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n-BUTYLSODIUM: THE PREPARATION, PROPERTIES AND NMR SPECTRA OF A HYDROCARBON- AND TETRAHYDROFURAN-SOLUBLE REAGENT

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Summary

n-Butylsodium (BuNa), synthesized via n-butyllithium and sodium t-butoxide by metal exchange and precipitation, is readily soluble in hexane after adding solvating ligands such as *N,N,N',N'*-tetramethylenediamine (TMEDA) or tetrahydrofuran (THF). The resulting solutions can be used for homogenous metallation of weak hydrocarbon acids; crystalline products suitable for X-ray analysis often are obtained. High field NMR studies of BuNa in THF suggest only one form to be present at low temperatures.

Well-defined organometallic compounds of the heavier alkali metals have found relatively limited synthetic use as compared with their lithium counterparts [1—3]. The availability and tractability of hydrocarbon-soluble n-butyllithium (BuLi) on the one hand, and the mixed-metal LIKOR-type reagents on the other [3], are responsible for their widespread application. In contrast, the alkyl derivatives of the heavier alkali metals are reported to be insoluble in nonpolar solvents [1,4] and heterogenous conditions [3] must be employed. For example, n-butylsodium (BuNa) evidently forms an insoluble mixed aggregate with NaCl if prepared from n-butyl chloride and sodium metal. Efforts to solubilize such systems [4] led to the conclusion that the ligands like TMEDA have a "dispersing rather than solubilizing effect" [4b]. The superior metallating qualities of these systems were attributed to catalysis by the ligand.

Hydrocarbon-soluble reagents like sodium t-pentoxide [5], sodium bis(trimethylsilyl)amide [6] or complexed compounds like the phenylalkalimagnesium 2-ethoxide reagents [7] are weaker bases, and hence are of more limited use.

Our search for a convenient synthetic route to crystalline organosodium compounds [2], has led to the development of a soluble sodium reagent which can

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be obtained easily by adding a donating ligand like TMEDA to a hexane dispersion of BuNa. The latter is synthesized from BuLi by the well known metal—metal exchange reaction [1d,3,8].

$$\mathrm{BuLi + NaO^tBu \rightarrow BuNa + LiO^tBu}$$

Since BuNa is insoluble in hexane, it can be separated easily from the soluble lithium alcoholate by filtration and is obtained in reasonably pure condition. When a donating ligand like TMEDA is added to a BuNa suspension in hexane, a clear solution of high metallating capability forms immediately. Other donors, e.g. *N,N,N',N'*-tetramethyl-1,2-diaminocyclohexane, which coordinate sodium more effectively [4a], show the same behavior. BuNa solutions can be obtained in concentrations of 1—4 *M* or more, by adjusting the TMEDA/hexane ratio employed.

The metallating properties of the reagent are quite similar to those of BuLi/TMEDA in hexane. At −78°C a white precipitate (probably a $(\text{n-BuNa})_n$-$(\text{TMEDA})_m$ complex) forms, which redissolves at higher temperatures. Precipitation also precludes the determination of the degree of aggregation by cryoscopy in THF [9]. At 25°C in hexane the exothermic metallation of TMEDA begins after only a few minutes. The integrity of the BuNa/TMEDA reagent below 0°C was shown by reaction with triphenylsilyl chloride; only n-butyltriphenylsilane and unreacted TMEDA were found by NMR analysis.

The BuNa/TMEDA/hexane reagent readily deprotonates weak organic acids, and often leads to crystalline rather than powdery products [10]. Thus yellow needles of $[\text{benzylsodium}\cdot\text{TMEDA}]_4$ formed after addition of an equimolar amount of the BuNa reagent to a solution of toluene in hexane. (The composition was determined by quenching with CD_3OD and NMR analysis, as well as by X-ray analysis [11].)

Addition of tetrahydrofuran (THF) to the BuNa precipitate also leads to clear solutions which are fairly stable at dry ice temperatures, but solvent attack occurs above about −40°C. The high field part of the 400 MHz ^{1}H NMR spectra of BuNa and of BuLi in THF-d_8 at −75°C are compared in Fig. 1. The chemical shifts observed are nearly the same, but BuNa shows no evidence for the equilibrating dimers and tetramers found for BuLi [12]. The terminal CH_2-metal chemical shift (−1.09 ppm) and ^3J(H—C(1)—C(2)—H)-coupling constant (8.8 Hz) closely parallel the −75°C BuLi data (dimer: −1.17 ppm/8.8 Hz; tetramer −1.05 ppm/9.2 Hz; at 0°C coalescence gives a triplet: −1.11 ppm/8.5 Hz) [12b]. In contrast to the spectra of BuLi, the α-CH_2 resonance of BuNa is not separated into several signals; the β- and γ-CH_2-methylene and methyl resonances also are not split (besides the HH coupling). This simplification of the complex AA'XX' splitting seen in BuLi [12b] to a triplet indicates magnetic equivalence of the BuNa α-CH_2 protons. A plausible explanation might be facile inversion at the α-carbon, suggesting a weaker α-CH_2—Na interaction than that in BuLi. Either only one modification of BuNa is present under these conditions or a rapid equilibrium between several forms far from coalescence takes place even at −75°C (the coalescence temperature of the terminal $LiCH_2$ signal for BuLi is above −40°C at 400 MHz [12b].

The ^{13}C chemical shifts of BuNa in THF-d_8 at −95°C at 100 MHz (δ in ppm 9.8, α-CH_2; 14.8, δ-CH_3; 35.9, 37.5, other CH_2's) are quite similar to those of

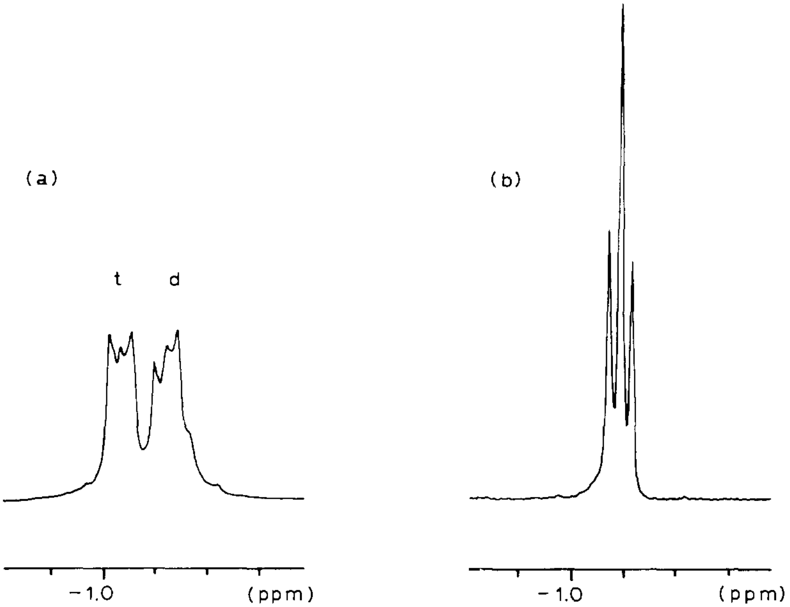

Fig. 1. High field region of the 400 MHz ^{1}H NMR spectra of BuLi (a) and of BuNa (b) in THF-d_8 at −75°C; t = tetramer, d = dimer.

BuLi, but not the complex broadening and separation of signals which characterize the latter [12a]. Only at −121°C is a coalescence-like broadening of the α-CH_2 ^{13}C signal observed, but this may be due to the impending resolution of ^{23}Na—^{13}C coupling. The 106 MHz ^{23}Na NMR spectra of BuNa in THF-d_8 at temperatures below −75°C showed only one broad, intense signal (half height width 1030 Hz) at 19.6 ppm (relative to 1 *M* aqueous NaCl).

In preliminary experiments, similar behaviour was found for BuK when synthesized by the same metal—metal exchange-precipitation procedure. The BuK/TMEDA solutions in hexane metallate various hydrocarbons even more easily, but also decompose more readily. In addition, the ternary solutions of BuLi, TMEDA and KO^{t}Bu or NaO^{t}Bu in hexane are effective metallating agents [13].

Experimental

BuNa/TMEDA/hexane. n-Butylsodium was prepared under argon as described in ref. 14 but in a closed filtration vessel with glass frit. To a suspension of 9.5 g (0.10 mol) NaO^{t}Bu (obtained from refluxing HO^{t}Bu and sodium in hexane; the resulting crystalline NaO^{t}Bu was used after washing without further purification) in 50 ml hexane, 80 ml of 1.6 *M* BuLi in hexane (EGA) was added with stirring at 0°C. The powdery BuNa (6.8 g, 85 mmol) precipitate was washed thoroughly several times with hexane, and then suspended in 40 ml of the same solvent above the frit. Addition of up to 40 ml TMEDA below 0°C leads to a colourless or slightly yellow solution which can be used directly for homogeneous metallations. Addition of THF to the precipitate at −78°C also leads to clear solutions.

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