Journal of Organometallic Chemistry, 393 (1990) C40–C42
Elsevier Sequoia S.A., Lausanne
JOM 21145PC

Preliminary communication

Two new strongly basic systems prepared by activation of n-butyllithium with organopotassium compounds

Frederick Scott, Augustine M. Hamese and Helgard G. Raubenheimer

Department of Chemistry and Biochemistry, Rand Afrikaans University, P.O. Box 524, Johannesburg 2000 (Republic of South Africa)

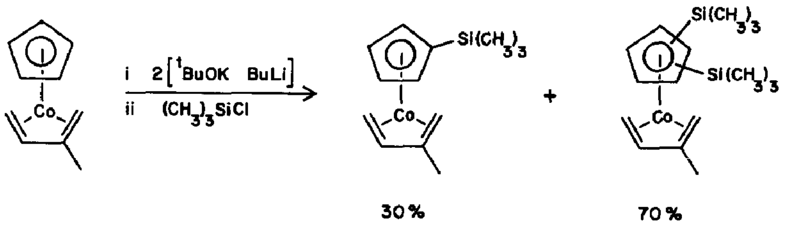
(Received May 30th, 1990)

Abstract

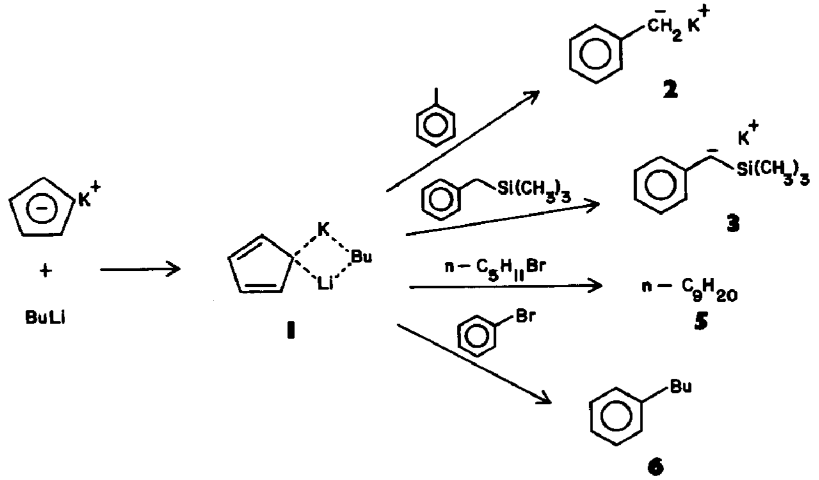
Treatment of n-butyllithium with potassium cyclopentadienide or potassium naphthalenide yields a strongly basic system. The activation of n-butyllithium with potassium cyclopentadienide also enhances its reactivity in nucleophilic substitution reactions.

The combination of alkyllithium compounds with potassium t-alkoxides in non-polar [1–3] or polar solvents [4] as well as in combination with *N,N,N,',N'*-tetramethylethylene diamine (TMEDA) [5] produces strongly basic reagents that are useful metallating agents in organic synthesis. The strong basicity of these mixtures, which are capable of deprotonating weak organic acids with pK_a values of up to 50, can be ascribed to the formation of organopotassium compounds (by transmetallation) [6] or aggregated potassium compounds (adduct formation) [4,7]. These extremely strong bases have previously also been used to produce di-, tri- and poly-anions of organic [3,8] and organometallic compounds, [9] (i.e. Scheme 1) [10].

The exchange between lithium and potassium is, however, not limited to the reaction between alkyllithium compounds and potassium t-alkoxides. This has been demonstrated in the reactions of lithium amides [11,12,13] and lithium enolates [14]



Scheme 1



Scheme 2

with potassium alkoxides, which give the corresponding potassium amides and potassium enolates. In a continuation of a study of deprotonation of organometallic compounds [15] we thought it of interest to attempt to generate strongly basic reagents free of alkoxide ions or complexing ligands. Our preliminary results showed that potassium cyclopentadienide functions as a convenient alternative source of potassium ions in an exchange or addition reaction with n-butyllithium (BuLi). An unidentified product, termed adduct **1**, which is capable of deprotonating weak CH acids, is formed (Scheme 2).

When a diethyl ether solution or a tetrahydrofuran (THF) suspension of potassium cyclopentadienide was treated with a molar equivalent of BuLi at room temperature in the presence of toluene, an immediate colour change to orange-red indicated the formation of the benzyl anion **2**. Quenching with carbon dioxide or chlorotrimethylsilane produced phenyl acetic acid and benzyltrimethyl silane in isolated yields of 55% and 65%, respectively. Deprotonation of toluene proceded more slowly in ether solution than in THF. No deprotonation of toluene occurred when the reaction was performed in hexane, which suggested that there was inhbition of the lithium–potassium exchange or adduct formation in this non-polar solvent.

The new basic potassium cyclopentadienide–BuLi reagent may be used in reactions with substrates which are sensitive to the alkoxide ion. The α-trimethylsilyl benzyl anion **3** [16] yielded bis(trimethylsilyl)phenyl methane, **4** (45%), when the cold reaction mixture was treated with an excess of chlorotrimethyl silane. The low yield of **4** when THF is used as solvent is probably due to slow deprotonation and cleavage of THF by the anion **3**. In diethyl ether the cation exchange occurs too slowly to be of any synthetic value, yielding **4** in only 15% yield after work-up with chlorotrimethyl silane.

The identity of the reactive organometallic reactant, represented stoichiometrically as complex **1**, is unknown. It also shows a markedly greater reactivity than BuLi in nucleophilic substitution reactions [17]. Thus coupling of **1** with bromopentane occurred when a hexane mixture of BuLi and bromopentane was treated with an ethereal solution of potassium cyclopentadienide. n-Nonane, **5**, was formed in

60% yield, and in a similar experiment with bromobenzene, butylbenzene, **6**, was produced in 50% yield.

Activation of BuLi was also achieved by treatment with a THF solution of potassium naphthalenide. A strongly basic reagent was again produced. In the presence of toluene the red benzyl anion **2** was formed and could be trapped with CO_2 or chlorotrimethylsilane. However, the yields of phenyl acetic acid (30%) and benzyltrimethyl silane (37%) were lower than before, due to the competitive deprotonation of the THF solvent and of the naphthalene used as alkali metal carrier. Our observations recall the historically important results of Bryce-Smith who described the deprotonation of benzene by alkyllithium compounds in combination with potassium–sodium alloy [18].

Activation of alkyl lithium compounds with potassium compounds other than potassium alkoxides may be used to deprotonate organic and organometallic acids that are destroyed by alkoxide ions. Alternatively, the new strong bases are useful reagents in deprotonation reactions in which strongly coordinating ligands such as TMEDA [19], which activate BuLi but also coordinate to other metals present [20], have to be avoided. We plan to see whether the lower reactivity of the potassium cyclopentadienide–BuLi mixture will allow selective deprotonation similar to that observed for the less active diphenyl magnesium–alkali metal alkoxide systems [21].

References

1 L. Lochmann, J. Pospisil and D. Lim, Tetr. Lett., (1966) 257; L. Lochmann and J. Trekoval, J. Organomet. Chem., 326 (1987) 1.
2 M. Schlosser, J. Organomet. Chem., 8 (1987) 9.
3 R.B. Bates, W.A. Beavers and B. Gordon III, J. Org. Chem., 44 (1979) 3800.
4 R. Lehmann and M. Schlosser, Tetrahedron Lett., (1984) 741; M. Schlosser and S. Strunk, ibid., (1984) 745.
5 H.D. Verkruijsse, L. Brandsma and P. von R. Schleyer, J. Organomet. Chem., 332 (1987) 99.
6 R. Pi, W. Bauer, B. Brix, C. Schade and P. von R. Schleyer, J. Organomet. Chem., 306 (1986) C1.
7 D. Wilhelm, T. Clark, P. von R. Schleyer, J.L. Courtneidge and A.G. Davies, J. Organomet. Chem., 273 (1984) C1.
8 D. Wilhelm, T. Clark, T. Friedl and P. von R. Schleyer, Chem. Ber., 116 (1983) 751.
9 A.G. Osborne and R.H. Whiteley, J. Organomet. Chem., 162 (1978) 79.
10 F. Scott, unpublished results.
11 L. Lochmann and J. Trekoval, J. Organomet. Chem., 179 (1979) 123.
12 P.A.A. Klusener, H.H. Hommes, H.D. Verkruijsse and L. Brandsma, J. Chem. Soc., Chem. Commun., (1985) 1677.
13 C. Margot and M. Schlosser, Tetrahedron Lett., (1985) 1038.
14 L. Lochmann, R.L. De and J. Trekoval, J. Organomet. Chem., 156 (1978) 307.
15 H.G. Raubenheimer, S. Lotz, G.J. Kruger, A. van A. Lombard and J.C. Viljoen, J. Organomet. Chem., 336 (1987) 349.
16 A.J. Hart, D.H. O'Brien and C.R. Russel, J. Organomet. Chem., 72 (1974) C19.
17 L. Lochmann and J. Trekoval, Collect Czech. Chem. Commun., 51 (1986) 1439.
18 D. Bryce-Smith and E.E. Turner, J. Chem. Soc., (1953) 861; D. Bryce-Smith, ibid., (1954) 1079.
19 G.G. Eberhardt and W.A. Butte, J. Org. Chem., 29 (1964) 2928.
20 G.J. Kruger, G. Gafner, J.P.R. de Villiers, H.G. Raubenheimer and H. Swanepoel, J. Organomet. Chem., 187 (1980) 333.
21 C.G. Screttas and M.-Screttas, J. Organomet. Chem., 290 (1985) 1.