesis of Aryl Azides from Aryl-lead Triacetates Generated in situ from Arylboronic Acids.**—The arylboronic acid (2.0 mmol) was added over 15 min to a stirred solution of lead tetraacetate (2.0 mmol) and mercury(II) acetate (0.2 mmol) in chloroform (2 ml) at 40 °C, and the mixture was stirred at 40 °C overnight. The mixture was cooled to room temperature, sodium azide (3.0 mmol) in dry dimethyl sulphoxide (4 ml) was

added, and the mixture was stirred for 3 h in the dark. Chloroform (30 ml) was added and the mixture was washed with water (3 × 10 ml). The chloroform solution was filtered through Celite and evaporated under reduced pressure. The residue was then dissolved in ether (200 ml) and the solution washed with water (3 × 50 ml) and saturated brine (50 ml). The ether solution was dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated at room temperature to yield the aryl azide.

The following compounds were prepared by the above method. (i) *p*-Methoxyphenyl azide (2a) (0.212 g, 71%), identical (IR and NMR spectra) with the above material.

(ii) Phenyl azide (2b) (0.14 g, 59%), identical (IR and NMR spectra) with the above material.

(iii) *p*-Tolyl azide (2c) (0.184 g, 69%), identical (IR and NMR spectra) with the above material.

(iv) *p*-Fluorophenyl azide (2d) (0.20 g, 73%), identical (IR and NMR spectra) with the above material.

(v) 3,4-Dimethoxyphenyl azide (2f) (0.29 g, 82%), m.p. 35–36.5 °C (from methanol) (Found: C, 56.0; H, 5.2; N, 23.4. C<sub>8</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub> requires C, 56.3; H, 5.1; N, 23.5%),  $\nu_{\max}(\text{KBr})$  2 120, 1 515, 1 246, and 1 025 cm<sup>-1</sup>;  $\delta_{\text{H}}(\text{CDCl}_3)$  3.86 (3 H, s, OCH<sub>3</sub>), 3.87 (3 H, s, OCH<sub>3</sub>), 6.53 (1 H, d, *J*<sub>2,6</sub> 2.5 Hz, 2-H), 6.61 (1 H, dd, *J*<sub>5,6</sub> 8.8 Hz, *J*<sub>2,6</sub> 2.5 Hz, 6-H), and 6.84 (1 H, d, *J*<sub>5,6</sub> 8.8 Hz, 5-H).

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### References

- D. H. R. Barton, D. M. X. Donnelly, J.-P. Finet, and P. J. Guiry, *Tetrahedron Lett.*, 1989, **30**, 1539.
- D. J. Ackland and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2695 and references therein.
- D. H. R. Barton, J.-P. Finet, C. Giannotti, and F. Halley, *J. Chem. Soc., Perkin Trans. 1*, 1987, 241.
- H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Tetrahedron Lett.*, 1974, 853.
- D. H. R. Barton, D. M. X. Donnelly, J.-P. Finet, and P. J. Guiry, *Tetrahedron Lett.*, 1989, **30**, 1377.
- H. R. Crawford and J. T. Pinhey, unpublished results.
- A. McKillop, J. S. Fowler, M. I. Zelesko, J. D. Hunt, E. C. Taylor, and G. McGillivray, *Tetrahedron Lett.*, 1969, 2427.
- V. I. Lodochnikova, E. M. Panov, and K. A. Kocheshkov, *Zh. Obshch. Khim.*, 1964, **34**, 946 (*Chem. Abstr.*, 1964, **60**, 15906).
- M. E. C. Biffin, J. Miller, and D. B. Paul in 'The Chemistry of the Azido Group,' ed. S. Patai, John Wiley, London, 1971, p. 156.
- N. Kornblum in 'The Chemistry of the Functional Groups, Supplement F,' ed. S. Patai, John Wiley, New York, 1982, p. 361.
- J. Morgan and J. T. Pinhey, *J. Chem. Soc., Perkin Trans. 1*, preceding paper.
- R. P. Kozyrod and J. T. Pinhey, *Org. Synth.*, 1984, **62**, 24.
- R. P. Kozyrod, J. Morgan, and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 1147.
- H. C. Bell, J. R. Kalman, J. T. Pinhey, and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1521.
- F. R. Bean and J. R. Johnson, *J. Am. Chem. Soc.*, 1932, **54**, 4415.
- E. Lieber, T. S. Chao, and C. N. R. Rao, *J. Org. Chem.*, 1957, **22**, 654.
- J. E. Leffler and R. D. Temple, *J. Am. Chem. Soc.*, 1967, **89**, 5235.
- J. E. Leffler and H. E. Gibson, *J. Am. Chem. Soc.*, 1967, **89**, 4117.

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