are presumably identical, so that the reaction must follow the pathway indicated in eq 4. Alternatively, alkyl displacement of the chloride must be rapid, possibly catalyzed by the aminoborane itself.

The use of alkyldichloroboranes provides for the first time a highly useful stereospecific synthesis of secondary amines. The reaction is rapid and gives excellent yields for a wide variety of alkyl and aryl groups. However, for this reaction to be synthetically useful, we required a simple general preparation of the alkyldichloroboranes. The successful development of such a synthesis is reported in the accompanying communication.[2] Aryldichloroboranes may be readily prepared by the method of Hooz and Calgada.[3]

(12) (a) National Science Foundation Predoctoral Fellow, 1970–1972; (b) Postdoctorate Research Associate on Grant No. GM 10937 from the National Institutes of Health.

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Received December 22, 1972

Reaction of Representative Olefins with Dichloroborane Ethyl Etherate Induced by Boron Trichloride. An Exceptionally Simple, General Synthesis of Alkyldichloroboranes and Alkylboronic Acid Derivatives *via* Hydroboration

Sir:

Representative olefins fail to react in pentane with dichloroborane diethyl etherate, $BHCl_2:OEt_2$, at any significant rate. However, the addition of 1 mol equiv of boron trichloride induces a rapid reaction. This procedure provides a simple, general synthesis of alkyldichloroboranes, $RBCl_2$, and their derivatives. The alkyldichloroboranes are easily isolated by distillation after separating the solution from the precipitated solid. Alternatively, they can be converted to the corresponding boronic acid esters by adding the alcohol to the reaction mixture and the esters recovered. Consequently, this procedure provides a simple and straightforward synthesis of monoalkyl boron derivatives.

Monochloroborane diethyl etherate, $BH_2Cl:OEt_2$, in diethyl ether solution readily reacts with a variety of olefins, providing an exceptionally simple synthesis of dialkylchloroboranes.[1] The need for representative monoalkyldichloroboranes in our studies[2] led us to explore the possible reaction of dichloroborane, $BHCl_2$, with olefins as a route to these compounds. The reaction of olefins with $BHCl_2$ is extremely slow in THF.[3,4] We discovered that the reaction is also slow in diethyl ether, in contrast to the fast reaction of BH_2Cl in this solvent. In benzene solution, or neat, dichloroborane diethyl etherate, $BHCl_2:OEt_2$, reacted with terminal olefins almost completely in several hours at 25°. However, the product was mainly dialkylchloroborane, R_2BCl, and not the desired $RBCl_2$.

Presumably, the reason for the low reactivity of $BHCl_2:OEt_2$ toward olefins is the strong complexation between the strongly acidic $BHCl_2$ and the basic Et_2O components, considerably larger than that involved in the case of BH_2Cl. It was thought that the complexed ether molecule could be removed by using a stronger Lewis acid. If so, the synthesis of undisproportionated $RBCl_2$ might be achieved. Indeed, the presence of boron trichloride in a mixture of the olefin and reagent in inert solvents resulted in a rapid reaction (eq 1).

$$BHCl_2:OEt_2 + \text{olefin} + BCl_3 \longrightarrow RBCl_2 + BCl_3:OEt_2 \quad (1)$$

For example, addition of $BHCl_2:OEt_2$ to a benzene solution of equivalent amounts of 1-octene and BCl_3 at 0° resulted in the uptake of 99% of the olefin in 5 min. When 1-butene was used in place of 1-octene, the quantitative formation of *n*-$BuBCl_2$ was observed (*n*-$BuBCl_2$ was analyzed by glpc as *n*-$BuB(OCH_3)_2$ after methanolysis). However, the solubility of $BCl_3:OEt_2$ introduced difficulties in the isolation of $RBCl_2$ in pure form from the benzene solution. The use of pentane as the reaction medium circumvented these difficulties.

Addition of $BHCl_2:OEt_2$ to a mixture of olefin and BCl_3 in pentane at 0° resulted in the precipitation of a white, thick solid, $BCl_3:OEt_2$, on the sides of the flask. Within 5 min after the addition of $BHCl_2:OEt_2$, 90% of the olefin had undergone the reaction at 0°. On warming to room temperature, the remaining olefin was converted within 15 min. Simple distillation of the pentane solution, after separation from the solid $BCl_3:OEt_2$, provides the monoalkyldichloroborane in yields of 80–90%. Alternatively, the alkylboronic acid esters can be obtained by simply adding excess alcohol at 0°. The reaction is quite general, as shown by the fact that olefins of such a wide range of structure as 1-octene, *cis*-2-octene, 2-methyl-1-pentene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, cyclohexene, and styrene all were readily converted into the corresponding alkyldichloroboranes or the esters. The results are summarized in Table I.

Table I. Synthesis of Alkyldichloroboranes and Dimethyl Alkylboronates by the Hydroboration of Olefins with Dichloroborane Ethyl Etherate Induced by Boron Trichloride

Alkyldichloroborane or Dimethyl Alkylboronate	Yield, %	Bp, °C (mm Hg)
$RB(OCH_3)_2$, R =		
1-Butyl	90[a]	
2-Butyl	88[a]	
2-Methyl-1-propyl	97[a]	
Cyclopentyl	76[b]	76–78 (40)
$RBCl_2$, R =		
2-Methyl-1-butyl	87[b]	110–112 (746)
1-Hexyl	81[b]	102–104 (100)
3-Hexyl	77[b]	88–90 (102)
Cyclopentyl	79[b]	136–138 (751)
trans-2-Methylcyclopentyl	80[b]	94–96 (110)
exo-Norbornyl	83[b]	95–98 (50)

[a] Glpc yield. [b] Isolated yield. The $RBCl_2$ was identified by methanolysis and characterizing the $RB(OCH_3)_2$ by pmr. The regiospecificity and the stereospecificity of the products were established by glpc analysis of the isomeric alcohols produced in the usual oxidation of the $RBCl_2$ with alkaline hydrogen peroxide.

The $BHCl_2:OEt_2$ was prepared by slowly adding with stirring a 1.3–1.5 *M* solution of lithium borohydride in diethyl ether to a 1.3–1.4 *M* solution of BCl_3 in diethyl ether at 0°,[5] in accordance with the reaction shown in

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eq 2. (Approximately 5–10% of excess BCl_3 was used

$$LiBH_4 + 3BCl_3 + 4Et_2O \longrightarrow 4BHCl_2{:}OEt_2 + LiCl\downarrow \quad (2)$$

to ensure that the product was free of BH_2Cl.) The mixture was stirred for 2 hr at 0° and kept overnight in a cold room (0–5°). The solution was then decanted or filtered from precipitated lithium chloride. The excess ether was removed at room temperature with a water aspirator (30 mm) until constant weight of the contents was realized (6–8 hr). The $BHCl_2{:}OEt_2$ thus obtained is a clear liquid. It is not stable at room temperature for more than 2 days, but can be stored in a cold room (0–5°) for 2 or so weeks without difficulty. The reagent was analyzed by hydrolyzing aliquots—the hydrogen gas evolved gave the hydride content and the hydrochloric acid formed gave the chloride content. The preparation used contained 4–6% excess $BCl_3{:}OEt_2$. The neat reagent is 6.6 *M* in $BHCl_2{:}OEt_2$.

The following procedure for the synthesis of cyclopentyldichloroborane and dimethyl cyclopentylboronate is representative. A dry 300-ml round-bottom flask kept under nitrogen was charged with 100 mmol (8.8 ml) of cyclopentene, 100 mmol of BCl_3 in pentane (50 ml), and 127 ml of dry pentane. The mixture was cooled in an ice bath and 100 mmol of $BHCl_2{:}OEt_2$ (15.1 ml) was slowly added over a period of 15 min, while vigorously stirring the contents of the flask. The stirring was continued for 15 min at 0°. Then the reaction mixture was brought to room temperature and stirred for another 15 min. The contents of the flask were cooled to 0° and the pentane solution was siphoned into another flask through a glass tube fitted with a fritted disk under a positive pressure of nitrogen. The $BCl_3{:}OEt_2$ in the reaction flask was washed twice with pentane at 0°, and the washings were collected along with the main solution. The pentane was then removed using a water aspirator. Cyclopentyldichloroborane was obtained in 79% yield by distillation at 136–138° (751 mm). The purity of the product was checked by methanolysis and analysis of the dimethylboronate by pmr.

For the synthesis of dimethyl cyclopentylboronate, the above procedure was followed. After stirring at room temperature for 15 min, the reaction mixture was cooled to 0° and 50 ml of methanol was added slowly while stirring. Stirring was continued for 0.5 hr at 0°. The solvent, HCl, and $B(OCH_3)_3$ were removed using a water aspirator and the dimethyl cyclopentylboronate was distilled at 76–78° (40 mm). The product was obtained in 76% yield. The material was identified by pmr and comparison with an authentic sample.

The conventional methods for the synthesis of $RBCl_2$ are the exchange reactions of BCl_3 and BR_3 in the presence of boron hydrides at elevated temperature,[6,7] the reaction of trialkylboroxines with BCl_3,[8] and the reaction of tetraalkyltin compounds with BCl_3.[9] These are time consuming multistep syntheses and generally the overall yields are low. More seriously, the exchange reaction often causes considerable isomerization involving migration of the boron atom.[7] The procedure reported here is much simpler and possesses the enormous advantage in that the $RBCl_2$ is obtained in pure form in pentane solution. Thus, these reagents can be used directly in pentane solution,[2] without isolation, or they can be easily isolated from such solution in the pure state.

The syntheses of trialkylboranes and dialkylboron derivatives *via* hydroboration have been previously accomplished.[1,10] The present development provides an exceptionally simple hydroboration procedure for the general synthesis of monoalkylboron derivatives. Thus, we are now in a position to synthesize tri-, di- and monoalkylboron compounds *via* hydroboration under mild conditions.

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Solvolysis of 1-Aryl-1-cyclopropyl-1-ethyl *p*-Nitrobenzoates. Evidence for Major Increases in Electron Supply by the Cyclopropyl Group with Increasing Electron Demand at the Cationic Center

Sir:

Increasing the electron demand at the carbonium ion center by varying the substituent on the aryl group results in major increases in rates of solvolysis of the *p*-nitrobenzoates of 1-aryl-1-cyclopropyl-1-ethyl as compared to the corresponding 2-aryl-3-methyl-2-butyl derivatives. This result is attributed to major increases in the electron supply by the cyclopropyl moiety, in contrast to that of the isopropyl groups, under the increasing demand by the cationic center. This result is in marked contrast to the behavior of the 2-aryl-2-*exo*-norbornyl *p*-nitrobenzoates, where the exo:endo rate ratios reveal no significant change in electron supply with increasing electron demand at the cationic center.

In the study of neighboring group effects, it has been postulated that the more stable the carbonium ion center, the less demand that center will make upon neighboring groups for additional stabilization through participation.[1] Gassman and Fentiman have shown that this postulate is valid for π participation in the 7-norbornenyl derivatives.[2] The ability of the π electrons in 7-aryl-7-*anti*-norbornenyl *p*-nitrobenzoates (I) to stabilize the developing carbonium ion center increases as a function of the electron demand of that center. Thus, the relative rate of I increases from 3.4 for *p*-anisyl to over 10^5 for 3,5-bis(trifluoromethyl)-phenyl in comparison to the corresponding 7-aryl-7-norbornyl derivatives (II).[2]

This postulate has never been tested for σ participation in carbon systems not containing π electrons. Therefore, we decided to examine the effect of increasing electron demand on the rates of solvolysis of the

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