



To test the utility of bromide **1** as a mechanistic probe, we applied it in the metal--halogen interchange reaction with tert-butyllithium. Despite numerous studies, the mechanistic course of such reactions remains an open question.<sup>10</sup> A recent study of the reactions of tert-butyllithium with various halides including 6-halo-1-hexene probes led to the conclusion that the reactions proceeded predominantly via SET pathways,<sup>11</sup> but the major pathway for cyclization from the 6-halo-1-hexenes is now known to be the anionic route shown in Eq 2.<sup>12</sup> When bromide **1** was treated with tert-butyllithium in ether--pentane or THF--pentane at -23 °C according to the reported procedure for the 6-halo-1-hexene reactions,<sup>11</sup> we obtained low yields of the rearranged product 4-methyl-1-pentene (13% and 7%, respectively). The product mixtures were complicated, containing coupling products from the probe and organolithium reagent, and it is clear that further studies are required. Nevertheless, the detection of 4-methyl-1-pentene suggests a lower limit for the extent of radical formation of ca. 10% in these reactions. Thus, an SET process or another route to alkyl radicals is required as at least a minor pathway in the reaction of bromide **1** with tert-butyllithium. Further, our detection of unrearranged 3,3-dimethyl-1-butene in 20-30% yield in reactions in THF--pentane requires that either (1) a metal--halogen exchange pathway not involving free radicals exists, (2) radical **6** was reduced in a bimolecular reaction which has a rate constant greater than  $1 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$  at -23 °C, or (3) radical **7** was reduced to an organolithium species which then rearranged to 2,2-dimethyl-3-buten-1-yl-lithium; we are now studying these possibilities.

In conclusion, the availability of 4-bromo-3,3-dimethyl-1-butene coupled with the well characterized, fast rearrangement of radical **6** formed from this probe<sup>5,6</sup> suggests numerous applications of the probe. It should be especially useful in studies where 6-halo-1-hexenes and their analogs have been shown to give cyclic products in reactions with bases or nucleophiles since radical **6** rearranges 20 times faster than 5-hexen-1-yl at 25 °C.<sup>6</sup> It is to be hoped that the application of probes such as **1** will help clarify the confused situation regarding possible SET pathways in reactions of alkyl halides with strong bases/nucleophiles.

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#### References and Notes

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