

Radical Anion Reactions in n-Butyl-lithium–Potassium t-Pentyl Oxide Mixtures

Dieter Wilhelm, Timothy Clark,* and Paul von Ragué Schleyer

Institut für Organische Chemie der Friedrich-Alexander-Universität, Erlangen-Nürnberg, Henkestrasse 42, D-8520 Erlangen, Federal Republic of Germany

Ethyl- or isopropyl-benzenes react with n-butyl-lithium–potassium t-pentyl oxide mixtures to give coupling products characteristic of styrene radical anions which are postulated to arise from one-electron oxidation of styrene dianion intermediates.

The 1:1 complex formed by mixing hexane solutions of n-butyl-lithium and potassium t-pentyl oxide ($\text{BuLi}/\text{KOCMe}_2\text{Et}$)¹ is an extremely active metallation reagent which also catalyses metal hydride eliminations.^{2–4} We now report a new type of reaction involving an unusual second metallation directed by the first metallic substituent. Subsequent electron transfer yields radical anions and coupling products.

In contrast to the well known^{1–4} metallation and elimination reactions observed for most substrates in $\text{BuLi}-\text{KOCMe}_2\text{Et}$, compounds such as ethyl- or isopropyl-benzenes, which have both α - and β -hydrogens, give high yields of dimeric products of the type obtained from one-electron reduction of substituted styrenes.⁵ This, together with the observation of an intense blue colour in the reaction mixture and the deposition

of a metallic mirror, suggests that styrene radical anions are being generated in the reaction.

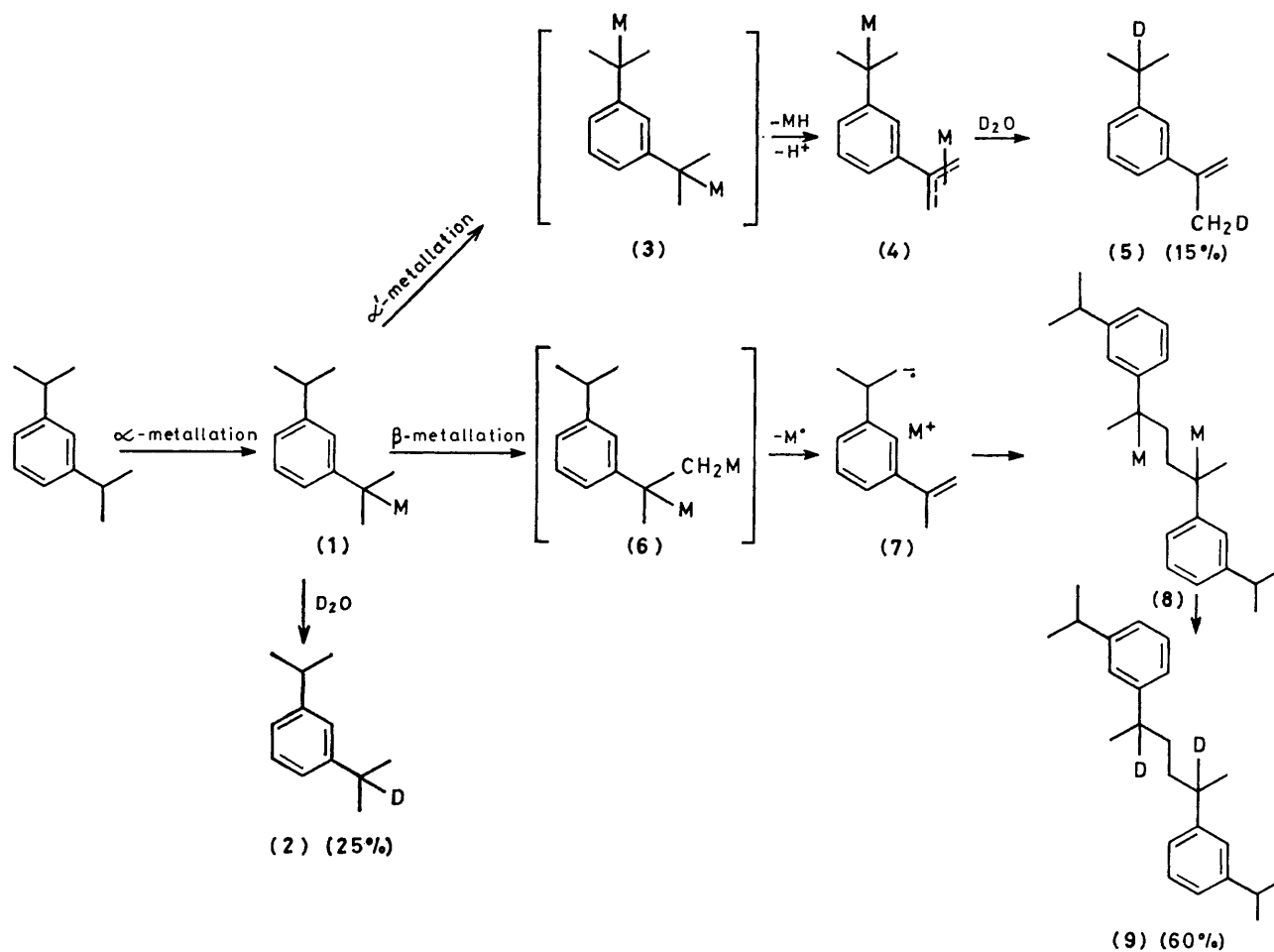
The products obtained from ethyl-, isopropyl-, methylisopropyl-, and di-isopropyl-benzenes (Table 1) can be rationalized by the mechanism depicted in Scheme 1. *m*-Di-isopropylbenzene has been chosen for illustration since the two alternative reaction pathways are followed.

Conventional α -metallation⁶ gives the benzyl anion salt (**1**) (M denotes either Li or K as the nature of the metallated species from $\text{BuLi}-\text{KOCMe}_2\text{Et}$ is uncertain). Metallation of *m*-di-isopropylbenzene with 4 equiv. of $\text{BuLi}-\text{KOCMe}_2\text{Et}$ for 24 h at reflux followed by quenching with D_2O yields 25% of (**2**). When the n-butyl-lithium–tetramethylethylenediamine complex ($\text{BuLi}-\text{TMEDA}$)⁶ is employed, only a low yield of (**1**)

Table 1. Reaction products^a isolated after 24 h refluxing in a 4-fold excess of BuLi-KOCMe₂Et followed by quenching with D₂O.

Starting material	Monometallation, %	α, α' -Dimetallation, % (eliminations)	α, β -Dimetallation, % (dimers)
Ethylbenzene	68	—	32
Isopropylbenzene	50	—	50
<i>p</i> -Methylisopropylbenzene	92	8	—
<i>m</i> -Methylisopropylbenzene	71	29	—
<i>p</i> -Di-isopropylbenzene	20	—	80
<i>m</i> -Di-isopropylbenzene	25	15	60

^a In all cases a total yield of at least 98% was obtained; the percentages given are relative to this total yield. All new compounds gave satisfactory elementary analyses, ¹H and ¹³C n.m.r. spectra, and mass spectra.



is obtained together with ring metallation products, and no further reaction occurs.

With BuLi-KOCMe₂Et, further conventional metal exchange of the second α -H (α, α' -dimetallation) yields dianion (3). This ion triplet, however, is not stable and undergoes metal hydride elimination²⁻⁴ and allylic metallation to give (4). The product from D₂O quenching (5) can be isolated in 15% yield. We know of no other examples of such eliminations of benzyl-type dianions in BuLi-KOCMe₂Et; such processes do not take place with the corresponding monoanions.⁴

The main reaction, however, occurs *via* two unusual steps, the first of which, (1) \rightarrow (6), competes with the α, α' -dimetallation, (1) \rightarrow (3). Although we have no direct evidence, the styrene dianion salt (6), obtained by a second metallation in

the β -position (α, β -dimetallation), is proposed as the intermediate. Precedents for such 'directed' second metallation reactions in which the first metal substituent controls the position of the subsequent proton abstraction are known.⁷⁻¹⁰ The step, (1) \rightarrow (6), may appear to be unlikely, but benzyl-lithium can be metallated a second time on the benzyl carbon⁷ and dilithiostilbene is known to be stable.¹¹ Furthermore, MNDO calculations¹² suggest a methyl proton in (1) ($M = Li$) to be the most acidic (the LUMO coefficient¹³ is an order of magnitude larger than for all other hydrogen atoms). The MNDO structure of (6) ($M = Li$) is doubly bridged, as shown in Figure 1. This energetically favourable arrangement is similar to that calculated⁸ and observed¹⁴ for *o, o'*-dilithiobiphenyl, which is also obtained *via* directed metallation.⁸

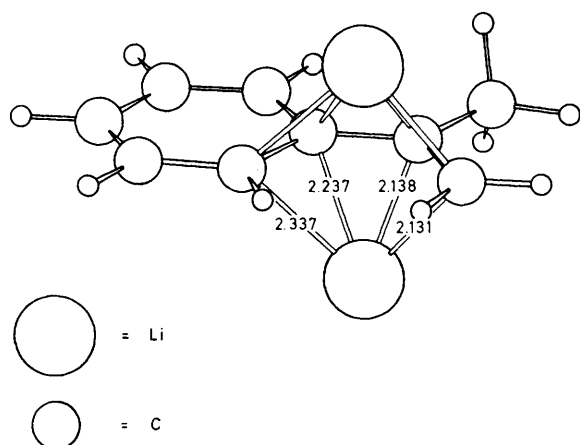


Figure 1. MNDO calculated structure for α,β -dilithioisopropylbenzene, which has been used as a model for (6) ($M = \text{Li}$).

The dianion salt (6) is, however, not stable under our reaction conditions and loses an electron in what appears to be a 'dark' reaction in an opaque reaction mixture to give the styrene radical anion derivative (7) which dimerises to (8). Dideuteriated (9) is obtained in 60% yield after quenching with D_2O . The electron transfer reaction (6) \rightarrow (7) can be demonstrated in related compounds.¹⁵ In this case a solid-state e.s.r. spectrum could be obtained from the heterogeneous reaction mixture, but styrene radical anions are too short-lived in solution for an isotropic e.s.r. spectrum to be observed.¹⁶ Alternative mechanisms involving hydride elimination from (1) to give a neutral styrene [as opposed to the anion involved in the elimination step (3) \rightarrow (4)] can be ruled out as no BuLi addition products are found.

The above mechanism can account for the products obtained from a series of starting materials, as shown in Table 1. *p*-Di-isopropylbenzene, for which the α,α' -dimetallation is less favourable than for the *meta*-isomer,¹⁷ gives only dimeric α,β -dimetallation products. *p*-Methylisopropylbenzene, on the other hand, is first metallated at the methyl group and therefore gives only α,α' -dimetallation products. The *meta*-isomer gives a higher yield of such products, as expected from the *m*- and *p*-di-isopropylbenzene results. Finally, ethyl- and isopropylbenzene, which do not eliminate and which only have one α -position, also give moderate yields of dimeric products.

Bates and Ogle¹⁸ have also recently observed radical anion products in quench reactions of xylene dianions with methyl iodide, once again illustrating the ease of oxidation of dilithium compounds. The metallation products of *p,p'*-dimethyl-

bibenzyl they report (67% dimetallation in the methyl groups, 9% dimetallation in the methylene groups, but no mixed products) are also consistent with our proposed activation of the β -position by the first metal substituent.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank Professor A. G. Davies and his coworkers for helpful discussions and for the e.s.r. experiments, which were performed during a visit to University College London financed by the British Council.

Received, 22nd November 1982; Com. 1339

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