The Anti-Markovnikov Hydrobromination of Alkenes Using a Hydroboration–Transmetallation–Bromination Reaction Sequence

By JOSEPH J. TUFARIELLO* and MARTIN M. HOVEY

(*Department of Chemistry, State University of New York at Buffalo, Buffalo, New York* 14214)

Summary The *unsym*-trialkylboranes derived from alk-1-enes and dicyclohexyl- or bis-(1,2-dimethylpropyl)-borane can be treated with aqueous alkaline mercuric oxide followed by *in situ* bromination to afford good yields of primary alkyl halides.

ONE long-recognized potential route to alkyl halides involves the *anti*-Markovnikov hydrohalogenation of alkenes through the intermediacy of the corresponding organoboranes. A convenient synthesis of primary alkyl iodides from the cleavage of trialkyl-boranes with iodine in the presence of sodium hydroxide has been reported;[1] however, all other direct,[2] or indirect[3] halogenations of organoboranes are exceedingly inefficient.

We report a convenient route to primary alkyl bromides from the bromination of the organomercurials derived from transmetallation reactions involving *unsym*-trialkylboranes and mercuric oxide.

$$R_2B\text{-n-alkyl} + HgO \xrightarrow[H_2O]{OH^-} (\text{n-alkyl})_2Hg \xrightarrow{Br_2} \text{n-alkyl-Br}$$

The transmetallation of *sym*-trialkylboranes with mercuric oxide has been described;[4] however, only a maximum of two of the alkyl groups can be transferred from trialkylboranes to mercury (*i.e.* to afford dialkylmercurials). This sharply limits the yields of alkyl bromides obtainable from *sym*-trialkylboranes. We have found, however, that primary alkyl groups exhibit a pronounced transmetallation aptitude over s- or t-alkyl groups in the organoborane–mercuric oxide reaction. This has enabled us to hydroborate terminal olefins with the selective hydroborating agents (*e.g.* dicyclohexyl-[5] or bis-(1,2-dimethylpropyl)-borane[5]) and remove the primary alkyl groups selectively with mercuric oxide. Subsequent bromination of the resultant dialkylmercurials *in situ* provides an efficient synthesis of primary alkyl bromides.

Anti-Markovnikov hydrobromination of olefins by hydroboration–transmetallation–bromination sequence

Alkene	Product	Yield,[a] %
hex-1-ene	1-bromohexane	22[b]
hex-1-ene	1-bromohexane	75[c]
hex-1-ene	1-bromohexane	73[d]
hex-1-ene	1-bromohexane	44[e]
non-1-ene	1-bromononane	77[c]
3,3-dimethylbut-1-ene	3,3-dimethyl-1-bromobutane	42[c]
cyclohexene	bromocyclohexane	20[b]

[a] The yields, determined by g.l.p.c., are based on starting olefin in a reaction using a 1·5 : 1 molar ratio of mercuric oxide to trialkylborane. [b] The alkene was hydroborated using borane in tetrahydrofuran to the trialkylborane stage. [c] The alkene was hydroborated using dicyclohexylborane. [d] The alkene was hydroborated with bis-(1,2-dimethylpropyl)borane. [e] The alkene was hydroborated with 1,1,2-trimethylpropylborane.

The Table summarizes the results for a series of representative alkenes. It can be readily seen that primary alkyl bromides can be obtained in good yield (approx. 75%) from the transmetallation–bromination of the *unsym*-trialkylboranes[5] derived from a alk-1-ene and dicyclohexyl- or bis-(1,2-dimethylpropyl)-borane. In each case, the yield of alkyl bromide corresponds to the transfer of approximately one of the boron-bound groups. This corresponds to the transmetallation efficiency observed[4] for the reaction between mercuric oxide and tri-n-hexylborane to produce di-n-hexylmercury, where only 33% of the boron-bound alkyl groups were transferred to mercury.

In each of the reactions of *unsym*-trialkylboranes with mercuric oxide, bromination resulted in the formation of only primary alkyl bromide and in no case was more than a trace of s- or t-alkyl bromide detected.

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