Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

ORGANOBORANES
XI. A STUDY OF THE MERCURATION OF ORGANOBORANES CONTAINING SECONDARY ALKYL GROUPS

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(Received July 17th, 1970)

SUMMARY

The reaction of mercury(II) salts with trialkylboranes containing secondary alkyl groups is far more sluggish than the corresponding reaction of trialkylboranes with primary alkyl groups and only two of the three secondary alkyl groups react. The relative rates of reaction of a variety of mercury(II) salts with tricyclopentylborane are reported. The reactivities of a representative series of tri-sec-alkylboranes towards mercuric benzoate were found to decrease in the order: cyclopentyl > cyclohexyl > cyclooctyl > sec-butyl > norbornyl. The mercuration of tri-*exo*-norbornylborane proceeds with predominant retention of configuration. The reaction of mercuric benzoate with tricyclopentyl- and tricyclohexylboranes gives good yields of the corresponding alkylmercuric salts, but organoboranes containing more bulky alkyl groups exhibit exceedingly slow rates and the resulting decomposition of the organomercurials limits the synthetic utility of the reaction.

INTRODUCTION

Organoboranes derived from terminal olefins via hydroboration undergo a rapid quantitative reaction with mercuric acetate at room temperature in tetrahydrofuran (THF) to give the corresponding alkylmercuric acetates[1] (eqn. 1).

$$2\,RCH{=}CH_2 + BH_3 \xrightarrow{THF} (RCH_2CH_2)_3B \xrightarrow[THF]{3\,Hg(OAc)_2} 3\,RCH_2CH_2HgOAc + B(OAc)_3 \quad (1)$$

This development provides a major new route to a variety of organomercurials, including those containing functional substituents. Organoboranes containing secondary alkyl groups, such as sec-butyl and cyclopentyl, do not react under such mild conditions.

Recent work has confirmed the facile reaction of primary trialkylboranes with mercury(II) salts and indicated that tri-sec-alkylboranes will also react[2]. Thus, Tufariello and Hovey report that 20% yields of bromocyclohexane can be obtained by

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* National Science Foundation Fellow 1967–1970.

the mercuration/bromodemercuration of tricyclohexylborane. This work has prompted us to report in detail our work on the mercuration of organoboranes containing secondary alkyl groups.

RESULTS AND DISCUSSION

Introduction

Whereas tri-n-butylborane undergoes complete reaction with mercuric acetate in 5 min at 0°, tri-sec-butylborane gives only about 5% reaction after refluxing 15 h in THF. Tricyclopentylborane, however, undergoes complete reaction in 8 h under these same conditions*.


(2)

Only two of the three alkyl groups, however, were utilized (eqn. 2). The mercuration of tricyclopentylborane was studied more thoroughly to determine the effect of various reaction parameters and to see if a faster, more convenient procedure could be found in order that the reaction might be successfully extended to a wide variety of secondary aliphatic groups.

Effect of solvent

The effect of the following solvents on the reaction of tricyclopentylborane and mercuric acetate at 65–70° was studied: n-hexane, THF, diglyme, and *N,N*-dimethylformamide (DMF). Diglyme and THF required 7–8 h for complete reaction. n-Hexane was very much slower, apparently the result of the very low solubility of mercuric acetate in this solvent. Although mercuric acetate was completely soluble in DMF, the reaction was not significantly faster than in THF and only one alkyl group reacted. This interesting result appears to be due to strong coordination of the solvent with the mercuric acetate, reducing its electrophilicity. Mercuric acetate reacts relatively rapidly at 65° with dimethyl sulfoxide (DMSO), making this an undesirable solvent. Methanol was not used because of the earlier observation that the reaction of tri-n-butylborane and mercuric acetate in this solvent effectively halts after the cleavage of only one alkyl group, instead of the usual three. Ether solvents would appear to strike a reasonable compromise between solubility and electrophilicity of the mercuric acetate.

Effect of temperature

The effect of increasing the temperature on the rate of reaction and on the product stability was examined. THF (b.p. 66°), 1,4-dioxane (b.p. 101°), and diglyme (b.p. 162°) were chosen as suitable ether solvents of increasing boiling point. Two and three equivalents of mercuric acetate were used. The reaction proceeded very rapidly at 120° and 162° in diglyme, but did not give complete reaction of two alkyl groups even with three equivalents of mercuric acetate. Colored solutions and insoluble mercurous salts appeared during these reactions. Decreasing the temperature of the

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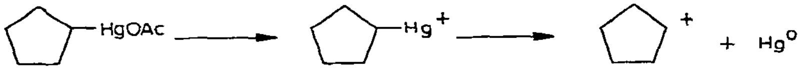
* The extent of reaction was determined by following the disappearance of the alkyl groups attached to boron.

reaction led to slower but more complete reaction. Refluxing dioxane and THF gave complete reaction of two alkyl groups using three equivalents of mercuric acetate, but even refluxing THF gave only about 82% reaction when only two equivalents were used. The product apparently decomposes at elevated temperatures perhaps via the following pathway (eqn. 3). The solvolysis of alkylmercuric salts has been



(3)

$$Hg^0 + Hg(OAc)_2 \longrightarrow Hg_2(OAc)_2$$

suggested to follow a similar path[3], and in at least one case the solvolysis reaction has been found to be first order in mercuric acetate[4]. Temperatures above 66° do not appear feasible in the mercuration of tri-sec-alkylboranes.

Effect of mercury salt

The reactivities of a variety of mercury(II) salts were investigated to determine the relative reactivities and product stabilities. The following approximate order of decreasing reactivity of the mercury(II) salt towards tricyclopentylborane was found:

nitrate $\geqslant$ trifluoroacetate $>$ benzoate $>$ n-butyrate $\geqslant$ fluoride $>$ acetate $>$ phthalate

The rate of reaction of mercury(II) salts with tricyclopentylborane roughly parallels the strength of the conjugate acids, exceptions being in part due to varying solubilities in THF. Although mercuric nitrate and trifluoroacetate give the fastest reaction at room temperature, even at this temperature these salts undergo considerable decomposition before the reaction is complete. The much greater rate of decomposition in reactions of these salts over that of mercuric acetate is what one would expect if the decomposition proceeds through ionization to an alkylmercuric ion as in eqn. (3). Mercuric fluoride also undergoes a very slow reaction at room temperature, but gives 68% reaction after refluxing for 1 h in THF. Here again considerable decomposition occurs and the reaction appears to be of little synthetic use.

The much greater product stability in the reaction of mercuric acetate allowed the use of the higher temperature of refluxing THF to achieve a greatly enhanced rate. However, the rather low solubility of mercuric acetate in THF still appeared to hinder the rate of the reaction, and suggested that perhaps more soluble mercury salts of other organic acids might provide a more convenient rate of reaction. The following salts were prepared and treated with tricyclopentylborane to test this hypothesis: mercuric benzoate, mercuric n-butyrate, and mercuric phthalate. Indeed, greatly enhanced rates were realized with mercuric benzoate and n-butyrate, both of which proved to be highly soluble under the reaction conditions. Mercuric phthalate, however, was much less soluble in refluxing THF and was therefore less satisfactory. In the reactions of mercuric acetate, n-butyrate and benzoate, some decomposition of the product occurs, and this prevents achieving complete reaction of the two alkyl groups with only two equivalents of the salt. Of the three salts, mercuric benzoate gives the fastest reaction and proceeds to transfer about 91% of two alkyl groups to mercury. Thus, mercuric benzoate appears to be the most desirable mercury salt for the conversion of tri-sec-alkylboranes to the corresponding monoalkylmercurials.

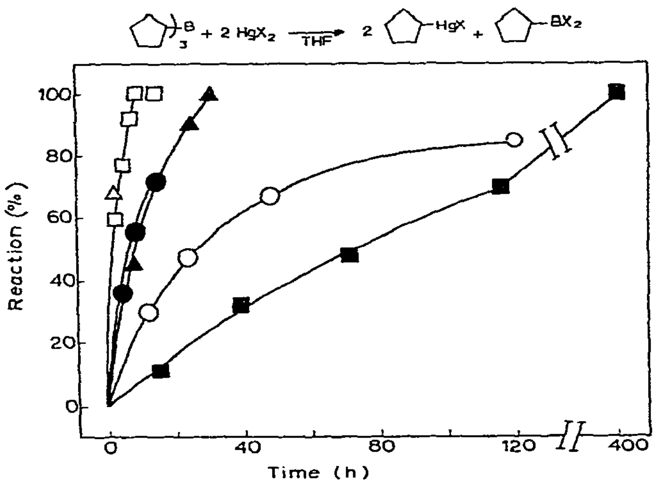


Fig. 1. Effect of mercury(II) salt (3 equivalents): ▲, $Hg(NO_3)_2$ 25°; △, HgF_2 66°; ■, $Hg(OAc)_2$ 25°; □, $Hg(OAc)_2$ 66°; ●, $Hg(O_2CCF_3)_2$ 25°; ○, $Hg(O_2CCF_3)_2$ 0°.

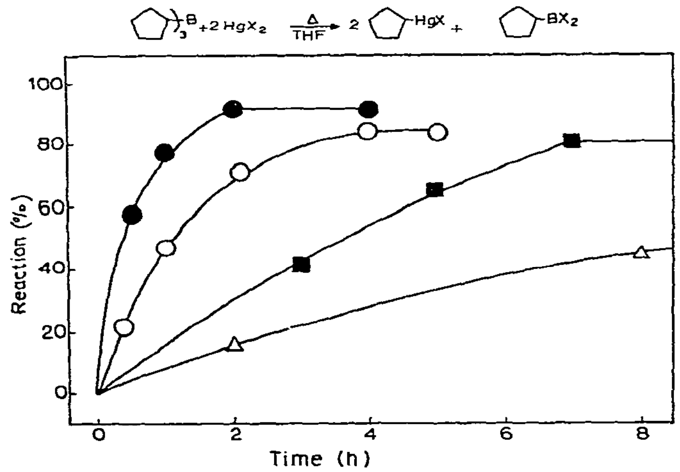
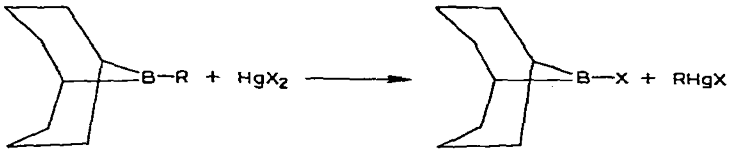


Fig. 2. Effect of mercury(II) carboxylates: ●, $Hg(O_2CC_6H_5)_2$; ○, $Hg(O_2CCH_2CH_2CH_3)_2$; ■, $Hg(OAc)_2$; △, $Hg[(O_2C)_2C_6H_4]$.

Mercuration of unsymmetrical secondary alkylboranes

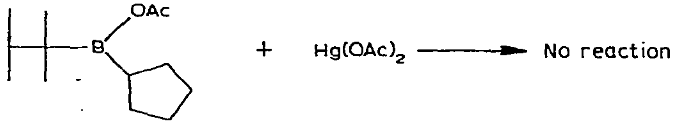
This procedure limited the yield of alkylmercuric salt to a maximum of 66%, based on starting olefin. It was hoped that the use of a suitable organoborane for the hydroboration stage might make possible the complete conversion of starting olefin to organomercurial.

Unfortunately, the presently applied dialkylboranes do not appear to be suitable for effecting the complete utilization of starting olefin. Primary dialkylboranes are unsatisfactory, because of the rapid transfer of primary alkyl groups in preference to secondary groups[1]. Moreover, the mercuration of trialkylboranes derived from di-sec-alkylboranes would be expected to exhibit little selectivity among the three sec-alkyl groups. It was hoped, however, that the reaction of *B*-sec-alkyl-9-borabicyclo[3.3.1]nonanes[5] (*B*-alkyl-9-BBN) might proceed with preferential cleavage of the desired sec-alkyl group, leaving the bridgehead secondary groups intact (eqn. 4). Numerous reactions of *B*-alkyl-9-BBN's are known to proceed in such a manner[6]. Consequently, the reaction of *B*-cyclopentyl-9-BBN with one equivalent of mercuric acetate at room temperature was investigated. The reaction proceeded remarkably rapidly, probably the result of the openness of the boron atom in these compounds. However, analysis revealed that approximately 90% of the cyclopentyl groups were still attached to the boron. Consequently, the fast reaction must involve a rupture of the cyclooctyl–boron bond, possibly favored by the relief of strain in the bicyclic system*.



(4) .

It was then hoped that the use of organoboranes derived from the mono-tert-alkylborane, thexylborane[7], might lead to preferential attack at the sec-alkyl group. Accordingly, thexylcyclopentylboron acetate (I) was prepared, and its reaction with mercuric acetate investigated. However, compound (I) gave no transfer of the cyclopentyl group in 18 h of refluxing in THF (eqn. 5). The steric hindrance of the thexyl group is apparently sufficient to prevent any reaction from occurring.



(5)

(I)

Dimethyl alkylboronates are now readily available by the reaction of trialkylboranes with trimethyl borate in the presence of a catalytic amount of "borane"[8] (eqn. 6). Unfortunately, dimethyl cyclopentylboronate gave no reaction in 16 h of refluxing with mercuric benzoate. It thus appears that ordinary sec-alkylboronic esters are also unreactive towards mercury(II) salts**.

$$R_3B+2\,B(OCH_3)_3 \xrightarrow{\text{cat. }BH_3} 3\,RB(OCH_3)_2 \tag{6}$$

Thus far all attempts to bring about the complete conversion of starting olefin to organomercurial have failed. Mercuric benzoate, however, provides a means of converting two of the three alkyl groups of tri-sec-alkylboranes to alkylmercuric salts.

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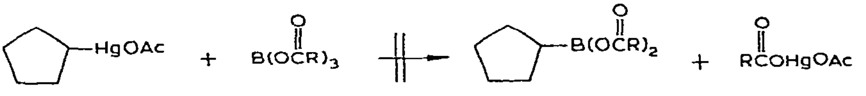
* B-n-Hexyl-9-BBN was found to give about 88% attack at the n-hexyl group and 12% attack at the bridgehead carbon atoms[1].

** sec-Benzylboronic esters react very readily, however. See ref. 9.

Kinetics vs. thermodynamics

The question still remains as to why only two of the three sec-alkyl groups of tri-sec-alkylboranes react relatively slowly, while all three alkyl groups react with remarkable ease in the case of primary trialkylboranes[1]. We were interested in establishing whether the incomplete reaction of the secondary derivative had its origin in kinetic or thermodynamic considerations. For example, is the difficulty in transferring the third secondary alkyl group merely a kinetic problem, or does the equilibrium actually favor retaining the last secondary alkyl group on boron rather than mercury.

We therefore refluxed cyclopentylmercuric acetate with boron triacetate* and boron tribenzoate* for 24 h to see if we could effect transfer of the cyclopentyl group from mercury to boron (eqn. 7). Oxidation of the alkyl groups on boron gave only a

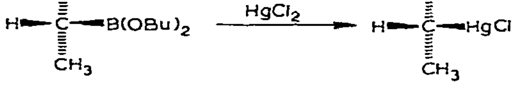


(7)

6% yield of cyclopentanol in both cases. An identical amount of elemental mercury was also present, suggesting that even this minor amount of cyclopentanol had probably arisen from decomposition of the organomercurial as in eqn. (3). The failure to achieve reaction does not rule out the thermodynamic argument. However, we presently feel that the failure to obtain transfer of the third sec-alkyl group in the reaction of tri-sec-alkylboranes is probably not due to the inability of the third group to react, but is due to the extremely slow rate of reaction of these groups.

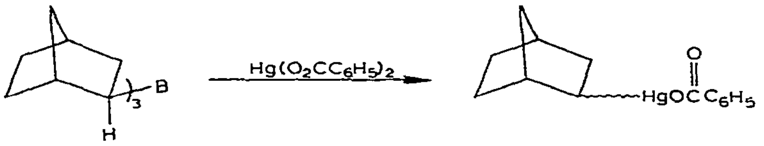
Stereochemistry

Matteson and Bowie have previously reported that the mercuri-deboronation of (*R*)-(−)-dibutyl 1-phenylethaneboronate (II) (eqn. 8) proceeds with net retention of configuration[11]. However, because of the optical instability of the product only 11–14% retention was found. We have attempted to determine the stereochemistry of the organomercurial formed in the mercuration of tri-*exo*-norbornylborane (>99% *exo*) (eqn. 9). Bromination in pyridine at −40° of aliquots of crude norbornylmercuric benzoate obtained after 12 and 24 h of reaction gave approximately 93/7 and 88/12 mixtures of *exo*/*endo* norbornyl bromides respectively. Bromination under these



(8)

(II)



(9)

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* We are aware of the possible dismutation of these compounds. See ref. 10.

conditions proceeds with complete retention of configuration[12]. Thus, the mercuration of trialkylboranes appears to proceed with predominant retention of configuration.

The *endo*-norbornyl bromide might have arisen in several different ways. Firstly, the reaction itself might proceed with some inversion, although we consider this unlikely. Secondly, the bromination step might be affected by impurities present in the crude product, since this reaction is known to be quite sensitive to solvent effects and radical initiators[13]. Finally, the rather strenuous reaction conditions required to obtain even a very minor amount of product quite likely leads to isomerization of the initially formed organomercurial. Since mercury has been found to have no conformational preference in the norbornyl system[4], isomerization of the initially formed *exo*-norbornylmercuric benzoate would lead to some *endo* product. The apparent increase in *endo*-norbornyl bromide with time suggests isomerization is in fact occurring. Thus, mercuration most likely proceeds with complete retention as in the presumably analogous protonolysis reaction[14].

Relative reactivities of representative tri-sec-alkylboranes

The relative reactivities of the following representative tri-sec-alkylboranes towards mercuric benzoate (two equivalents) were studied: cyclopentyl, cyclohexyl, cyclooctyl, sec-butyl, and norbornyl. The rates of reaction of these trialkylboranes were followed by watching the disappearance of alkyl groups attached to boron. The results of this study are illustrated in Fig. 3. The following order of decreasing reactivity was found:

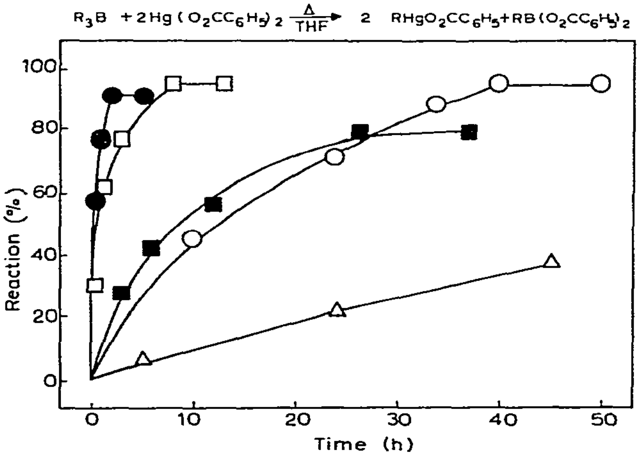

Fig. 3. Relative reactivities of tri-sec-alkylboranes: ●, cyclopentyl; □, cyclohexyl; ■, cyclooctyl; ○, sec-butyl; △, norbornyl.

cyclopentyl > cyclohexyl > cyclooctyl > sec-butyl > norbornyl.

The difference in reactivity of the different alkyl groups reflects the expected steric hindrance about the boron atom. Similar results were found with primary trialkylboranes[1]. The percent reaction at which each of these reactions appeared to level off was as follows: cyclopentyl, 91 %; cyclohexyl, 95 %; cyclooctyl, 79 %; sec-butyl, 95 %;

and norbornyl 50–60 %. These percentages reflect the extent of reaction of the trialkylborane, but not the amount of the product present.

Mechanism

The mercuration of organoboranes exhibits all the characteristics of an electrophilic substitution reaction. The following order of decreasing reactivity appears to hold in this reaction: aryl, vinyl > prim-alkyl > sec-alkyl > tert-alkyl. Although there is no way of predicting a priori such a reaction sequence for electrophilic reactions, similar substituent effects have been observed in each of the following well characterized electrophilic cleavage reactions: bromination of organotin compounds[15], acid cleavage of unsymmetrical dialkylmercurials[16] and alkylmercuric iodides[17], and the "one-alkyl exchange" reaction between alkylmercuric salts and mercuric salts[18]. Numerous deviations in this pattern have been observed, however, and the role of steric effects is not yet clear.

Other presumably electrophilic cleavage reactions of organoboranes also follow this reactivity sequence. Secondary alkyl groups undergo protonolysis less readily than primary[19]. In the base induced bromination[20] and iodination[21] of organoboranes, secondary alkyl groups are again less reactive than primary. In fact, although the halogenation reactions are extremely fast, primary trialkylboranes transfer one more alkyl group than secondary trialkylboranes.

The more ionic mercuric salts also tend to accelerate the rate of mercuration. Similar results have been found in the "one-alkyl" and "two-alkyl" exchange reactions of organomercurials[22].

The nature of the transition state in the mercuration of organoboranes cannot be determined from present data. However, the effect of various mercuric salts, the relative reactivities of various organoboranes, and the stereochemistry of the mercuration reactional suggest that the mercuration of organoboranes is an electrophilic substitution reaction which proceeds with retention of configuration.

Isolated yields

To determine the actual synthetic utility of the mercuration of tri-sec-alkylboranes, we have run preparative scale reactions (0.05 mole) and attempted to isolate the organomercurials as sec-alkylmercuric halides. The following trialkylboranes were refluxed with two equivalents of mercuric benzoate until the reaction was complete (reaction time in hours): cyclopentyl (2.5), cyclohexyl (7), cyclooctyl (28) and sec-butyl (48). Treatment with the appropriate sodium halide and subsequent work-up gave crude cyclopentylmercuric chloride and cyclohexylmercuric chloride in 93 % and 98 % yields respectively. The cyclohexyl compound did not appear to be as pure however. In the attempted synthesis of sec-butylmercuric iodide and cyclooctylmercuric chloride, only a small amount of sec-butylmercuric iodide was obtained upon recrystallization from 95 % ethanol, and none of the cyclooctyl compound could be obtained. The longer reflux times for these compounds apparently lead to considerable decomposition and limit the synthetic utility of this reaction.

EXPERIMENTAL SECTION

Materials

All glassware was dried thoroughly in a drying oven and cooled under a stream of nitrogen. THF and diglyme were dried over lithium aluminum hydride, distilled and kept under nitrogen. The n-hexane, DMF, DMSO, and all olefins were used directly as obtained commercially. The borane/tetrahydrofuran solution was prepared by the procedure of Brown and Sharp[23].

Preparation of mercury salts

Reagent-grade mercuric acetate, anhydrous mercuric nitrate, and mercuric fluoride were used directly as obtained commercially. Mercuric trifluoroacetate[24], mercuric benzoate[25], and mercuric n-butyrate[25] were prepared according to literature procedures.

The mercuric benzoate was dried either one week over calcium sulfate under a good vacuum or 1 h at 125° in an air oven; m.p. 161–162° (lit.[26] m.p. 160°). (Found: C, 36.82; H, 2.36. $C_{14}H_{10}HgO_4$ calcd.: C, 37.97; H, 2.28%.)

Mercuric n-butyrate was also prepared according to the literature procedure[25], but was recrystallized from n-butyric acid; m.p. 102–103°. (Found: C, 25.61; H, 3.69. $C_8H_{14}HgO_4$ calcd.: C, 25.64; H, 3.76%.)

Mercuric phthalate was prepared as follows. A solution of 20.42 g of potassium acid phthalate (0.10 mole) in 400 ml of water was slowly dripped into a well stirred solution of 31.87 g of mercuric acetate (0.10 mole) in 400 ml of water. The white precipitate was collected by vacuum filtration, washed with water and air dried. Drying 3 h in an air oven at 125° yields 33.6 g (92%) of mercuric phthalate; m.p. >300°. (Found: C, 26.12; H, 1.34. $C_8H_4HgO_4$ calcd.: C, 26.35; H, 1.11%.)

Mercuration of tricyclopentylborane

A 1 *M* stock solution of tricyclopentylborane in THF was prepared in the usual manner. A typical procedure involved addition of 10 ml of the stock solution (10 mmoles of organoborane) to 20 ml of THF. The mercuric salt (20 or 30 mmoles) was added to this solution under nitrogen and allowed to react at the appropriate temperature. The solvent was changed by removal of the THF under vacuum and addition of the new solvent. Analysis was accomplished by reducing the organomercurial with alkaline sodium borohydride and oxidizing the remaining organoborane[1]. GLC analysis of the cyclopentanol on a 5% Ucon 50 LB 550X column using n-undecane as an internal standard indicated the amount of unreacted alkyl groups.

Mercuration of unsymmetrical secondary alkylboranes

The mercuration of *B*-cyclopentyl-9-BBN was carried out by adding 30 mmoles of mercuric acetate (9.56 g) to 60 ml of a 0.5 *M* solution of the organoborane in THF[5].

Thexylcyclopentylboron acetate (I) was prepared by the following procedure. Twenty mmoles of thexylborane[7] (16.7 ml of 1.2 *M* THF solution) at 0° was added to 1.37 g of cyclopentene (20 mmoles) at 0° under nitrogen in a 100 ml roundbottom flask fitted with a reflux condenser. After stirring 1 h at 0°, this solution was added dropwise to a solution of 1.20 g of acetic acid (20 mmoles) in 5 ml of THF at 0°. After stirring 1 h, 20 mmoles of mercuric acetate was added and brought to reflux.

GLC analysis as above for cyclopentanol indicated no reaction.

Dimethyl cyclopentylboronate (30 mmoles) was refluxed with mercuric benzoate (30 mmoles) in 60 ml of THF. GLC analysis as above at 16 h showed no reaction.

Kinetics vs. thermodynamics

The boron tricarboxylates were prepared by adding 1.15 ml of 2.60 *M* BH_3/THF (3.0 mmoles) to 9 ml of 1 *M* carboxylic acid (9.0 mmoles) in THF under nitrogen at room temperature over 10 min. Quantitative hydrogen evolution was obtained*. Three mmoles of cyclopentylmercuric acetate (m.p. 54–54.6°) was added and the solution refluxed 24 h. n-Undecane was used as an internal standard. Reduction, oxidation, and GLC analysis were carried out as described earlier. Metallic mercury was filtered out, washed with acetone, and weighed.

Stereochemistry

The mercuration of tri-*exo*-norbornylborane was carried out as with tricyclopentylborane, and 1 ml aliquots were removed at 12 and 24 h and placed in vials. After removal of THF on a vacuum pump, 2 ml of pyridine was added, and 1 ml of 1 *M* bromine in pyridine was dripped in slowly at $-40°$. Workup was as described previously[1]. GLC analysis was carried out on a $20' \times \frac{1}{4}''$ 5% Zonyl E-7 column at 85°.

Relative reaction rates of representative tri-sec-alkylboranes

These rates were followed as in the case of tricyclopentylborane using an appropriate internal standard.

Isolated yields

The following procedure is typical. Fifty mmoles of mercuric benzoate (22.2 g) was added to 75 ml of 0.33 *M* organoborane and refluxed the appropriate length of time. This solution was then poured into 400 ml of ice water, and the THF removed under vacuum. One hundred ml of a 1 *M* solution of the appropriate sodium halide was added dropwise. After neutralization of the acidic solution, the solid was collected by filtration, washed with water, 3 x 50 ml of 50% glycerin, more water, and dried in a vacuum desiccator overnight. A crude yield was obtained, and the solid was recrystallized from 95% ethanol. Cyclopentylmercuric chloride (93%), m.p. 111.5–112° (lit.[27] m.p. 108.5°). Cyclohexylmercuric chloride (98%), m.p. 158–159° (lit.[28] m.p. 158°). Sec-butylmercuric iodide, m.p. 54° (lit.[29] m.p. 54°).

ACKNOWLEDGEMENT

This work was supported by funds from a National Science Foundation Fellowship.

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* Pelter *et al.* failed to obtain quantitative hydrogen evolution with benzoic acid, because of their more dilute solutions (private communication). See ref. 10.

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