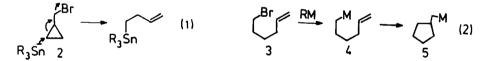
4-BROMO-3, 3-DIMETHYL-1-BUTENE: A NEW PROBE FOR RADICAL INTERMEDIATES IN REACTIONS IN STRONGLY BASIC MEDIA

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<u>Summary</u>: The preparation, isolation and purification of the title bromide (1) are described, and the application of 1 as a mechanistic probe is demonstrated in the metal--halogen interchange reaction with tert-butyllithium.

Mechanistic probes are becoming increasing popular tools for studies of the details of reactions which might involve free radical intermediates.² In studies in strongly basic or nucleophilic media, two well characterized radical rearrangements, the cyclopropylcarbinyl ring opening and the 5-hexen-1-yl cyclization, have been widely exploited. However, the probes used, the cyclopropylcarbinyl halides (2) and 6-halo-1-hexenes (3), are inherently flawed for studies in such media. For example, the cyclopropylcarbinyl halides apparently react with trialkyltin anionoids in what is the equivalent of a homo-S_N2 reaction (Eq 1),³ and the 6-halo-1-hexenes and their various analogs might suffer metal--halogen exchange in strongly basic media to give acyclic organometals **4** which can cyclize to cyclopentylcarbinylmetals (Eq 2).⁴ In each case a false positive test for a radical intermediate results.



Thus, the recently reported, fast rearrangement^{5,6} of the 2,2-dimethyl-3-buten-l-yl radical (6) to the 2-methyl-4-penten-2-yl radical (7) was well received. It was apparent that 4-bromo-3,3-dimethyl-1-butene (1) could be quite useful as a mechanistic probe for reactions in strongly basic media. Formation of radical 6 from this probe could, after rearrangement, lead to products from radical 7, but, if an organometal reagent is formed from 1, rearranged products would not be expected (Scheme 2 in ref 6). As an added attraction, the neopentyl-like structure of probe 1 will lead to slow S_N^2 reactions and no E2 reactions; the probe is open to reactions with nucleophiles by single electron transfer (SET) or attack at halogen.

Bromide 1 was prepared from 2,2-dimethyl-3-buten-1-ol $(8)^7$ by a conventional method,⁸ but our initial attempts to distill 1 failed to give the product even when a vacuum transfer was attempted. Apparently bromide 1 reacted with triphenylphosphine when the reaction mixture became concentrated. Dilution of the reaction mixture with a high boiling solvent followed by flash distillation afforded crude 1 which was purified by preparative gc. The survival of 1 on the gc column demonstrated that the compound is inherently robust. Bromide 1 (>98% pure by analytical gc) was characterized by its ¹H NMR spectrum and high resolution mass spectrum.⁹

<u>Procedure:</u> To alcohol **8** (0.10 mol) and Ph_3P (0.12 mol) in 70 mL of CH_2Cl_2 at 0 °C was added CBr_4 (0.11 mol) in portions. The mixture was allowed to warm to 25 °C over 2 h and was then diluted with 100 mL of tetraglyme. Flash distillation (25-70 °C bath, 4 Torr) gave crude 1 (ca. 65% yield) which was purified by preparative gc (0V-101 on Chromosorb G, 140 °C).

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.¹⁰ 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, 11 but the major pathway for cyclization from the 6-halo-1-hexenes is now known to be the anionic route shown in Eq 2.12When 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, 11 we obtained low vields of the rearranged product 4-methy1-1-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 4methyl-l-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-dimethy1-1-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 $\mathbf{6}$ was reduced in a bimolecular reaction which has a rate constant greater than 1×1 10⁷ M⁻¹ sec⁻¹ at -23 °C, or (3) radical **7** was reduced to an organolithium species which then rearranged to 2,2-dimethy1-3-buten-1-yllithium; 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^{5,6} 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 nucleo-philes since radical **6** rearranges 20 times faster than 5-hexen-1-yl at 25 °C.⁶ 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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