

Preliminary communication

n-BUTYLPOTASSIUM: PREPARATION, SYNTHETIC USE AND NMR PROPERTIES IN HEXANE AND TETRAHYDROFURAN SOLUTION

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Summary

Precipitated n-butympotassium (BuK), prepared by metal—metal exchange between n-butyllithium and potassium-t-amylate, dissolves in hexane after addition of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The homogeneous solution is an effective metallation reagent. High-field NMR studies in THF-*d*₈ solution at low temperatures, considered alongside analogous data for alkylsodium derivatives, indicate that like the latter, BuK is monomeric under these conditions.

We have extended our study of the preparation and the properties of n-butylna (BuNa) [1] to n-butympotassium (BuK). Earlier investigations indicated that both alkylpotassium and alkylsodium species are insoluble in hydrocarbons [2–6]. In contrast, we achieved homogeneous solutions of BuNa in hexane by addition of donor ligands like *N,N,N',N'*-tetramethylethylenediamine (TMEDA). Thus, BuNa now provides an alternative to butyllithium (BuLi) or mixed n-BuLi/ROK ("LIKOR"-type) reagents [3]. BuK can be obtained via similar metal—metal exchange (eq. 1) [4–6] in hexane at –50°C and with ROK = potassium-t-amylate (or better potassium-(–)-(1R)-menthoxide [6]). We now report our experience with this compound.



When prepared via eq. 1, BuK is insoluble in hexane and, like BuNa [1], can be separated and washed easily by filtration in a closed vessel equipped with a glass frit. Addition of a donating ligand such as TMEDA to a BuK/hexane suspension at –50°C gives a clear solution of high metallating power. Thus

toluene is rapidly deprotonated (<1 min at -30°C), yielding red crystals, and subsequent treatment with CD_3OD reveals the crystal composition to be $(\text{benzylpotassium} \cdot \text{TMEDA} \cdot 0.5 \text{ toluene})_x$. As TMEDA is attacked faster by BuK than by BuNa [7], temperatures below ca. -70°C must be maintained during storage, even then, a brown precipitate forms after several days.

The BuK/TMEDA in hexane was also used to metallate benzylic and bi-phenyl-substituted carbon atoms in cross-linked polystyrene derivatives, and this gave deeply colored polymetallated polymers [8a]. The concentration of the polystyrene-bound carbanionic centres can be determined by direct titration [8b] or by microanalysis after quenching with an electrophilic reagent.

During dissolution of the precipitated BuK in octadeutero-tetrahydrofuran ($\text{THF-}d_8$) at -100°C (for the NMR experiments), partial attack on the solvent occurred, to give small amounts of $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{D}$. However, this reaction does not proceed to any further significant extent on warming to -60°C . However, at -30°C BuK is completely deuterated by $\text{THF-}d_8$. A 1/1-mixture of both solid BuK and ROK brings about immediate dedeuteration of $\text{THF-}d_8$ when dissolved in it at -100°C ; only monodeuterobutane was detected in both the ^1H and ^{13}C NMR spectrum at that temperature.

The reaction of BuK with THF precludes determination of the molecular weight by cryoscopy [9]; such determination was also prevented for BuNa by solubility problems at -108°C [1]. However, we found cryoscopically that the degree of aggregation of n-octylsodium in THF is $n = 0.9 \pm 0.1$ (formal concentration $c = 50.7 \text{ mm}$), i.e. only a pure monomer is present. By analogy, n-BuNa also must be a monomer in THF-solution which accounts for the NMR observations [1].

The 400 MHz ^1H NMR spectrum of BuK in $\text{THF-}d_8$ at -60°C is quite similar to that of BuNa [1]. The chemical shifts and coupling constants are shown in Table 1.

TABLE 1

 ^1H NMR CHEMICAL SHIFTS (ppm) OF BuM, M = Li, Na, K IN $\text{THF-}d_8$

(Multiplicities and coupling constants (in Hz) when measurable are given in parentheses)

| | H(1) | H(2) | H(3) | CH_3 | Temperature ($^{\circ}\text{C}$) | Literature |
|-------------------|---------------------|------------------------|------------------------|------------------|------------------------------------|-------------|
| n-BuK | -1.17 (t; 7.9) | 1.54 (tt; 7.9, 7.1) | 1.27 (qt; 7.1, 7.1) | 0.82 (t; 7.1) | -60 | this work |
| n-BuNa | -1.09 (t; 8.8) | 1.51 (tt; 8.8, 7.3) | 1.17 (qt; 7.3, 7.3) | 0.81 (t; 7.3) | -75 | [1] |
| n-BuLi (tetramer) | -1.03 (9.2) [15] | 1.38 | 1.17 | 0.81 | -75 | [10b], [12] |
| n-BuLi (dimer) | -1.14 (8.8) [15] | 1.44 | 1.18 | 0.81 | -75 | [10b], [12] |

As was the case for BuNa, no evidence for the equilibrating dimers and tetramers found for n-BuLi [10] can be detected in the BuK NMR spectra: the α -, β -, γ - and CH_3 -protons appear as distinct sets of signals and show no

TABLE 2

¹³C NMR CHEMICAL SHIFTS (ppm) OF n-BuM, M = Li, Na, K IN THF-*d*₈

| | C(1) | C(2) | C(3) | CH ₃ | Temperature (°C) | Literature |
|-------------------|------|------|------|-----------------|------------------|-------------|
| n-BuK | 21.4 | 36.9 | 39.4 | 15.0 | -91 | this work |
| n-BuNa | 9.8 | 35.9 | 37.5 | 14.9 | -95 | [1] |
| n-BuLi (tetramer) | 10.5 | 33.9 | 35.4 | 14.7 | -96 | [10a], [11] |
| n-BuLi (dimer) | 12.4 | | | | | [10a], [14] |

splitting apart from intramolecular H-H coupling. Table 2 shows the ¹³C chemical shifts for BuK, BuNa and the n-BuLi tetramer.

As in the ¹H NMR spectrum the observation of one set of signals indicates the presence of only one form of n-BuK, and we take this to be the monomer. Whereas in BuNa the chemical shift of the α-carbon is slightly upfield as compared to that of the n-BuLi tetramer, a relatively strong downfield shift is observed for n-BuK. A small chemical shift difference between BuLi and BuNa and the correspondingly large difference between BuNa and BuK also has been described for the 5,5-dimethyl-2-hexenyl-alkali metal derivatives [13]: (α-C) 31.0 (Li), 35.7 (Na), 45.0 (K) ppm. The downfield shift of the α-carbon in BuK can be attributed to the more pronounced *sp*²-character of the anionic centre due to the larger ionic radius of K⁺ over those of Na⁺ and Li⁺. A little covalent character (10–20%) may contribute to the bonding in BuLi, and in BuNa.

Experimental

NMR spectra were recorded on a JEOL GX400 spectrometer (¹H: 400 MHz; ¹³C: 100.5 MHz). The chemical shifts are relatively to TMS and are based on the solvent signals: residual proton in THF-*d*₈ δ 3.85 ppm; α-carbon in THF-*d*₈ δ 67.4 ppm.

BuK/TMEDA. To 78.0 ml of a potassium-*t*-amylate solution in hexane (obtained from refluxing 0.15 mol *t*-amyl alcohol and 0.15 mol potassium in hexane), 120.0 ml (0.20 mol) of n-BuLi in hexane (1.6 m) was added dropwise with stirring at -50°C (dry-ice cooled filtration vessel with glass frit in an argon counter current [9]). BuK separated as a white powder. After 2 h at -50°C the mixture was stirred for 30 min at 0°C and then filtered. The powdery BuK was washed thoroughly with cooled hexane and suspended in 120 ml of hexane at -50°C. Addition of 70 ml (0.47 mol) TMEDA yielded a clear solution, which was used directly for metallation reactions. The temperature must be kept below ca. -40°C to prevent metallation of TMEDA. THF or THF-*d*₈ can also be used to dissolve the BuK precipitate (see text), but the temperature must be kept below -90°C.

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References and Notes

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- 14 Due to the high concentration of the ^{13}C NMR sample the BuLi dimer—tetramer equilibrium is strongly shifted to the tetramer side. The small signals of the dimer could not be distinguished unambiguously from impurity peaks. The α -carbon of the n-BuLi dimer in a ^{13}C enriched sample resonates at 12.4 ppm [10a].
- 15 Coupling constants determined from partly deuterated species, cf. lit. 10b.