thus apparent that the rate-limiting step involves loss of the sulfonate group, which would not be observed if there were rate-limiting Cope rearrangements to a highly reactive allylic sulfonate ester. Furthermore, the silver-assisted rearrangement of **3** or **5** occurs rapidly at −15°, while Cope rearrangement of **10** is rapid only above 140°.

The most attractive mechanism consistent with these data is that **3**, **5**, **7**, or **8** ionizes to carbonium ions in which Cope rearrangement to ions like **4** is then extremely rapid. An alternative path for the overall rearrangement involves solvolytic fragmentation of **3**, **5**, **7**, or **8** to an allylic cyclopentenyl cation bonded to a cyclopentadiene (**11**). Such a cation could then cyclize again to a cation like **4**. The major argument against this mechanism is that **11** could also have cyclized to **12**, the less-hindered exo isomer, and no product derived from this is detected in any of our solvolytic studies. If some special overlap is invoked in the cyclization of **11** to favor endo closing, the bonding (**13**) for the cyclization transition state would be similar to that in the Cope rearrangement transition state. Some slight participation of the double bond in the solvolyses is indicated by our finding that the solvolysis rate of nosylate **8** is 1.5 times the rate for its 2,3-dihydro analog; this would be consistent with either the fragmentation or the Cope rearrangement mechanism.

Although this is the first example of an apparent solvolytic Cope rearrangement, studies[3,5,6] on 8-ketones related to **10** indicate that they undergo relatively rapid Cope rearrangements and that these rearrangements are facilitated by protonation of the carbonyl oxygen. It is not surprising that these processes are facilitated by a conjugating carbonium ion as a substituent on a Cope rearrangement system: the six delocalized electrons of the Cope transition state can conjugate with the external carbonium ion much as the six electrons of a benzene ring stabilize (and *ipso facto* are stabilized by) the positive carbon in a benzylic cation. An alternate description is that the carbonium ion formed begins to fragment toward a structure like that of **11**, but the new bond then begins to form before the fragmentation is complete.

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Ronald Breslow,* Jacob M. Hoffman, Jr.
Department of Chemistry, Columbia University
New York, New York 10027
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Rapid Reaction of Representative Olefins with Monochloroborane Diethyl Etherate. A Simple, Convenient Synthesis of Dialkylchloroboranes and Dialkylborinic Acid Derivatives

Sir:

Monochloroborane diethyl etherate, conveniently prepared by the reaction of boron trichloride diethyl etherate with lithium borohydride in diethyl ether, readily hydroborates a variety of olefins at 0° to give the corresponding dialkylchloroboranes in excellent yields. The dialkylchloroboranes thus formed are easily isolated as such by distillation under reduced pressure. Alternately, they are readily converted into borinic acid esters *in situ* by treatment with alcohols. This provides a very simple and convenient general synthesis of dialkylchloroboranes and its derivatives *via* hydroboration.

The redistribution of trialkylboranes with boron trichloride and boric acid esters, generally at elevated temperatures, provides the basis for the methods generally used in the past for the synthesis of dialkylchloroboranes and dialkylborinic acid esters, respectively.[1,2] Unfortunately, these methods are often difficult to apply, especially for the synthesis of relatively large amounts required as synthetic intermediates. Recent developments[3-6] in our laboratory have established that these compounds are exceptionally valuable synthetic intermediates. Consequently, we sought a convenient synthesis of dialkylchloroboranes and dialkylborinates. Since hydroboration of olefins with BH_3 etherates provides an exceptionally simple synthesis of trialkylboranes,[7] it appeared that hydroboration by monochloroborane etherates[8] might provide an analogous simple route to dialkylchloroboranes.

Actually, studies of the hydroboration of olefins by monochloroborane, BH_2Cl, have already been reported.[9-11] These studies utilized BH_2Cl in tetrahydrofuran. In this solvent the reaction of olefins with BH_2Cl is very slow and incomplete. We undertook to overcome this difficulty by increasing the concentrations of the reactants and the reaction temperature. The reaction rates were greatly improved. However, analysis of the reaction products revealed that the reactions were not proceeding to the formation of the desired R_2BCl products, as had been assumed previously.[9]

For example, from 4 *M* 1-butene and 2 *M* BH_2Cl in THF at 0° (6 hr) there was obtained 35% *n*-Bu_3B, 20% *n*-Bu_2BCl, and 45% *n*-$BuBCl_2$. Similarly, at 25° (12 hr) 2 *M* 1-butene and 1 *M* BH_2Cl in THF yielded a product which analyzed for 60% *n*-Bu_3B, 10% *n*-Bu_2BCl, and 30% *n*-$BuBCl_2$. Under the same conditions *cis*-2-butene yielded 62% *sec*-Bu_3B, 1% *sec*-Bu_2BCl, and 37% *sec*-$BuBCl_2$.[12]

It occurred to us that the reason for this very low reactivity of BH_2Cl in THF could be the strong complexation of the reagent with the highly basic THF, rendering the boron atom much less reactive toward the olefin. The rate and relatively long reaction times could also be responsible for the observed complexity of the prod-

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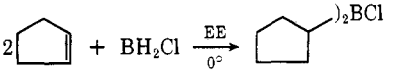
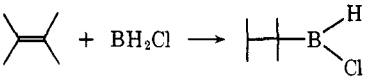
ucts. Accordingly, we undertook to investigate the reaction of olefins with BH_2Cl in less basic solvents, such as diethyl ether and diglyme. Indeed, it was observed that the reaction of 1-hexene with BH_2Cl is very fast, both in diethyl ether and in diglyme. Even more important, the products were the simple dialkylchloroboranes we desired. Since diethyl ether is a more convenient medium for preparative reactions than diglyme, the former was selected for detailed study.

The rates of reaction of the representative olefins (1.0 *M*), 1-hexene, *cis*-3-hexene, 2-methyl-2-butene, norbornene, cyclopentene, styrene, cyclohexene, and tetramethylethylene, with BH_2Cl (0.5 *M*) in diethyl ether at 0°, were examined. In the case of 1-hexene, *cis*-3-hexene, 2-methyl-2-butene, cyclopentene, and norbornene, 2 mol of olefin/mol of BH_2Cl was taken up in 1 hr. The reactions with cyclohexene and styrene were more sluggish, requiring 2 and 16 hr, respectively. In these cases, the product of the reaction is the dialkylchloroborane, established by distillation and characterization of the reaction products (eq 1).



(1)

In the case of tetramethylethylene, 1 mol of olefin/mol of BH_2Cl was utilized in 15 min. No more olefin was consumed over a considerably additional period of time, indicating that the probable product in this case is the monoalkylchloroborane (eq 2).



(2)

Although these studies ulilized solutions which were 0.5 *M* in BH_2Cl and 1.0 *M* in olefin, it was established that the initial concentration of the reagents is not critical. We later standardized on solutions which were approximately 2.0 *M* in olefin and 1.0 *M* in BH_2Cl. Under these conditions the great majority of olefins reacted completely in 1 hr at 0°.

Table I. Synthesis of Dialkylchloroboranes and Methyl Dialkylborinates by the Hydroboration of Representative Olefins with Monochloroborane in Diethyl Ether at 0°

Dialkylchloroborane or methyl dialkylborinate	Yield, %	Bp, °C (mm)	$n^{20}D$
Di-*n*-hexylchloroborane	84[a]	74–76 (0.3)	
Methyl di-*n*-butylborinate	93,[b] 77[a]	56–58 (5.0)	1.4144
Methyl di-*sec*-butylborinate	99[b]		
Methyl diisobutylborinate	96[b]		
Dicyclopentylchloroborane	80[a]	68–69 (1.0)	
Methyl dicyclopentylborinate	84[a]	82–84 (2.0)	1.4705
Methyl di-*exo*-norbornylborinate[c]	83[a]	96–100 (0.5)	1.5044

[a] Isolated. [b] Glpc. [c] Stereochemistry assumed from the known stereochemistry of hydroboration of norbornene.

These experiments clearly establish that the hydroboration of olefins with BH_2Cl in diethyl ether provides a simple convenient method for the preparation of dialkylchloroboranes. Moreover, since chloroboranes are easily solvolyzed by addition of water or alcohols, this method can also be adapted to the preparation of dialkylborinic acids and esters (eq 3 and 4).

$$R_2BCl + H_2O \longrightarrow R_2BOH + HCl \quad (3)$$

$$R_2BCl + R'OH \longrightarrow R_2BOR' + HCl \quad (4)$$

Accordingly, a series of representative dialkylchloroboranes and/or the corresponding methyl dialkylborinates were synthesized and isolated using this facile reaction of BH_2Cl in ethyl ether with olefins. The results are summarized in Table I.

Since the reaction goes to completion in practically all cases, the crude product obtained by the removal of the solvent can usually be used directly for further synthetic applications. If needed, the pure products are easily isolated by distillation under reduced pressure.

The reagent was prepared for our studies by the reaction of lithium borohydride in diethyl ether with boron trichloride diethyl etherate at 0°, as indicated in eq 5. Excess diethyl ether was used as the solvent.

$$LiBH_4 + BCl_3 + 2Et_2O \longrightarrow LiCl + 2BH_2Cl{:}OEt_2 \quad (5)$$

This solution of monochloroborane etherate containing suspended lithium chloride can be used directly for the hydroboration and the isolation of the product. However, in cases where one would like to use the crude hydroboration product or its derivatives prepared *in situ* without isolation, the lithium chloride is essentially insoluble in the reaction mixture and can readily be separated by filtration or decantation.

The following procedure for the synthesis of dicyclopentylchloroborane and methyl dicyclopentylborinate is illustrative. To 25 mmol of boron trichloride in diethyl ether (1.58 *M*), taken in a 100-ml flask, previously flushed with nitrogen and kept at 0°, was added 25 mmol of lithium borohydride in diethyl ether (1.45 *M*) slowly, over a period of 15–20 min. The mixture was stirred at 0° for 15 min. Cyclopentene (100 mmol) was added to the stirred solution and the reaction mixture was maintained at 0° for 1 hr. The ether was then removed under vacuum and the dicyclopentylchloroborane was isolated by distillation at 68–69° (1.00 mm). The yield was 80%.

The methyl dicyclopentylborinate was prepared as follows. The above procedure was followed. One hour after the addition of the cyclopentene to the BH_2Cl solution, 100 mmol of methanol was added and the reaction mixture was stirred for 15 min at 0°. The solvent and the hydrogen chloride formed by the methanolysis of the dicyclopentylchloroborane were removed under vacuum, with a water aspirator. The methyl dicyclopentylborinate was isolated by distillation at 82–84° (2.0 mm). The product was obtained in 84% yield.

The present development thus provides a very simple, convenient, general procedure for the synthesis of dialkylchloroboranes and borinic acid derivatives. This is now of special significance in view of the valuable applications in organic synthesis now being discovered for these intermediates.[3–6]

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Herbert C. Brown,* N. Ravindran[13]
Richard B. Wetherill Laboratory
Purdue University, Lafayette, Indiana 47907
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