

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

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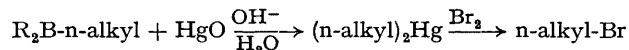
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Summary The *unsym*-trialkylboranes derived from alkenes and dicyclohexyl- or bis-(1,2-dimethylpropyl)-borane can be treated with aqueous alkaline mercuric oxide followed by *in situ* bromination to afford good yields of primary alkyl halides.

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 indirect³ 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.



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)-borane⁶) 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 ^e
3,3-dimethylbut-1-ene	3,3-dimethyl-1-bromobutane	42 ^e
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.

¹ H. C. Brown, M. W. Rathke, and M. M. Rogić, *J. Amer. Chem. Soc.*, 1968, **90**, 5038.

² (a) J. R. Johnson, H. R. Snyder, and M. G. Van Campen, jun., *J. Amer. Chem. Soc.*, 1938, **60**, 115; (b) L. H. Long and D. Dollimore, *J. Chem. Soc.*, 1953, 3902, 3906.

³ J. Sharefkin and H. Banks, *J. Org. Chem.*, 1965, **30**, 4313.

⁴ J. Honeycutt and J. Riddle, *J. Amer. Chem. Soc.*, 1959, **81**, 2593; *ibid.*, **82**, 3051 (1960).

⁵ H. C. Brown and A. W. Moerikofer, *J. Amer. Chem. Soc.*, 1962, **84**, 1478.

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*-trialkylboranes⁵ 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 observed⁴ 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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