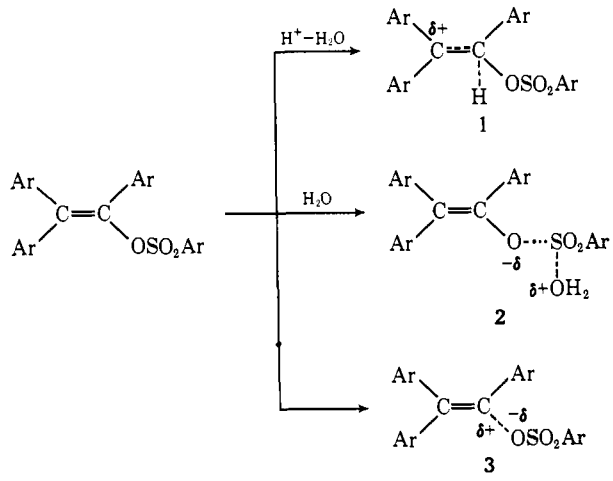

The *m* value is low for an SN1 process and this may be due to the presence of the α-anisyl group[1j,16] or to considerable solvent participation in **3**.[17] The most likely explanation is, however, severe hindrance to solvation of **3**, since one lobe of the incipient cationic p orbital is directed toward the highly crowded *cis*-stilbene unit while the other lobe is shielded by the leaving group and the *cis* group.[18] It is interesting that the k_{OTs}/k_{Br} ratio of 32 is higher than those assigned to SN2 processes,[19] but is still low compared to ratios in substrates reacting by the SN1 mechanism, excluding neophyl and *p*-methoxyneophyl systems. Whether this is due to solvent participation, to "early" transition state for the tosylate, to reduced solvation, or to different electron donation by the leaving groups to the reaction center is not yet known.

Further studies in this and related systems are in progress and will be soon reported.

at 50% reaction of, *e.g.*, 0.008 *M* [RX] and 0.016 *M* [lutidine], $[H^+] \sim 5.8 \times 10^{-6}$ *M* (using $pK_{BH^+} = 5.77$ in 50% ethanol). At this acid concentration the pseudo-first-order rate coefficient for the addition of H_3O^+ to *p*-amino-α-bromostyrene in water at 50° is *ca.* 10^{-9} sec^{-1}.[15] The extrapolated (by the *mY* relationship) k_1 value in water at 50° for the solvolysis of trianisylvinyl brosylate is *ca.* 3×10^{-4} sec^{-1}, *i.e.*, five orders of magnitude faster, without taking into account that bromine stabilizes a positive charge better than brosylate. Since according to the addition–elimination mechanism the *p*-aminophenyl derivative should be *more* reactive than the anisyl derivative, the addition–elimination route is unimportant under our conditions.

(15) W. M. Schubert and G. W. Barfknecht, *J. Amer. Chem. Soc.*, **92**, 207 (1970).

(16) S. Winstein and R. Heck, *ibid.*, **78**, 4801 (1956).

(17) Neither solvent nor β-aryl participation is reflected in the stereochemistry of the solvolysis of triarylvinyl halides in acetic acid or in 80% ethanol.[11]

(18) The steric hindrance to solvation is lower in α-halostyrenes, and indeed α-bromostyrene[1a] and α-bromo-*p*-methoxystyrene show higher *m* values.[13] We want to emphasize that in an electrophilic solvent (*e.g.*, acetic acid), where solvation of the leaving group is important, the hindrance to solvation by the *cis*-aryl group is small and higher *m* values are expected.

(19) H. M. R. Hoffmann, *J. Chem. Soc.*, 6753, 6762 (1965).

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Transmetallations Involving Mercury(II) Salts. A Convenient Anti-Markovnikov Alkene Hydrobromination Procedure

Sir:

Although there has been considerable effort devoted toward investigations of the chemistry of organoboranes, there are relatively few known reactions which can efficiently functionalize all three boron-bound groups under mild conditions. Examples include certain oxidations[1] and carbonylations[2] of organoboranes and their reactions with silver oxide[3] and carboxylic acids.[4]

We should like to report herein that the reaction of primary trialkylboranes with certain mercury(II) salts results in a facile transmetallation and produces the corresponding primary alkyl mercury salts in excellent yield and under mild conditions.

$$R_3B + HgX_2 \longrightarrow RHgX + BX_3$$

Our research efforts in this direction were prompted by attempts to develop a convenient method for the *anti*-Markovnikov hydrohalogenation of olefins. While iodine has been shown to react with primary trialkylboranes in the presence of sodium hydroxide to cleave up to two of the boron-bound groups,[5] all other direct[6] and indirect[7] halogenations of trialkylboranes investigated to date have proven to be exceedingly inefficient. The successful transmetallation procedure involving mercury(II) salts, which is described below, provides the means of halogenating all three of the boron-bound groups

$$RCH{=}CH_2 \xrightarrow[THF]{BH_3} (RCH_2CH_2)_3B \xrightarrow{Hg(OAc)_2} RCH_2CH_2HgOAc$$

$$RCH_2CH_2HgOAc \xrightarrow{Br_2} RCH_2CH_2Br$$

When a THF solution of primary trialkylborane, obtained from the hydroboration of 1-alkene, was refluxed with 3 mol equiv of mercuric acetate, primary alkyl mercuric acetate was produced. The reaction can be followed by observing the disappearance of the insoluble mercuric acetate. The alkylmercuric acetate can be isolated at this stage by removal of the solvent and dissolution of the product mixture in refluxing pentane, resulting in the crystallization of the alkylmercuric acetate upon cooling. In the case of tri-*n*-hexylborane, a 73% yield of *n*-hexylmercuric acetate, mp 49–50° (lit.[8] mp 50°), is produced. While transmetallations involving organoboranes and compounds of mercury (*e.g.*, mercuric oxide) have been reported previously,[9] the yields of the dialkylmercurials produced suggest the transfer of only one or, at best, two of the alkyl groups from boron.

The alkylmercuric salts can be conveniently brominated[10] *in situ* to afford primary alkyl bromides in 71–86% yield. The results derived from similar studies of a number of organoboranes are summarized in Table I. From these results, it is clear that primary trialkylboranes give good yields of primary alkyl bromides in this one-flask sequence of reactions. Secondary trialkyl-

(1) (a) H. C. Brown "Hydroboration," W. A. Benjamin, New York, N. Y., 1962; (b) J. R. Johnson and M. G. Van Campen, Jr., *J. Amer. Chem. Soc.*, **60**, 121 (1938); (c) H. C. Brown and C. P. Garg, *ibid.*, **83**, 2951 (1961); (d) R. Köster and Y. Morita, *Ann.*, **704**, 70 (1967).

(2) H. C. Brown, *Accounts Chem. Res.*, **2**, 65 (1969).

(3) H. C. Brown and C. H. Snyder, *J. Amer. Chem. Soc.*, **83**, 1001 (1961).

(4) H. C. Brown and K. Murray, *ibid.*, **81**, 4108 (1959).

(5) H. C. Brown, M. W. Rathke, and M. M. Rogić, *ibid.*, **90**, 5038 (1968).

(6) (a) J. R. Johnson, H. R. Snyder, and M. G. VanCampen, Jr., *ibid.*, **60**, 115 (1938); (b) L. H. Long and D. Dollimore, *J. Chem. Soc.*, 3902, 3906 (1953).

(7) J. Sharefkin and H. Banks, *J. Org. Chem.*, **30**, 4314 (1965).

(8) K. H. Slotta and K. R. Jacobi, *J. Prakt. Chem.*, **120**, 249 (1929).

(9) J. Honeycutt and J. Riddle, *J. Amer. Chem. Soc.*, **81**, 2593 (1959).

(10) F. R. Jensen and L. Gale, *ibid.*, **82**, 147, 148 (1960).

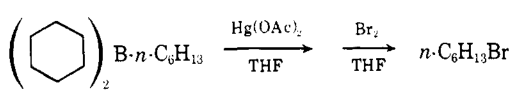
Table I. Anti-Markovnikov Hydrobromination of Olefins by Hydroboration–Transmetallation–Bromination Sequence

Alkene[a]	Product[b]	Yield,[c] %
1-Hexene	1-Bromohexane	79[d]
1-Octene	1-Bromooctane	75
1-Nonene	1-Bromononane	86
2,4,4-Trimethyl-1-pentene	2,4,4-Trimethyl-1-bromopentane	76
3,3-Dimethyl-1-butene	3,3-Dimethyl-1-bromobutane	71
Cyclohexene	Bromocyclohexane	22[d]

[a] The hydroboration was carried out as usual using borane in THF solution; see G. Zweifel and H. C. Brown, *Org. React.*, **13**, 1 (1963). [b] The products were characterized by direct comparison of their physical and chemical properties with those reported in the literature. [c] The yields, determined by glpc, are based on starting trialkylborane in a reaction using a 1:1 molar ratio of mercuric acetate to trialkylborane. [d] A 73% yield of *n*-hexylmercuric acetate was isolated when the reaction sequence was interrupted prior to the bromination step. Similarly, a 25% yield of cyclohexylmercuric acetate was obtained.

boranes such as tricyclohexylborane, however, afford greatly diminished yields of secondary bromides.

It is noteworthy that dicyclohexyl-*n*-hexylborane[11] affords a 90% yield of 1-bromohexane when exposed to this transmetallation–bromination sequence. This indicates that primary alkyl groups possess a greater transmetallation facility than secondary alkyl groups in this case.



We have found that the reaction of organoboranes with mercuric salts appears to depend on the ionic character of the salt. The reaction is exceedingly facile with mercuric nitrate, being essentially complete in 10 min at room temperature. The trifluoroacetate and fluoride salts are at least as rapid as mercuric acetate; however, mercuric chloride and bromide failed to react under the same conditions.

A general procedure for the generation of alkyl bromides from organoboranes using the transmetallation sequence is included.

1-Nonene (3.8 g, 30 mmol) in 24 ml of THF is hydroborated in the usual manner[12] with borane in THF. The tri-*n*-nonylborane solution is treated with mercuric acetate (9.56 g, 30 mmol) and refluxed for 4 hr to ensure complete reaction. The mixture is cooled in an ice bath and bromine (6–8 g in 10 ml of CCl_4) is added dropwise until the color persists for several minutes. The solvent is removed at reduced pressure and then 40 ml of hexane and 80 ml of water are added. The precipitated mercuric bromide is removed by suction filtration. The organic layer is separated and the aqueous layer is extracted three times with hexane. The combined extracts are dried over magnesium sulfate. After filtration and removal of solvent, distillation of the crude product affords 4.20 g (69%) of 1-bromonane, bp 102–105° (1.8 mm).

We are currently exploring the corresponding iodination and chlorination procedures.[13] In addition, we found that the *in situ* reduction of *n*-nonylmercuric acetate, prepared as described above, using sodium

$$(n\text{-}C_9H_{19})_3B \xrightarrow[\text{THF}]{\text{Hg(OAc)}_2} \xrightarrow[\text{OH}^-\text{–H}_2\text{O}]{\text{NaBH}_4} n\text{-}C_9H_{20}$$

borohydride[14] leads to the formation of *n*-nonane in 72% yield based on trialkylborane, suggesting that the hydroboration–transmetallation–borohydride reduction sequence provides a valuable alternative to the protonolysis procedure for the reductive cleavage of organoboranes.

Acknowledgment. We thank the U. S. Army Research Office (Durham) (DA-ARO-31-124-G-889) for generous support of this work.

(11) H. C. Brown and A. W. Moerikofer, *ibid.*, **84**, 1478 (1962).
(12) See Zweifel and Brown, Table I, footnote *a*.
(13) The halogenation of organomercurials has been reviewed: F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials," McGraw-Hill, New York, N. Y., 1968.
(14) H. C. Brown and P. Geoghegan, Jr., *J. Amer. Chem. Soc.*, **89**, 1522 (1967).

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The Preparation of Lithio Ethyl Acetate. A Simple Procedure for the Conversion of Aldehydes and Ketones to β-Hydroxy Esters

Sir:

Addition of ethyl acetate to a solution of lithium bis(trimethylsilyl)amide in tetrahydrofuran at −78° results in essentially quantitative formation of lithio ethyl acetate,[1] I. At the same low temperature, I reacts

$$LiN[Si(CH_3)_3]_2 + CH_3CO_2C_2H_5 \longrightarrow HN[Si(CH_3)_3]_2 + LiCH_2CO_2C_2H_5 \quad (1)$$

almost instantly with aldehydes or ketones to give, after hydrolysis, excellent yields of the corresponding β-hydroxy esters (eq 2).

$$LiCH_2CO_2C_2H_5 + RC(=O)R' \longrightarrow R\text{–}C(OLi)(R')\text{–}CH_2CO_2C_2H_5 \xrightarrow{H_2O} R\text{–}C(OH)(R')\text{–}CH_2CO_2C_2H_5 \quad (2)$$

Solutions of lithio ethyl acetate are stable indefinitely at −78°, but decompose rapidly if allowed to warm to 0°. Thus a solution prepared according to eq 1 remains colorless at −78° and quenching with water after 4 hr gives 95% recovery of ethyl acetate. However, warming a solution to 0° produces an immediate deep yellow color and quenching gives only 2% recovery of ethyl acetate.

Previous workers[3] have shown that sodium bis(trimethylsilyl)amide converts ethyl acetate to sodio ethyl acetate. This anion is much less stable than the corresponding lithium derivative. Thus, quenching a tetrahydrofuran solution of sodium bis(trimethylsilyl)-

(1) Lithio ethyl acetate has previously been made by the addition of ethyl bromoacetate to butyllithium in a hexane–ether solvent at −75°.[2] However, quenching of such solutions with water indicates the conversion to I is less than 15%.
(2) W. M. Jones and R. S. Pyron, *Tetrahedron Lett.*, 479 (1965).
(3) C. R. Kruger and E. G. Rochow, *J. Organometal. Chem.*, **1**, 476 (1964).