## A Simple, High-yielding Preparation of Sodium Diisopropylamide and other Sodium Dialkylamides

## Donald Barr, <sup>a</sup> Andrea J. Dawson<sup>b</sup> and Basil J. Wakefield\*<sup>b</sup>

<sup>a</sup> The Associated Octel Company Ltd., PO Box 17, Oil Sites Road, Ellesmere Port, South Wirral L65 4HF, UK <sup>b</sup> Department of Chemistry and Applied Chemistry, Cockcroft Building, University of Salford, Salford M5 4WT, UK

Sodium dialkylamides are prepared by the reaction of sodium dispersion with secondary amines in the presence of isoprene.

Lithium diisopropylamide (LDA) is a very important nonnucleophilic base<sup>1</sup> and potassium diisopropylamide (KDA) has proved a useful 'superbase'.<sup>2</sup> Surprisingly, little work has been reported on sodium diisopropylamide (NDA).<sup>3</sup> The most commonly-used route to these substances starts from butyllithium (Scheme 1). This route is efficient, but expensive. Moreover, the reagents are usually used without purification, and often contain lithium as well as the other alkali-metal.

An alternative route to LDA is the reaction of lithium with diisopropylamine with the aid of an electron carrier such as styrene or isoprene.<sup>4</sup> One report on the reaction of sodium, diisopropylamine and isoprene, described the formation of myrcene (*ca.* 10% yield) but not of NDA.<sup>5</sup>

We now report that under the right conditions, NDA may be prepared in high yield as an isolable solid, by the reaction of sodium with diisopropylamine in the presence of isoprene. In a typical procedure, a Schlenk tube was purged with dry, oxygen-free nitrogen and charged with cyclohexane (30 ml), diisopropylamine (140 mmol) and isoprene (140 mmol). The mixture was stirred under nitrogen at room temperature, and sodium dispersion (average particle size 40 µm; ca. 30% w/w in n-octane; 100 mmol) was added. The mixture was stirred at ambient tmperature until no grey tinge of metallic sodium was visible and the suspension was pale beige in colour; approximately 5 h was required. The mixture was filtered under nitrogen and dried in vacuo. The product (98% yield) was a white, infusible (m.p. >300 °C) solid, highly pyrophoric on exposure to air. (Found C, 59.2; H, 11.3; N, 11.1; Na, 18.7; C<sub>6</sub>H<sub>14</sub>N Na requires C, 58.5; H, 11.5; N, 11.4%; Na, 18.65%). It was appreciably soluble in tetrahydrofuran (THF) in which it is presumably present as an associated THF complex. The NMR spectra of the solute in  $[{}^{2}H_{8}]$ THF were measured:  $\delta_{H}$ 1.015 (12H, d, J 6 Hz), 2.90 (2H, septet, J 6 Hz);  $\delta_{\rm C}$ 25.0, 47.0.



Scheme 1 Reagents: i, Bu<sup>t</sup>ONa or other sodium tert-alkoxide; ii, Bu<sup>t</sup>OK or other potassium tert-alkoxide

GC-MS analysis of the filtrate from the reaction mixture showed several products, including a trace of a compound corresponding to a dimer of isoprene, but not myrcene, though myrcene was detected in the products from some other experiments.

Reaction took place with sodium wire in place of dispersion, but it was slower and yields were much lower.

Our procedure is suitable for preparing other sodium dialkylamides; we have prepared sodium dicyclohexylamide (95%) and sodium dibenzylamide (80%).

Preliminary results indicate that the reactivity of NDA, prepared by our method, is high (*cf.* ref. 3). For example, diphenylmethane (200 mmol) was added to a stirred mixture of NDA (200 mmol), THF (9 ml) and cyclohexane (25 ml). The mixture was stirred at room temperature for 30 min, and then poured on to solid carbon dioxide. Conventional work-up gave diphenylacetic acid in *ca.* 80% yield. Under similar conditions LDA gave 15% yield.

We thank the Associated Octel Company for financial support. The results described in this communication are the subject of a patent application.

Received, 1st August 1991; Com. 1/04009J

## References

- B. J. Wakefield, Organolithium Methods, Academic Press, London, 1988; Dictionary of Organometallic Compounds, ed. J. E. Macintyre, Chapman and Hall, London, 5th suppl., 1989; L. Brandsma and H. Verkruijsse, Preparative Polar Organometallic Chemistry, Springer-Verlag, Berlin, 1987, vol. 1.
- J. Hartmann and M. Schlosser, *Helv. Chim. Acta*, 1976, **59**, 453; S. Raucher and G. A. Koolpe, *J. Org. Chem.*, 1978, **43**, 3794; M. Schlosser and S. Strunk, *Tetrahedron Lett.*, 1984, **22**, 741; P. A. A. Klusener, L. Tip and L. Brandsma, *Tetrahedron*, 1991, **47**, 2041.
- 3 L. Lochmann, J. Organomet. Chem., 1979, 179, 123; 1989, 364, 281 and 1989, 376, 1.
- 4 M. T. Reetz and W. F. Maier, *Liebigs Ann. Chem.*, 1980, 1471; F. Gaudemar-Bardone and M. Gaudemar, *Synthesis*, 1979, 469; R. C. Morrison, R. W. Hall, and T. L. Rathman, US Pat., 4595779, 1986 (*Chem. Abs.*, 1986, **105**, 78512).
- 5 K. Tanabe, A. Agata, T. Katagiri and J. Tanaka, *Synthesis*, 1977, 307.