Crystalline Alkyl-lithiums from α -Trimethylsilyl-substituted o-Xylenes; X-Ray Crystal Structure of $[{o-C_6H_4(CHSiMe_3)_2}{Li(tmeda)}_2]$ (tmeda = Me₂NCH₂CH₂NMe₂)

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Reaction of $[o-C_6H_4(CHRR')(CHR''R''')]$ (R, R', R'', R''' = H or SiMe₃) with LiBuⁿ in n-hexane in the presence of Me₂NCH₂CH₂NMe₂ (tmeda) or MeN(CH₂CH₂NMe₂)₂ (pmdeta) results in selective lithiation of the α -carbon in a manner dependent on the nature of the associated substituents and the tertiary amine to afford novel crystalline lithium alkyls; a single-crystal X-ray structure determination of $[{o-C_6H_4(CHSiMe_3)_2}{Li(tmeda)}_2]$ shows each lithium to interact with both the α - and adjacent ring carbon atoms from opposite sides of the *o*-xylidene plane.

We report the selective lithiation of o-xylene or a variously α -trimethylsilyl-substituted o-xylene using n-butyl-lithium in the presence of the tertiary polyamine tetramethylethylenediamine (tmeda) or, especially, pentamethyldiethylenetriamine (pmdeta). The principal features of interest are (i) the selectivity, (ii) the superiority in selectivity (for monolithiation) and reactivity of pmdeta compared with tmeda, (iii) a novel 1,6carbanionic rearrangement [(5) \rightarrow (6), see Scheme 1], (iv) the availability and potential of these *crystalline lithium alkyls* as alkylating agents, and (v) the X-ray structure of the first α, α' -dilithio-alkane, which shows the organic moiety to be conjugated and planar.

The metallation experiments are summarised in Scheme 1; this refers to $o-\text{MeC}_6\text{H}_4\text{Me}$, $o-\text{ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$, and $o-\text{MeC}_6\text{H}_4\text{CH}_2\text{Cl}$ as starting materials, crystalline lithium alkyls [(2), (4)—(6), (8), (10), and (11)], and various trimethylsilyl o-xylenes [(1), (3), (7), (9), and (12)]. Selective high-yield monolithiation, by use of LiBuⁿ-pmdeta, of $o-\text{MeC}_6\text{H}_4\text{Me}$, $o-\text{MeC}_6\text{H}_4\text{CH}_2\text{SiMe}_3$ (1), $o-\text{MeC}_6\text{H}_4\text{CH}(\text{SiMe}_3)_2$, (3), $o-\text{C}_6\text{H}_4$ -(CH₂SiMe₃)₂, (7), or $o-\text{Me}_3\text{SiCH}_2\text{C}_6\text{H}_4\text{CH}(\text{SiMe}_3)_2$, (12),



Scheme 1. Reagents and conditions ($R = SiMe_3$): i, Mg-thf, then ClSiMe_3; ii, LiBuⁿ (ca. 1.6 M in n-C₆H₁₄) + tmeda (Me₂NCH₂CH₂NMe₂) or pmdeta [MeN(CH₂CH₂NMe₂)₂], 12 h at 20 °C for tmeda or $< \frac{1}{2}$ h at 20 °C for pmdeta; iii, ClSiMe₃, OEt₂, 0 °C; iv, benzene, 80 °C, 2 h. Crystalline (2), (4)-(6), (8), (10), and (11), and liquids (3) and (12) yielded satisfactory microanalytical and ¹H and ¹³C n.m.r. spectroscopic data; compound (5) was isolated as colourless crystals whereas all other lithium complexes were yellow.



Figure 1. A single molecule of $[\{o-C_6H_4(CHSiMe_3)_2\} \{Li(tmeda)\}_2\},$ (8). Each molecule has pseudo-mm symmetry. Average values for the important distances (a-h) and angles $(a-\epsilon)$ designated are as follows (the e.s.d. of a *single* value is given in parentheses): distances (Å): $a, 1\cdot37(2); b, 1\cdot36(2); c, 1\cdot43(2); d, 1\cdot42(1); e, 2\cdot37(2); f, 2\cdot38(2); g, 2\cdot10(2); h, 1\cdot45(1); angles (deg.): <math>\alpha, 119\cdot6(11); \beta, 124\cdot1(10); \gamma, 116\cdot3(9); \delta, 122\cdot9(10); \epsilon, 86\cdot3(7).$

affords in each case a single crystalline α -lithiated derivative (4), (2b), (6), (11), or (10), respectively. These observations are rationalised by indicating that the relative α -proton thermodynamic acidities of *o*-xylene or a trimethylsilyl-*o*-xylene are governed by the following inequalities CH₂SiMe₃ > Me > CH(SiMe₃)₂. With *o*-MeC₆H₄CH(SiMe₃)₂, (3), an intermediate (5) on the pathway to *o*-Li(pmdeta)CH₂C₆H₄CH(SiMe₃)₂, (6), may be intercepted, which rearranges to (6) upon heating; thus in compound (3) a γ -proton is kinetically the most acidic.

The selectivity observed here for almost quantitative monolithiation, and isolability of crystalline material, using LiBuⁿpmdeta contrasts sharply with the mixed mono- and dimetallation of (i) *o*-xylene found previously in solution when using n-amylsodium-tmeda¹ or LiBuⁿ-tmeda,² or (ii) the now observed reactions of LiBuⁿ-tmeda with *o*-C₆H₄Me₂, (3), (7), or (12). However, with the latter, the important *di-lithiation* of *o*-(Me₃SiCH₂)₂C₆H₄, (7), to yield the title compound [{*o*-C₆H₄(CHSiMe₃)₂} {Li(tmeda)}₂], (8), was achieved.

The greater reactivity of LiBuⁿ-pmdeta compared with LiBuⁿ-tmeda is illustrated by the relative optimal reaction times for metallation (see Scheme 1), and is attributed either to the higher solution equilibrium concentration of monomeric (rather than associated) complex in pmdeta, or to greater steric weakening of the Li-C bond in pmdeta.

The use of tmeda in conjunction with an alkyl-lithium, such as LiBuⁿ, is now well established, and the importance of steric effects in lithiation is likewise documented. For example, whereas (Me₃Si)₃CH with LiBuⁿ-tmeda affords the *methyl*lithiated product,³ use of LiMe-thf-OEt₂ (thf = tetrahydrofuran) yields a solution containing (Me₃Si)₃CLi.⁴ Metallation with LiBuⁿ-pmdeta has been described for ferrocene as substrate^{5a} and for [Re(η -C₅H₅)₂H].^{5b} A recent example of a carbanionic rearrangement is Li[CH₂]₃SiMe₃ \rightarrow LiCH(SiMe₂)-[CH₂]₂CH₃.⁶

The potential of some of these crystalline organolithium tertiary polyamine complexes as alkylating agents has already begun to be realised;^{7,8} and an important feature is the possibility thereby of using exact stoicheiometries of highly pure starting materials.



The structure of $[\{o-C_6H_4(CHSiMe_3)_2\} \{Li(tmeda)\}_2], (8),$ (Figure 1) comprises two tmeda-co-ordinated lithium atoms, one each side of the planar o-xylidene moiety. Each lithium is associated with four sp²-hybridised carbon atoms: the two α - and their adjacent aromatic carbon atoms, at distances of 2.34-2.41 Å [for the C(α) atoms] and 2.32-2.42 Å [for the ring atoms C(ar)]. This represents the first structurally characterised dilithio-alkane. An interesting feature is the delocalisation of the charge, as also evident from the short $C(\alpha)$ -C(ar) distances, 1.41 and 1.43(1) Å, suggestive of a π -delocalised dianion and anion-cation interaction, as opposed to either electron-deficient bonding, (13), or σ -bonding, (14). There are no significant intermolecular contacts in (8). The lithium environments, and especially their interaction with the carbanion, are very similar to those observed in the Z,Z-hexatriene dianion, similarly ion-paired with lithium tmeda's⁹ and the corresponding complex of the naphthalene dianion.¹⁰

Crystal data: C₂₆H₅₆Li₂N₄Si₂, M = 494.8, monoclinic, space group P2₁, a = 10.936(3), b = 17.229(5), c = 9.995(3) Å, $\beta = 115.24(2)^{\circ}$, Z = 2. The specimen was mounted in a capillary under argon and the structure was solved from 1006 'observed' diffractometer reflections (Mo- K_{α} radiation) and refined to R = 0.054.[†]

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[†] Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.