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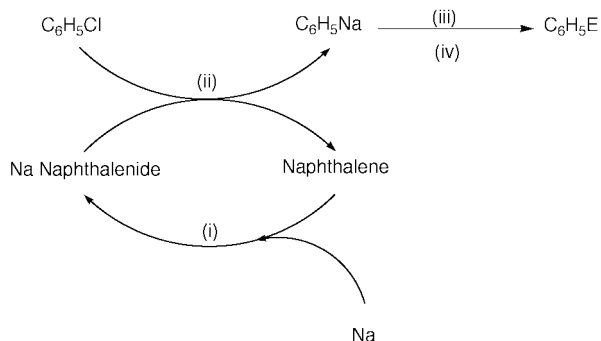
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Received (in Cambridge, UK) 10th August 1999, Accepted 31st August 1999

2-Methyl-1-phenylpropan-1-ol and phenyltrimethylsilane were prepared in yields >85%, using naphthalene catalysed sodium reactions, whereby phenylsodium, prepared from the reaction of chlorobenzene, sodium powder and naphthalene (5%), was quenched with isobutyraldehyde or chlorotrimethylsilane respectively.

The use of alkali metal arene radical anion complexes,  $\text{ArH}^-\text{M}^+$ , as soluble sources of metal in the formation of organoalkali metal species from organic halides is well established with early work focusing on the use of lithium naphthalenide.<sup>1</sup> Many radical anion derivatives of lithium have been prepared in recent years. The 4,4'-di-*tert*-butylbiphenyl (DBB) complex is particularly noteworthy, in that while it acts as a source of lithium, removal of the DBB by-product is facilitated by its low volatility.<sup>2</sup> Other approaches to overcoming the objection of having solutions of the target organolithium species loaded with the arene by-product are the use of a catalytic amount of arene,<sup>3</sup> macromolecular supported lithium naphthalenide complexes<sup>4</sup> and polymer supported arene-catalysed reactions.<sup>5</sup> Each of these approaches prove quite successful in the generation of lithium complexes from a range of organic compounds including: halogenated compounds, allylic and benzylic alcohols, or their silylated derivatives.<sup>3-7</sup>

Sodium arene radical anion complexes have received much less attention than the lithium counterparts although they do afford organosodium complexes in relatively high yields.<sup>8</sup> As with their lithium counterparts, the solutions of these reagents are loaded with the arene by-product. We have developed a method for the preparation of sodium reagents using polymer supported sodium naphthalenide, generating high yields of the desired sodium complexes, which are readily removed from the recyclable polymer by-product by filtration.<sup>4,7</sup> A drawback of this method is that the polymer supported sodium complex is quite unstable, resulting in reduced yields, limiting the value of the polymer as a useful reagent for the generation of sodium complexes. The work presented here follows from the successes of the above processes in developing a technique for the preparation of sodium complexes *via* arene-catalysed reactions (Scheme 1).



**Scheme 1** Reagents and conditions: (i)  $-78^\circ\text{C}$ , THF, 20 min, (ii)  $-78^\circ\text{C}$ , 1 h, (iii)  $\text{E}^+ = \text{H}_2\text{O}$ ,  $\text{Pr}^i\text{CHO}$  or  $\text{ClSiMe}_3$ ,  $-78$  to  $25^\circ\text{C}$ , 3 h, (iv)  $\text{H}_2\text{O}$ .

**Table 1** Yields of phenylsodium from the reaction of sodium powder with catalytic amounts of naphthalene at  $-78^\circ\text{C}$  for 1 h, and the reaction with an electrophile,  $\text{E}^+$ <sup>a</sup>

Arene (%)	$\text{E}^+$	Yield (%) <sup>b</sup>	Yield (%) <sup>c</sup>
10	$\text{H}_2\text{O}$	98	90
5	$\text{H}_2\text{O}$	99	90
2	$\text{H}_2\text{O}$	90	85 <sup>d</sup>
1	$\text{H}_2\text{O}$	90	85 <sup>d</sup>
5	$\text{Pr}^i\text{CHO}$	95	85
5	$\text{ClSiMe}_3$	95	85

<sup>a</sup> Average of three runs. <sup>b</sup> Yield of phenylsodium, established by quenching an aliquot with 0.1 M HCl, back-titrating with 0.1 M NaOH, average of three titrations. <sup>c</sup> Isolated yield of the quenched product. <sup>d</sup> Due to the small scale of reaction, percentages lower than 5% were difficult to perform accurately. Therefore the average of two runs is given.

Prior to the investigation of the reaction of sodium metal with catalytic amounts of arene, an investigation into the optimum reaction conditions was carried out. The variables considered were the type of arene (naphthalene, biphenyl and 4,4'-di-*tert*-butylbiphenyl), reaction temperatures ( $-78$ ,  $-30$  and  $0^\circ\text{C}$ ) and the reaction time (0.5, 1, 2 and 4 hours) for step (ii) in Scheme 1. The results of the trial indicated the best conditions were sodium with naphthalene at  $-78^\circ\text{C}$  for 1 hour.<sup>9</sup> Following this, an investigation into the use of sodium metal with varying percentages of arene was carried out.<sup>9</sup> The sodium metal is not completely consumed in these reactions; particle size of the metal is indeed known to be a controlling factor in the formation of organoalkali metal compounds.<sup>10</sup> Hence the use of sodium powder (<0.1 mm particle size) was investigated. Sodium powder with catalytic amounts of naphthalene was tested for the ability to form phenylsodium (Table 1).<sup>†</sup> Phenylsodium was quenched with different electrophiles;  $\text{H}_2\text{O}$ ,  $\text{ClSiMe}_3$  and  $\text{Pr}^i\text{CHO}$ , affording the desired compounds, benzene, phenyltrimethylsilane and 2-methyl-1-phenylpropan-1-ol respectively, in high yields. Noteworthy is the absence of other by-products often generated in these reactions. Early studies on the reaction of sodium naphthalenide with phenylhalides, resulted in the formation of biphenyl and terphenyls, derived from the intermediate anion radical, as well as the expected product, benzene.<sup>11</sup> The use of the arene in only catalytic quantities has eliminated the generation of these higher arenes.

The generation of the organosodium reagent and subsequent formation of the quenched compounds can be followed by a simple colour change. Initially the reaction mixture shows the dark green colour of the sodium arene; after the addition of the chlorobenzene the colour gradually changes to that of the organosodium reagent, dark red. The quenching of the organosodium reagent causes the disappearance of the colour of the organosodium reagent and the formation of the final products (usually affording a clear-pale yellow solution). Thus it is not necessary to follow the reaction through spectroscopic or chromatographic means.

We have thus developed a more practical method for generating organosodium complexes: the preparation of the sodium

radical anion complex is avoided, the reaction is clean and easy to follow through colour changes, and the work up is simplified, with reduced quantities of arene by-products for removal.

We thank M. L. Williams for helpful discussions and Griffith University for support of this project.

## Notes and references

† In a typical experiment: to a cooled ( $-78^{\circ}\text{C}$ ) green suspension of sodium powder ‡ (0.27 g, 11.7 mmol) and naphthalene (0.075 g, 0.58 mmol) in THF (60 ml) was slowly added a solution of chlorobenzene (1.05 g, 9.36 mmol) in THF (40 ml) and the resulting deep red mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h. The excess of sodium powder was filtered, at  $-78^{\circ}\text{C}$ , affording the deep red-purple organosodium reagent, phenylsodium. The activity of the solution was determined by titration. The remaining solution of phenylsodium was then quenched by addition of the desired electrophile,  $\text{H}_2\text{O}$ ,  $\text{ClSiMe}_3$ , or  $\text{Pr}^t\text{CHO}$ . The resulting solutions were subsequently hydrolysed, extracted into diethyl ether and/or hexane, filtered, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent was removed *in vacuo* affording benzene, phenyltrimethylsilane and 2-methyl-1-phenylpropan-1-ol respectively (85–90%, purity checked by  $^1\text{H}$  NMR spectroscopy).

‡ Sodium powder was obtained as a slurry in toluene (30 wt% <0.1 mm particle size). It was filtered and dried *in vacuo* and stored under argon, prior to use.

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Communication 9/07037K