glpc. The original peak for **14** disappeared almost completely and two new peaks were identified as B-methoxyboracyclopentane (98%) and B-(1-butyl)boracyclopentane (100%). The carbonylation–oxidation of the reaction mixture was carried out as described above for the carbonylation of **3**.

Preparation of 1-(1-Butyl)cyclopentanol from Cyclopentanone. Cyclopentanone (4.2 g, 50 mmol) was added to 50 ml (60 mmol) of 1.2 *N* *n*-butyllithium at room temperature. After working up with aqueous ammonium chloride, distillation afforded 4.6 g (65%) of **19**, bp 110–112° (43 mm), $n^{20}\text{D}$ 1.4537 (lit.[24] bp 193° (760 mm), $n^{25}\text{D}$ 1.4535).

Preparation of 1,1-Bis(1-boracyclopentyl)butane (14) from B-Methoxyboracyclopentane and 1-Butyne. The compound was prepared in a manner similar to the preparation of **3** described above, except that 1-butyne was used instead of 1,3-butadiene; yield by glpc 53%.[16] The peak size for the product increased when III was added to the reaction mixture without showing any sign of splitting.

---

(24) C. R. McLellan and W. R. Edwards, Jr., *J. Amer. Chem. Soc.*, **66**, 409 (1944).

Organoboranes. X. A Fast Reaction of Organoboranes with Mercuric Acetate. A Convenient Procedure for the Conversion of Terminal Olefins into Alkylmercuric Salts *via* Hydroboration–Mercuration

Richard C. Larock[1] and Herbert C. Brown

Contribution from Richard B. Wetherill Laboratory, Purdue University, Lafayette, Indiana 47907. *Received September 20, 1969*

Abstract: Organoboranes derived from terminal olefins *via* hydroboration undergo a rapid quantitative reaction with mercuric acetate at room temperature to give the corresponding alkylmercuric acetate. The fact that secondary alkyl groups do not react under these mild reaction conditions makes possible the use of dicyclohexylborane for selective hydroboration–mercuration. Functional groups are readily accommodated in this reaction. The alkylmercuric acetates are easily converted into the corresponding alkylmercuric halides to give greater than 90% isolated yields. This development makes a whole range of alkylmercuric salts and dialkylmercurials readily available.

Mercury(II) salts have been shown to react with aryl and alkyl boronic acids,[2a,b] diaryl borinic acids,[2c] and triaryl- and trialkylboranes[2d,e] to yield a variety of organomercurials.

Until recently these reactions proved to be of no practical synthetic utility. Prior to 1956, these organoboron compounds were generally prepared by the reaction of the appropriate Grignard reagent with a boron halide or ester.[3] Since the organomercurials could be obtained directly through reaction of a Grignard reagent with a mercuric halide, there was no advantage to be gained by going through the organoboron intermediate[4,5] (eq 1).

$$\begin{aligned} \text{RMgX} + \text{HgX}_2 &\longrightarrow \text{RHgX} + \text{MgX}_2 \\ 2\text{RMgX} + \text{HgX}_2 &\longrightarrow \text{R}_2\text{Hg} + 2\text{MgX}_2 \end{aligned} \qquad (1)$$

In 1956 a wide variety of trialkylboranes became readily available through the hydroboration of olefins.[6] Of particular significance is the fact that many functional groups are readily accommodated in this reaction.[7] Thus, through hydroboration–mercuration, the organic chemist has for the first time a convenient route to a variety of organomercurials not previously available.

Honeycutt and Riddle established that the trialkylboranes could be utilized for the synthesis of dialkylmercurials.[2e] However, it is not clear from their work whether only two or all three alkyl groups can be transferred from boron to mercury, nor was the scope of the reaction determined. We were interested in extending this reaction to the synthesis of alkylmercuric salts and undertook a detailed study of this possibility.

Results

Hydroboration–Mercuration of Representative Olefins. 1-Butene, 2-butene, and isobutylene were selected as typical representatives of terminal and internal olefins. These olefins were converted into the corresponding trialkylboranes (eq 2) and treated with 3 equiv of mercuric acetate (eq 3). Aliquots were removed at various times and the alkylmercuric acetate reduced with alkaline sodium borohydride (eq 4). Oxidation of the

$$3\text{RCH}{=}\text{CH}_2 + \text{BH}_3 \xrightarrow{\text{THF}} (\text{RCH}_2\text{CH}_2)_3\text{B} \qquad (2)$$

$$(\text{RCH}_2\text{CH}_2)_3\text{B} + 3\text{Hg(OAc)}_2 \xrightarrow{\text{THF}} 3\text{RCH}_2\text{CH}_2\text{HgOAc} + \text{B(OAc)}_3 \qquad (3)$$

---

(1) National Science Foundation Fellow, 1967–1970.

(2) (a) A. Michaelis, *Ber.*, 27, 244 (1894); (b) K. Torssell, *Acta Chem. Scand.*, 13, 115 (1959); (c) W. Koenig and W. Scharrnbeck, *J. Prakt. Chem.*, **128**, 153 (1930); (d) G. Wittig, G. Keicher, A. Rueckert, and P. Raff, *Ann.*, **563**, 110 (1949); (e) J. B. Honeycutt, Jr., and J. M. Riddle, *J. Amer. Chem. Soc.*, **82**, 3051 (1960).

(3) E. Krause and R. Nitsche, *Ber.*, **54**, 2784 (1921).

(4) C. S. Marvel, C. G. Gauerke, and E. L. Hill, *J. Amer. Chem. Soc.*, **47**, 3009 (1925).

(5) C. S. Marvel and H. O. Calvery, *ibid.*, **45**, 820 (1923).

(6) H. C. Brown and B. C. Subba Rao, *ibid.*, **78**, 5694 (1956).

(7) (a) H. C. Brown and M. K. Unni, *ibid.*, 90, 2902 (1968); (b) H. C. Brown and R. M. Gallivan, Jr., *ibid.*, 90, 2906 (1968); (c) H. C. Brown and R. L. Sharp, *ibid.*, **90**, 2915 (1968).

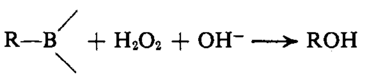
Table I. Conversion of Terminal Olefins into Primary Alkylmercuric Halides *via* Hydroboration–Mercuration

Olefin (100 mmol)	Mercuric acetate, mmol	Temp, °C	Time, min	Product	Isolated yield,[a] %	Mp,[b] °C (lit. mp)	Ref
1-Butene	94	0	5	*n*-Butylmercuric chloride	93	127.5 (127.5)	*d*
Isobutylene	100	0	30	Isobutylmercuric chloride	94	48.5–48.7 (49)	*e*
1-Butene	94	25	1	*n*-Butylmercuric chloride	93	127.5–127.8 (127.5)	*d*
1-Butene	94	25	1	*n*-Butylmercuric bromide	92	130–130.5 (129)	*d*
1-Butene	94	25	1	*n*-Butylmercuric iodide	91	114–114.5 (117)	*d*
1-Hexene	94	25	2	*n*-Hexylmercuric chloride	95	121.8–122 (125)	*f*
1-Dodecene	94	25	15	*n*-Dodecylmercuric chloride	98	114–114.7 (114.5)	*g*
α-Methylstyrene	100	25	15	2-Phenyl-1-propylmercuric chloride	97	55.5–56.0	
β-Pinene	100	25	30	*cis*-Myrtanylmercuric chloride	98	127–127.4	
3,3-Dimethylbutene-1	94	25	240	3,3-Dimethyl-1-butylmercuric chloride	94	133.8–134.0 (133–133.5)	*h*
Methyl 10-undecenoate	94	25	2	Methyl 11-chloromercuriundecanoate	97	97.5–98.0[c]	

[a] Based on mercuric acetate. [b] Recrystallized from 95% ethanol. [c] Recrystallized from methanol. [d] Reference 4. [e] Reference 9 [f] Reference 10. [g] Reference 11. [h] Reference 12.

$$RHgOAc + BH_4^- \longrightarrow RH + Hg^0 \qquad (4)$$

residual organoborane with alkaline hydrogen peroxide (eq 5) and gas chromatographic examination of



$$R{-}B\langle + H_2O_2 + OH^- \longrightarrow ROH \qquad (5)$$

the resulting alcohols indicated the extent of reaction.

Tri-*n*-butylborane gave no 1-butanol and 6% 2-butanol after 5 min of reaction at 0°. Consequently, all of the primary alkyl groups had reacted, leaving unreacted the 6% of secondary alkyl groups formed in the hydroboration.[8]

Triisobutylborane required 30 min at 0° for complete reaction of all alkyl groups.

Tri-*sec*-butylborane gave no reaction at 0° and less than 5% reaction after refluxing for 15 hr, indicating the inertness of the *sec*-alkyl groups.

Reaction of tri-*n*-butylborane and triisobutylborane with mercuric acetate at room temperature gives an extremely rapid exothermic reaction, but signs of decomposition are soon apparent.

Preparation of Alkylmercuric Halides *via* Hydroboration. This extraordinarily rapid reaction of the organoboranes derived from 1-butene and isobutylene with mercuric acetate suggested that this reaction should be quite general for terminal olefins. A number of terminal olefins were hydroborated in tetrahydrofuran and the resulting organoboranes were treated at room temperature with sufficient mercuric acetate to convert only the primary alkyl groups to the corresponding alkylmercuric acetate. These compounds were readily converted into the more easily handled alkylmercuric halides[9–12] by addition of water and reaction with the appropriate sodium halide. The resulting precipitate was collected, washed with water, and dried in a vacuum desiccator. Greater than 90% isolated yields were obtained in all cases. The results are summarized in Table I.

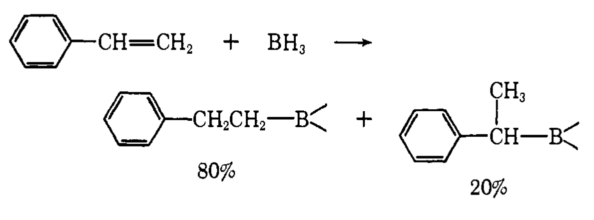
In the case of low-melting alkylmercuric halides, such as isobutylmercuric chloride (mp 49°), the tetrahydrofuran must be removed under vacuum before addition of the aqueous sodium halide solution in order to isolate a solid product.

The structural proof of all new compounds was accomplished by bromo- or iododemercuration of the organomercurial in pyridine according to the procedure of Jensen[13] (eq 6) and comparison of the alkyl halide

$$RHgX + X_2 \longrightarrow RX + HgX_2 \qquad (6)$$

by glpc with an authentic sample obtained by direct bromination[14] or iodination[15] of the organoborane. Elemental analysis for carbon, hydrogen, and mercury provided further proof of structure.

Hydroboration–Mercuration of Styrene. Hydroboration of styrene places 20% of the boron on the secondary carbon atom[8] (eq 7). It was of interest to know if



(7)

the benzylic alkyl group would react with mercuric acetate. Under experimental conditions similar to those of 1-butene earlier, the organoborane derived from styrene was mercurated at room temperature. Gas chromatographic examination of the α- and β-phenylethyl alcohols indicated the reaction was over in 5 min. At that time 87% of both primary and benzylic groups had reacted, indicating that the benzylic group is extremely reactive. Repetition of this ex-

---

(8) H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.*, **82**, 4708 (1960).

(9) W. K. Wilde, *J. Chem. Soc.*, 73 (1949).

(10) K. H. Slotta and K. R. Jacobi, *J. Prakt. Chem.*, **120**, 272 (1929).

(11) R. N. Meals, *J. Org. Chem.*, **9**, 211 (1944).

(12) F. C. Whitmore and H. Bernstein, *J. Amer. Chem. Soc.*, **60**, 2626 (1938).

(13) F. R. Jensen and L. H. Gale, *ibid.*, **82**, 148 (1960).

(14) H. C. Brown and C. F. Lane, unpublished data.

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

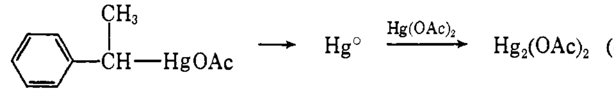
Table II. Conversion of Terminal Olefins into Primary Alkylmercuric Halides *via* Hydroboration–Mercuration using Dicyclohexylborane

Olefin (100 mmol)	Time, min	Product	Isolated yield, %	Mp,[a] °C (lit. mp)	Ref
1-Hexene	5	*n*-Hexylmercuric chloride	98	121.5–121.8 (125)	*b*
Styrene	3	2-Phenylethylmercuric chloride	99	165.5–166 (165)	*c*
α-Methylstyrene	5	2-Phenyl-1-propylmercuric chloride	96	55.2–55.5	
4-Vinylcyclohexene	5	2-(4-Cyclohexenyl)ethylmercuric chloride	93	112.8–113	

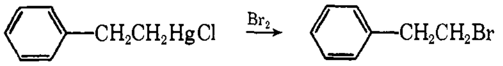
[a] Recrystallized from 95% ethanol. [b] Reference 11. [c] Reference 18.

periment using only enough mercuric acetate for the primary groups to react (80%) indicated only 55% reaction of the primary group and 81% reaction of the benzylic group after 10 min. These results suggest that the benzylic alkyl group reacts competitively if not faster than the primary alkyl group.

The incomplete reaction appears to be due to removal of mercuric acetate by reaction with metallic mercury, formed by decomposition of the benzylic mercurial (eq 8). The total amount of unreacted alkyl groups in both experiments corresponds closely to the amount of benzylic groups which have reacted, as one would expect.


(8)

Consistent with this view is the fact that only 2-phenylethyl bromide was obtained upon bromodemercuration of the once recrystallized alkylmercuric chloride (95% ethanol) obtained from styrene (eq 9). Metallic mercury and insoluble mercury salts were also present in the crude reaction product.


(9)

Mercuration Using Dialkylboranes. The difficulties with styrene suggested the use of dialkylboranes as hydroborating agents in the conversion of terminal olefins to alkylmercuric halides. 9-Borabicyclo[3.3.1]nonane (9-BBN),[16] disiamylborane,[17] and dicyclohexylborane[17] are dialkylboranes of large steric requirements which exhibit high selectivity in the hydroboration of terminal olefins, placing 99% of the boron at the terminal position. The apparent inertness of secondary alkyl groups suggested that after hydroboration with these reagents the primary alkyl group should react preferentially. 1-Hexene was chosen as a representative terminal olefin and hydroborated with each of these dialkylboranes.

The mercuration of B-*n*-hexyl-9-BBN was followed by our previously mentioned reduction–oxidation technique. The reaction with 1 equiv of mercuric acetate was very fast (1 or 2 min), presumably due to the openness of the boron atom. Analysis after 5 min, however, showed 12% of the *n*-hexyl groups unreacted and a similar amount of cyclooctanol (from reduction of the cyclooctylmercury compound obtained by opening of the 9-BBN bicyclic ring system). Similar ring opening has been observed in a number of reactions involving 9-BBN.

n-Hexyldisiamylborane undergoes a very slow reaction with mercuric acetate with some slight decomposition apparent. However, a 94% isolated yield of *n*-hexylmercuric chloride was obtained after 24 hr.

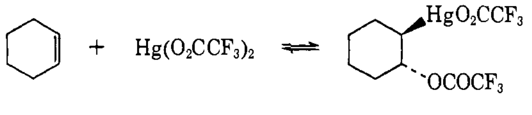
n-Hexyldicyclohexylborane, being a less hindered borane than that of disiamylborane, was found to give a very rapid quantitative reaction. Work-up after 5 min reaction time gave a 98% isolated yield of *n*-hexylmercuric chloride.

Several representative olefins were hydroborated with dicyclohexylborane, treated with mercuric acetate, and worked up as previously mentioned. A simple washing with cold pentane (0°) removed the dicyclohexylborinic acid and gave excellent yields of the corresponding alkylmercuric halides.

Use of dicyclohexylborane solved the difficulty with styrene and a 99% yield of 2-phenylethylmercuric chloride[18] was realized. Dicyclohexylborane is also highly valuable in achieving selective hydroboration of dienes[17] and of many olefins containing reactive functional groups near the double bond, as in allyl cyanide, ethyl vinylacetate, and allyl benzoate.[19] Consequently, this approach should be very valuable for such derivatives. The applicability of dicyclohexylborane for such selective reactions was tested with 4-vinylcyclohexene. The results are summarized in Table II.

Again, removal of the tetrahydrofuran on a vacuum pump prior to sodium halide addition was necessary to obtain solid material when low-melting compounds were involved (*e.g.*, 2-phenyl-l-propylmercuric chloride, mp 55.5–56°). A simple pentane (−50°) wash then removed most of the dicyclohexylborinic acid and gave a 96% yield of product.

It was of particular interest to us to know if mercuration of an organoborane could be accomplished in the presence of a double bond. It has been found in this laboratory that mercuric trifluoroacetate reacts rapidly and reversibly with olefins in aprotic solvents[20] (eq 10).


(10)

Such a reaction with mercuric acetate would make the synthesis of unsaturated alkylmercuric salts impossible. Fortunately, mercuric acetate was found to give only 8% reaction with cyclohexene in tetrahydrofuran after 42 hr.[20] This result now makes possible the synthesis of derivatives containing residual double bonds,

---

(16) E. F. Knights and H. C. Brown, *J. Amer. Chem. Soc.*, **90**, 5280, 5283 (1968).

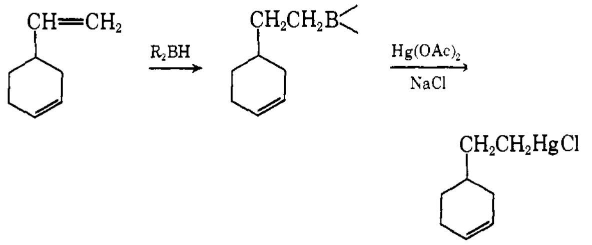
(17) G. Zweifel, N. R. Ayyangar, and H. C. Brown, *ibid.*, **85**, 2072 (1963).

(18) M. S. Kharasch and A. L. Flenner, *ibid.*, **54**, 674 (1932).

(19) H. C. Brown, G. W. Kabalka, and M. W. Rathke, *ibid.*, **89**, 4530 (1967).

(20) H. C. Brown and M.-H. Rei, *J. Chem. Soc., D*, 1296 (1969), and unpublished data.

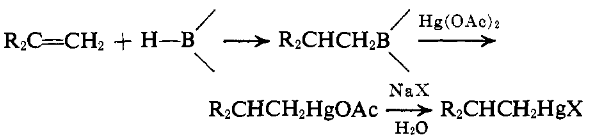
such as 2-(4-cyclohexenyl)ethylmercuric chloride (94% isolated yield), *via* selective hydroboration with dicyclohexylborane and mercuration of the organoborane (eq 11).



(11)

Discussion

Organoboranes derived from terminal olefins were found to undergo a rapid quantitative reaction with mercuric acetate at room temperature to give the corresponding alkylmercuric acetates. These compounds are readily converted into alkylmercuric halides by reaction with the appropriate sodium halide (eq 12).



$$R_2C{=}CH_2 + H{-}B\!< \longrightarrow R_2CHCH_2B\!< \xrightarrow{Hg(OAc)_2}$$

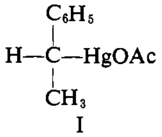
$$R_2CHCH_2HgOAc \xrightarrow[H_2O]{NaX} R_2CHCH_2HgX \quad (12)$$

This makes possible a simple procedure for the conversion of terminal olefins into primary alkylmercuric acetates and halides.

All three alkyl groups were found to react quite rapidly in tetrahydrofuran to give greater than 90% isolated yields in all cases (Table I). Secondary alkyl groups such as 2-butyl and cyclopentyl do not react under these reaction conditions. Thus, tri-*n*-butylborane which contains 6% *sec*-butylboron groups gives a 93% isolated yield of pure *n*-butylmercuric chloride.

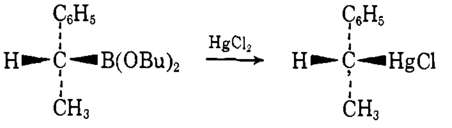
Mercuration followed by reduction might also provide a route *via* hydroboration to isomerically pure secondary organoboranes.

However, the secondary benzylic alkyl groups present in about 20% yield from the hydroboration of styrene proved to be very reactive, reacting competitively with the primary alkyl groups. This is not surprising since benzylboronic acid reacts more readily with mercuric chloride than do normal aliphatic boronic acids.[21] The apparent decomposition of 1-phenylethylmercuric acetate (I) in solution is similar to results found by Matteson and Bowie in their work on the stereochemistry of mercuri-deboronation of 1-phenylethaneboronic acid[22] (eq 13). They observed that when the reaction was run in aqueous acetone or dimethyl sulfoxide buffered with sodium acetate, the product II was contaminated with mercurous chloride. In fact mercurous chloride was the major product when the reaction was run in water alone. It seems likely that decomposition is initiated by solvolysis of the 1-phenylethylmercuric ion to mercury(0) and the 1-phenylethyl cation, a reaction characteristic of activated alkylmercuric ions.[23]



$$H{-}\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}{-}HgOAc$$

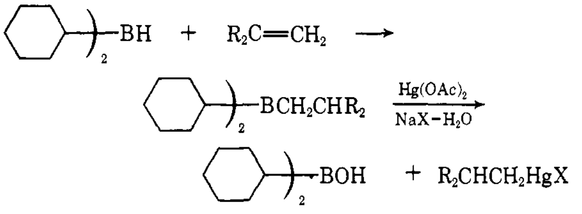
I



$$H\blacktriangleright\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}\blacktriangleleft B(OBu)_2 \xrightarrow{HgCl_2} H\blacktriangleright\overset{\displaystyle C_6H_5}{\underset{\displaystyle CH_3}{C}}\blacktriangleleft HgCl \quad (13)$$

II

Fortunately, the use of dicyclohexylborane circumvents the difficulties encountered with styrene (eq 14).

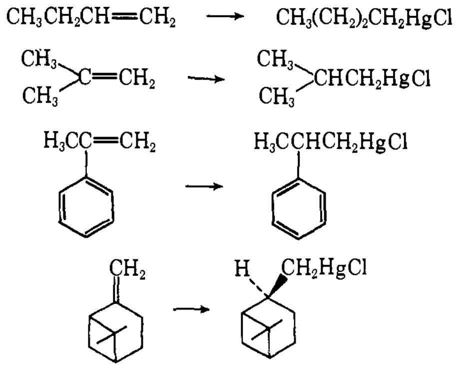


(14)

Excellent yields could be obtained with only a slight modification of the procedure using diborane (Table II). A simple washing with cold pentane or direct recrystallization of the solid gave pure alkylmercuric halides free of the borinic acid. The procedure using dicyclohexylborane is particularly desirable when a more selective hydroboration is required.

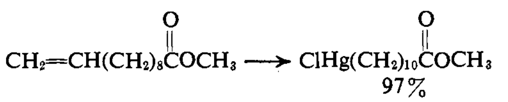
The mercuration reaction is tremendously sensitive to the steric hindrance about the boron atom. Tri-*n*-butylborane reacts in less than 5 min at 0°, while triisobutylborane requires 20–30 min at that temperature. Tri-*sec*-butylborane undergoes less than 5% reaction after refluxing for 15 hr in tetrahydrofuran. The organoborane derived from *t*-butylethylene also requires a surprisingly long time to react, presumably due to steric hindrance.

The reaction appears generally applicable as shown by the following transformations (eq 15).



(15)

It seems evident that many functional groups may be accommodated in this reaction which would not survive the standard procedures using a Grignard reagent. For example, hydroboration–mercuration of methyl 10-undecenoate gives a 97% isolated yield of the corresponding primary alkylmercuric chloride (eq 16). Double bonds are also readily accommodated as evidenced by the hydroboration–mercuration of 4-vinylcyclohexene (eq 17).



$$CH_2{=}CH(CH_2)_8\overset{\displaystyle O}{\overset{\|}{C}}OCH_3 \longrightarrow ClHg(CH_2)_{10}\overset{\displaystyle O}{\overset{\|}{C}}OCH_3 \quad (16)$$

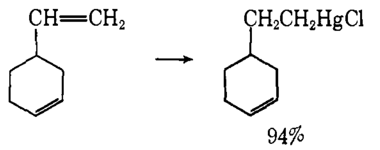
97%

---

[21] E. Khotinsky and M. Melamed, *Ber.*, **42**, 3090 (1909).

[22] D. S. Matteson and R. A. Bowie, *J. Amer. Chem. Soc.*, **87**, 2587 (1965).

[23] F. R. Jensen and R. L. Ouellette, *ibid.*, **83**, 4477, 4478 (1961).



(17)

Although we have only synthesized the alkylmercuric halides, it is obvious that this development makes a whole range of alkylmercuric salts readily available.

Jensen has established that alkylmercuric halides are reduced stereospecifically by magnesium to give high yields of dialkylmercury compounds with retention (85–97%) of configuration in both alkyl groups[24] (eq 18). The reaction does not appear to proceed

$$2R^*HgBr + Mg \longrightarrow R^*\text{-}Hg\text{-}R^* + MgBr_2 + Hg^0 \quad (18)$$

through a carbanion or Grignard reagent, and so should readily tolerate functional groups. Consequently, hydroboration–mercuration by the present procedure, followed by treatment with magnesium, should provide a convenient route to dialkylmercurials containing functional groups and retaining the stereochemistry present in the organoborane.[25] We are currently exploring the extension of the mercuration reaction to organoboranes containing secondary alkyl groups.

Experimental Section

Materials. All glassware was dried thoroughly in a drying oven and cooled under a stream of nitrogen. Tetrahydrofuran, diglyme, and all liquid olefins were dried over lithium aluminum hydride, distilled, and stored under nitrogen. 1-Butene, *cis*-2-butene, and isobutylene (99% pure grade) were obtained from the Phillips Petroleum Co. and used directly. Reagent grade mercuric acetate from J. T. Baker Chemical Co. was used. Sodium borohydride for the generation of diborane was obtained from Metal Hydrides, Inc.

Diborane Generation. Diborane was generated using the procedure of Brown and Sharp.[7c] Storage under nitrogen in the cold room for several months resulted in no measurable loss of hydride activity.

Hydroboration–Mercuration of Representative Olefins. Stock solutions of tri-*n*-butylborane, triisobutylborane, and tri-*sec*-butylborane (0.33 *M*) were prepared as follows. To a 250-ml volumetric flask flushed with nitrogen was added 35.5 ml of a 2.35 *M* solution of borane in tetrahydrofuran at 0° and 150 ml of tetrahydrofuran. Sufficient olefin was bubbled in at 0° to complete the hydroboration and the solution was stirred 1 hr at room temperature and filled to the mark.

Thirty-milliliter portions of the organoborane solution (10.0 mmol) were removed and placed in a 100-ml three-necked flask under a static pressure of nitrogen. Thirty millimoles of mercuric acetate (9.56 g) were added with vigorous stirring and 1-ml aliquots were removed at the appropriate times and added slowly to a well-stirred vial containing 0.5 ml of a 1 *M* sodium borohydride–3 *M* sodium hydroxide solution at 0°. After 15 min 1 ml of 6 *M* sodium hydroxide was added to the vial, followed by 1 ml of 30% hydrogen peroxide. The vial was warmed to 35–50° for 30 min to complete the oxidation. The alcohols were analyzed on a 5% Carbowax 20-M column using undecane as an internal standard.

Preparation of Alkylmercuric Halides *via* Diborane. A representative procedure is that utilized for the conversion of α-methylstyrene to 2-phenyl-1-propylmercuric chloride. A dry 300-ml flask equipped with septum inlet, thermometer well, side-arm flask, and magnetic stirrer, was flushed with nitrogen and then maintained under a static pressure of gas. The flask was charged with 82 ml of tetrahydrofuran and 11.8 g (100 mmol) of α-methylstyrene and placed in an ice bath. Hydroboration was accomplished by the dropwise addition of 17.9 ml of a 1.86 *M* solution of borane (100 mmol of hydride) in tetrahydrofuran. The solution was stirred for 1 hr at 25° and 31.9 g of mercuric acetate (100 mmol) was added from the attached flask. After stirring for 15 min, the suspension was poured into 400 ml of ice water, and 125 ml of a 1 *M* solution of the appropriate sodium halide (*i.e.*, sodium chloride) was added dropwise. The solid was collected by filtration, washed with generous quantities of water, and dried overnight in a vacuum desiccator. There was obtained 34.4 g (97% yield) of 2-phenyl-1-propylmercuric chloride, mp 55–56° (after two recrystallizations from 95% ethanol, mp 55.5–56°).

Anal. Calcd for $C_9H_{11}HgCl$: C, 30.43; H, 3.12; Hg, 56.47. Found: C, 30.21; H, 3.29; Hg, 56.37. Bromodemercuration yielded 2-phenyl-1-propyl bromide identical by glpc analysis with that obtained by direct bromination of the organoborane.[14]

By this procedure the following new compounds were prepared: *cis*-myrtanylmercuric chloride, mp 127–127.4° (*Anal.* Calcd for $C_{10}H_{17}HgCl$: C, 32.18; H, 4.59; Hg, 53.74. Found: C, 31.81; H, 4.56; Hg, 53.16); bromodemercuration gave *cis*-myrtanyl bromide identical by glpc with an authentic sample; methyl 11-chloromercuriundecanoate, mp 97.5–98° (*Anal.* Calcd for $C_{12}H_{23}O_2HgCl$: C, 33.11; H, 5.32; Hg, 46.08. Found: C, 33.18; H, 5.50; Hg, 46.32); bromodemercuration gave methyl 11-bromoundecanoate (glpc).

Isolation of isobutylmercuric chloride as a solid required removal of the tetrahydrofuran on a vacuum pump prior to addition of the sodium chloride solution. The results are summarized in Table I.

Bromo- and Iododemercuration. The following procedure is typical. One millimole of alkylmercuric chloride was dissolved in 4 ml of dry pyridine and 1 ml of 1 *M* bromine in pyridine was added at 0° and stirred for 1 hr. Ten milliliters of pentane was added and the solution poured into 10 ml of water. After filtration and separation of the organic layer, the aqueous phase was reextracted with 10 ml of pentane. The combined organic layers were washed consecutively with 10-ml portions of water, 10% hydrochloric acid, water, 5% sodium bicarbonate, and water. The pentane solution was dried over anhydrous magnesium sulfate and compared by glpc on a 10% SE-30 column with an authentic sample of alkyl halide.

Hydroboration–Mercuration of Styrene. A procedure identical with that described earlier for 1-butene, *cis*-2-butene, and isobutylene was employed. In individual experiments 30.0 mmol (100%) and 24.0 mmol (80%) of mercuric acetate were added. Analysis was by our previously described reduction–oxidation technique using *n*-hexadecane as an internal standard.

Mercuration Using Dialkylboranes. 9-BBN was prepared according to the procedure of Knights and Brown.[16] Twenty millimoles of 1-hexene (1.70 g) was added to 42 ml of a 0.48 *M* solution of 9-BBN in tetrahydrofuran. After stirring for 1 hr at room temperature, 6.38 g (20 mmol) of mercuric acetate was added and the reaction followed by the standard reduction–oxidation technique previously described.

Disiamylborane was prepared by slowly adding 14.16 g (200 mmol) of 2-methylbutene-2 (Phillips Petroleum Co., 99% pure grade) at 0° to 100 ml of a 1.0 *M* solution of borane in tetrahydrofuran and stirring for 24 hr at that temperature. One hundred millimoles of 1-hexene was added and the solution stirred for 1 hr at room temperature. One hundred millimoles of mercuric acetate (31.9 g) was added and the suspension stirred for 24 hr. The alkylmercuric acetate was worked up in the usual manner and the crude product washed with three 100-ml portions of cold pentane (0°) to wash out the dicyclohexylborinic acid. There was obtained 30.0 g of *n*-hexylmercuric chloride (94%), mp 121.8–122° (lit.[10] mp 125°).

The dicyclohexylborane was prepared in a manner identical with disiamylborane except the 1-hexene was added after 1 hr at 0° and the resulting solution stirred overnight at room temperature. Addition of mercuric acetate, 5 min of reaction, and a work-up identical with that of disiamylborane yielded 31.3 g of *n*-hexylmercuric chloride (98%) mp 121.5–121.8° (95% ethanol).

By a similar procedure the following compounds were prepared: β-phenylethylmercuric chloride (99%), mp 165.5–166° (lit.[18] mp 165°) and 2-(4-cyclohexenyl)ethylmercuric chloride (94%), mp 112.8–113°.

Anal. Calcd for $C_8H_{13}HgCl$: C, 27.83; H, 3.79; Hg, 58.10. Found: C, 27.69; H, 3.90; Hg, 58.40. Iododemercuration gave 2-(4-cyclohexenyl)ethyl iodide.

The low melting point of 2-phenyl-1-propylmercuric chloride necessitated removal of the tetrahydrofuran under vacuum prior to addition of the sodium halide in order to obtain a solid product. After a simple pentane (−50°) wash, a 96% yield was obtained, mp 55.2–55.5° (95% ethanol). The results of these reactions are summarized in Table II.

---

[24] F. R. Jensen and J. A. Landgrebe, *J. Amer. Chem. Soc.*, **82**, 1004 (1960).

[25] This and other routes to dialkylmercurials are currently under investigation in these laboratories by Jerry D. Buhler.