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TRANSFER REACTIONS INVOLVING BORON

XXVI*. A KINETIC STUDY OF THE LEWIS ACID CATALYZED DEALKOXYBORONATIONS OF β-ALKOXYORGANOBORANES*

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SUMMARY

The kinetics of the Lewis acid-catalyzed dealkoxyboronation of esters of *trans*-2-ethoxycyclohexaneboronic acid in a variety of donor solvents and with a variety of Lewis acids have been studied. It is concluded that the dealkoxyboronation reaction proceeds via a concerted *anti* elimination transition state in which probably two molecules of the donor solvent are intimately associated with the incipient boronium ion.

INTRODUCTION

β-Heterosubstituted organoboranes encountered in the hydroboration of vinyl[2,3] and allyl[4] derivatives can undergo three distinctly different types of β-elimination reactions: (1), *Syn* elimination occurring via a four-centered transition state: (2), *Anti* base-catalyzed elimination in which the base attacks the boron; and (3), *Anti* acid-catalyzed elimination in which a Lewis acid complexes with the β-heteroatom function to facilitate elimination[3].

The *syn* elimination has been shown to occur with β-alkoxyorganoboranes capable of attaining the appropriate geometry required for elimination[2a,3]. The base-catalyzed process was initially investigated by Matteson and Liedtke[5] in the base-catalyzed (water) debromoboronation of dibutyl *erythro*-2,3-dibromobutane-2-boronate and was shown to occur in a stereospecific *anti* manner. β-Chloro-, β-alkyl- and arylthio-, and β-alkoxy-organoboranes similarly have been shown to undergo *anti* base-catalyzed eliminations[3].

The acid-catalyzed process was first observed by Lewis and Pearce[6] in the carboxylic acid catalyzed elimination of *trans*-2-piperidinocyclohexaneboronic acid, and by Pasto and Cumbo[2a] in the boron trifluoride catalyzed dealkoxyboronation of β-alkoxyorganoboranes derived from ethoxycyclohexene and 1-ethoxy-4-tert-

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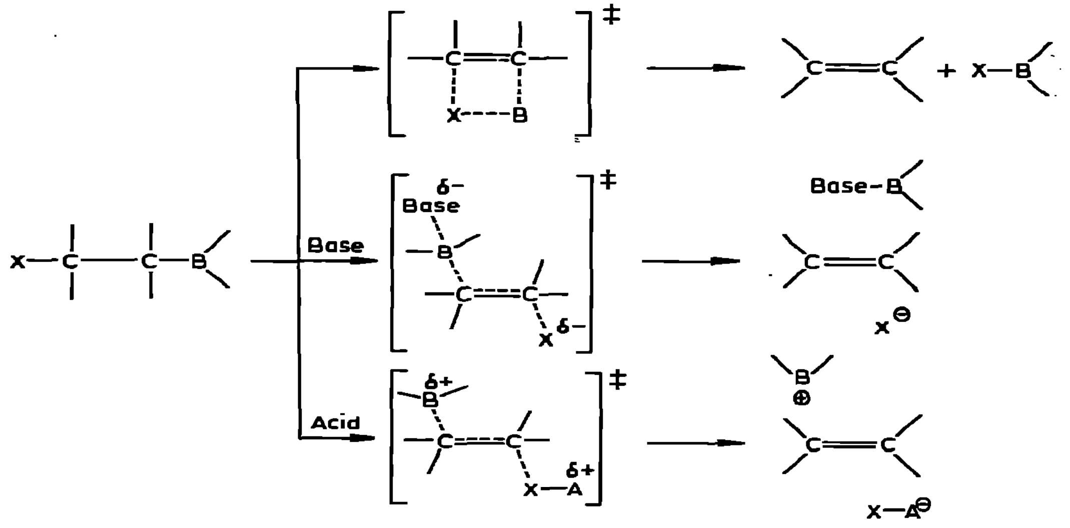


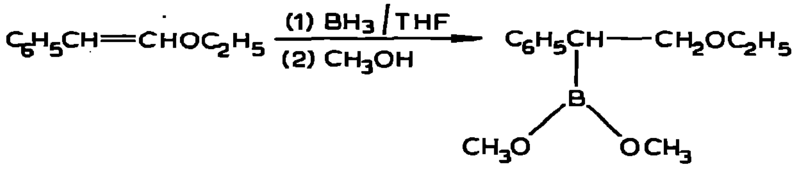
butylcyclohexene. The stereochemistry of the acid-catalyzed process was shown by Pasto and Snyder[3] to occur in a stereospecifically *anti* fashion.

The acid-catalyzed elimination process is formally analogous to the acid-catalyzed dehydration of alcohols in which the boron-containing moiety must initially be formed as a cationic species (boronium ion), a process which had not been previously investigated. Salts containing cationic boron species, however, had been prepared by Miller and Muetterties[7] and Ryschkewitsch and Garrett[8]; in all cases the cationic boron species (H_2B^+, $HClB^+$, or $HBrB^+$) being stabilized by coordination with two molecules of a donor ligand (*i.e.* $H_2BL_2^+$, etc., where L is a tertiary amine, phosphine, arsine, or a dialkyl sulfide).

The acid-catalyzed dealkoxyboronation reaction appeared to provide an excellent opportunity to study a process in which a boronium ion might be formed. A kinetic investigation of this reaction was thus undertaken to evaluate: (1), Effect of solvent on stabilization of the boronium ion; (2), Effect of substituents attached to boron on the stabilization afforded the boronium ion; and (3), Effect of the nature of the Lewis acid on the rate of elimination.

RESULTS

Initial efforts were directed toward the synthesis and study of dimethyl 2-ethoxy-1-phenyl-1-ethaneboronate (I), a substrate prepared and studied *in situ* in our earlier studies.

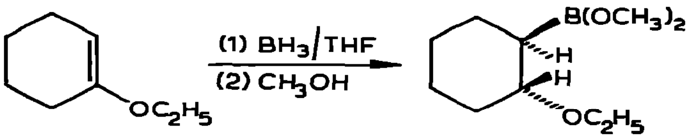


$$C_6H_5CH{=}CHOC_2H_5 \xrightarrow[(2)\ CH_3OH]{(1)\ BH_3/THF} C_6H_5\underset{\underset{CH_3O\ \ \ OCH_3}{B}}{CH}{-}CH_2OC_2H_5$$

(I)

Preparation of (I) by hydroboration of β-ethoxystyrene in tetrahydrofuran (THF) followed by methanolysis and attempted distillation produced styrene and trialkylborate. A more careful analysis revealed that on removal of the methanol and THF no elimination occurred until a 1/1 complex of (I) with THF (by NMR) was present. Attempted further distillation (even at high vacuum at 25°) resulted in decomposition of the 1/1 complex to give free (I) which then underwent the previously observed *syn* elimination. The two methoxy groups attached to the boron of (I) must not afford sufficient stabilization of the boron by resonance donation, further stabilization being afforded by complexation with THF which, on removal of the THF, must be provided by intramolecular (or possibly intermolecular) complexation with the ethoxy function ultimately resulting in elimination.

In order to circumvent this problem dimethyl *trans*-2-ethoxycyclohexaneboronate (II) was chosen for study. Boronate (II) was stable toward distillation and could be purified by vacuum distillation. The boronates (III) and IV) were prepared by treatment of *trans*-2-ethoxycyclohexylborane with excess ethylene glycol and phenol respectively. The borinate (V) was prepared by reaction of (II) with methylmagnesium iodide in ether at −78°C followed by hydrolysis, extraction with 1-butanol, and distillation [(V) could not be obtained in completely pure form, a small amount of the dibutyl ester of (II) being present].



(II)

The rates of the Lewis acid-catalyzed eliminations were measured by NMR techniques. Solutions of the organoborane and an internal standard (usually chloroform) in the appropriate solvent were placed in NMR tubes and a catalytic quantity (generally 2–5 mole per cent) of the Lewis acid-solvent complex[*] was added by means of a microsyringe. The rates of elimination were followed by periodic integration of the resonance signals of the internal standard and the vinyl hydrogen peaks of the product cyclohexene. The pseudo first-order rate constants were calculated in the usual manner using computer techniques. The second-order rate constants were calculated from the k_1's and the concentrations of the Lewis acid catalysts. The values of k_2 thus calculated were independent of the catalyst concentration (see Table 1).

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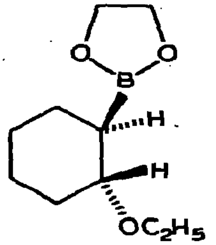
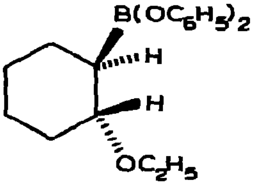
[*] It was demonstrated by ^{11}B NMR that redistribution between the ligands of the Lewis acids and the trialkylborate did not occur under the reaction conditions; i.e. the integrity of the Lewis acid catalyst was maintained during the course of the reaction. It was observed, however, that although ligand exchange between boron trifluoride and trimethylborate did not occur, ^{10}B–^{11}B redistribution occurs very rapidly (complete in < 1 min at 25°C in THF):

$$(CH_3O)_3\,{}^{*}B + {}^{11}BF_3 \xrightarrow[THF]{} (CH_3O)_3\,{}^{s}B + {}^{s}BF_3$$

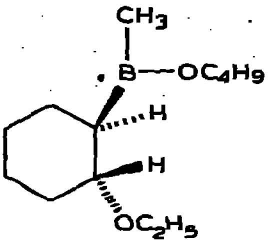
where *B indicates normal ^{10}B–^{11}B isotopic distribution and ^{s}B indicates a statistical isotopic distribution based on starting material isotopic contributions. (For a discussion of redistribution reactions in borane systems, see ref. 9).



(III)



(IV)



(V)

TABLE 1

RATE CONSTANTS FOR THE BF_3 CATALYZED DEALKOXYBORONATION OF (II) IN THF AT 42°C

(II) *(mol/l)*	*[BF_3·THF]* *(mol/l)*	k_1 *(sec⁻¹)*	k_2 *(l/(mol·sec))*
0.438	0.018	7.44×10^{-5}	4.11×10^{-3}
0.424	0.177	7.45×10^{-4}	4.20×10^{-3}
0.424	0.183	7.62×10^{-4}	4.17×10^{-3}

In general, two, or more, values of k_2 were determined, the values of k_2 appearing in the tables being average values.

The rate constants for the BF_3·THF catalyzed dealkoxyboronation in THF at various temperatures were determined (Table 2) giving $\Delta H^{*} = 1.4 \pm 0.4$ kcal·mol^{-1} and $\Delta S^{*} = -64 \pm 4$ cal/(mol·K) (standard state of l/(mol·sec) at 298 K).

TABLE 2

RATE CONSTANTS FOR THE CATALYZED DEALKOXYBORONATION OF (II) IN THF AT VARIOUS TEMPERATURES

T (K)	k_2 *(l/(mol·sec))*
300	3.77×10^{-3}
312	4.18×10^{-3}
331	4.44×10^{-3}
336	5.07×10^{-3}

The rate constants for the boron trifluoride catalyzed eliminations in various ether solvents are given in Table 3. Rate constants for the acid-catalyzed eliminations of (II) by various Lewis acids in THF are given in Table 4.

Rate constants for the BF_3·THF catalyzed dealkoxyboronations of (III), (IV) and (V) are given in Table 5.

DISCUSSION

In our initial investigation of the acid-catalyzed dealkoxyboronation reaction[2a]

TABLE 3

RATE CONSTANTS FOR THE BF_3 CATALYZED DEALKOXYBORONATION OF (II) IN VARIOUS ETHER SOLVENTS

Ether	*T* (°C)	$k_2 \times 10^3$ (l/(mol·sec))
Diisopropyl ether	40	2.11
Tetrahydrofuran	42	4.18
Diethyl ether	42	5.72
Tetrahydropyran	37	9.07
Dibutyl ether	40	9.73
Dipropyl ether	40	10.66

TABLE 4

SECOND-ORDER RATE CONSTANTS FOR THE DEALKOXYBORONATION OF (II) WITH VARIOUS LEWIS ACIDS IN THF AT 45°C

Lewis acid	*Relative Lewis acidity*[a]	k_2 (l/(mol·sec))
$(C_4H_9)_3B$	0[b]	[c]
$SbCl_3$	27	5.79×10^{-5}
BF_3	61	4.18×10^{-3}
$AlCl_3$	81	1.48×10^{-3}
BCl_3	100	7.3×10^{-3}[d]

[a] See ref. 10. [b] NMR evidence indicates that tributylborane does not complex with THF (see ref. 10 and 11). [c] No catalysis observed. [d] Approximate value only, extensive cleavage of THF by BCl_3 occurring under the reaction conditions. The value cited is for short reaction times.

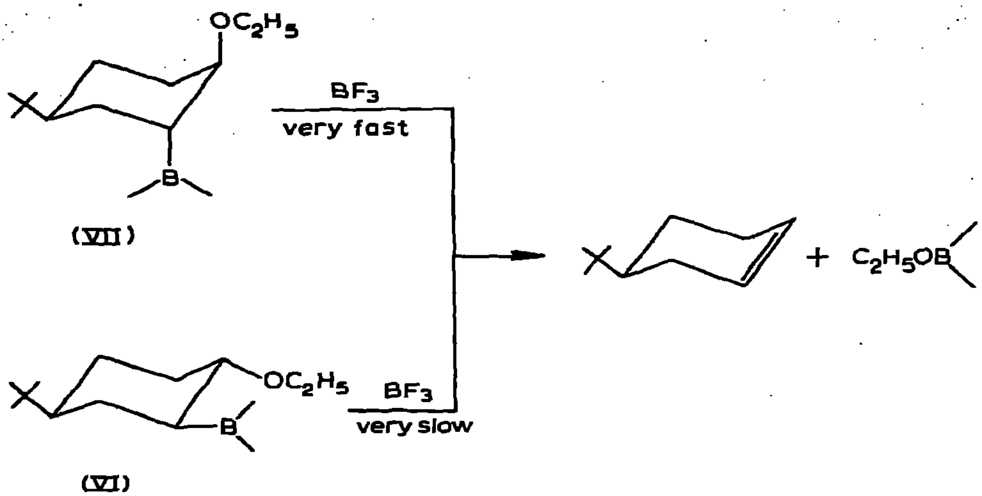
TABLE 5

RATE CONSTANTS FOR THE BF_3 CATALYZED DEALKOXYBORONATION OF (III), (IV) AND (V) IN THF AT 41°C

Substrate	k_2 (l/(mol·sec))
(II)	4.18×10^{-3}
(III)	4.83×10^{-6}
(IV)	1.49×10^{-4}
(V)	1.2×10^{-3}[a]

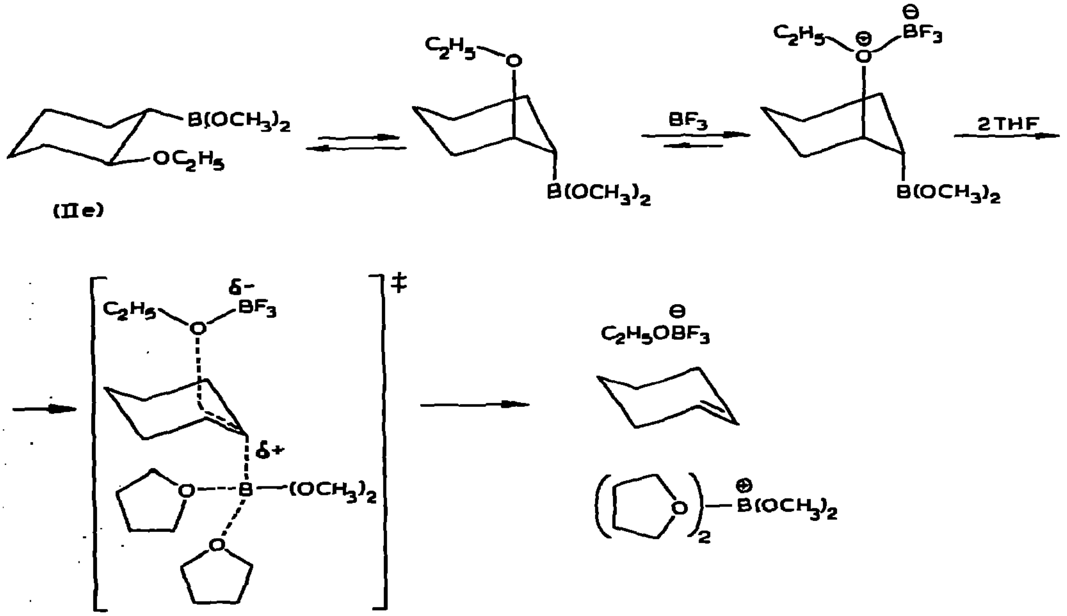
[a] Rate constant determined on a mixture of (V) with dibutyl *trans*-2-ethoxycyclohexaneboronate (see Experimental).

it was shown that of the two isomeric *trans*-2-ethoxy-5-tert-butylcyclohexylboranes (VI) and (VII) formed in hydroboration of 1-ethoxy-4-tert-butylcyclohexene, the diaxial isomer (VII) undergoes acid-catalyzed elimination considerably faster (≥100 times) than the diequatorial isomer (VI). This was attributed to better orbital overlap in the transition state for elimination with (VII) compared to (VI). It seems entirely reasonable, therefore, that in the present study the dealkoxyboronation of (II) occurs via the diaxial conformation (IIa).



The activation parameters for the BF$_3$-catalyzed dealkoxyboronation of (II) in THF, at first glance, appear to be highly unusual. The $\Delta S^{\ddagger}$ is unusually highly negative and suggests that extensive ordering of solvent must be occurring in the transition state. From the observations of Miller and Muetterties[7] and Ryschkewitsch and Garrett[8], and the magnitude of $\Delta S^{\ddagger}$, it would appear reasonable to suggest that two molecules of solvent may be intimately involved in the solvation stabilization of the incipient boronium ion as indicated in the transition state illustrated in Scheme 1.

SCHEME 1



The transition state illustrated in Scheme 1 suggests that changes in the donor ability of the solvent should result in substantial changes in the rate of reaction. Inspection of the results given in Table 3, however, does not wholly conform to expectation; the total range of rate constants is rather limited (< 10), and the sequence of rate constants not being that expected on the basis of the donor abilities of the solvent molecules. The effect of the solvent on the stabilization of the incipient boronium ion in the transition state is undoubtedly masked by the change in the "effective acidity" of the boron trifluoride; *i.e.* the greater the donor ability of the solvent, the more tightly is the boron trifluoride complexed with the solvent with the result that less of the substrate–BF_3 complex is formed thus producing a smaller apparent k_2: *i.e.* Substrate + Solvent–BF_3 $\rightleftarrows$ Substrate–BF_3 + Solvent.

The effect of the strength of the Lewis acid on the rate of elimination is much more obvious; the stronger the acid, the faster the rate of dealkoxyboronation (Table 4).

The effects of changing the nature of the functions attached to the boron atom present interesting comparisons. The k_2 for the BF_3-catalyzed dealkoxyboronation of the diphenyl boronate (III) is approximately 10^3 less than for the dimethyl boronate (II). The powerful inductive and resonance withdrawing effects of the phenyl groups, as well as their increased steric bulk, significantly reduce the stabilization afforded to the cationic boron by intra- and intermolecular means. Replacement of one methoxyl group by the non-donor methyl function reduces the rate of reaction only slightly; the stabilization provided by the remaining methoxyl and the two solvent molecules in the transition state offsetting the loss of the one methoxyl group.

The replacement of the two methoxyl groups by the ethylenedioxy function in (IV) results in a significant reduction in the rate of elimination. This is not unexpected. Kotz, Vanderzanden, and Cooks[12] have inferred from mass spectral studies that linear boronium ions are more easily formed than are non-linear species. This observation is consistent with theoretical predictions which indicate that species of the general type $\overset{+}{C}AB$ which contain 16 or fewer valence electrons are most stable when in a linear configuration[13]. The dialkoxyboronium ions contain 16 valence electrons about boron and the two oxygen atoms and, consequently, are expected to be most stable when linear. The interaction of the two solvent molecules in the transition state undoubtedly offsets the full effect of the dependence of the geometry of the species on the number of valence electrons present. The very distinct substituent effect is, thus, definitely consonant with the proposed concerted nature of the elimination process.

EXPERIMENTAL

Dimethyl trans-2-ethoxycyclohexaneboronate (II)

A solution of 15.0 g (0.12 mol) of ethoxycyclohexene in 25 ml of tetrahydrofuran was added dropwise to 72 ml of 1.87 *M* borane/tetrahydrofuran solution. The reaction mixture was stirred under a nitrogen atmosphere and maintained between 0 and −5°C by means of an ice/salt bath. Upon completion of the addition, the mixture was allowed to stir 10 min and a large excess of anhydrous methanol (40 ml, 1.2 mol) was carefully added. The solvent, excess methanol and trimethyl borate were removed under reduced pressure under a nitrogen atmosphere. The residue was distilled at

46.5–47.5°C at 0.60 mmHg (50 to 75% yield). NMR ($CDCl_3$) δ 1.12 (t, 3, $C\underline{H}_3CH_2$–), 1.50 (m, 9, ring hydrogens), 3.33 (m, 1, $C\underline{H}O$–), 3.54 (q, 2, –$C\underline{H}_2CH_3$), and 3.59 ppm (s, 6, $C\underline{H}_3O$–); ^{11}B NMR (neat) −32.2 ppm (s) (rel. to BF_3–etherate). Found: C, 60.25; H, 10.45; B, 5.58. $C_{10}H_{21}BO_3$ calcd.: C, 60.10; H, 10.57; B, 5.40%.)

2-(trans-2-Ethoxycyclohexyl)-1,3,2-dioxaborolane (III)

A solution of 1-ethoxycyclohexene (12.6 g, 0.10 mol) in 25 ml of dry tetrahydrofuran was added dropwise over a period of two hours to 75 ml of 1.47 *M* (0.11 mol) borane/tetrahydrofuran solution contained in a 3-neck flask maintained under a nitrogen atmosphere at −5° to 0°C and stirred. The reaction mixture was allowed to stir at 0°C for 15 min after the addition was complete. Ethylene glycol (6.2 g, 0.10 mol) dissolved in 50 ml of dry tetrahydrofuran was slowly added while the temperature of the reaction vessel was allowed to rise to room temperature. Following an additional two hours of stirring at room temperature 2 ml of methanol were added to quench any unreacted borane.

The reaction mixture was fractionally distilled using a vacuum jacketed distillation apparatus giving 14.3 g (72.2%) of 2-(2-*trans*-ethoxycyclohexyl)-1,3,2-dioxaborolane (III) which by NMR analysis was shown to contain a small amount of ethylene glycol. The distillate was dissolved in 20 ml of dry tetrahydrofuran and placed in a 50 ml 3-neck flask equipped with a stopper, nitrogen inlet, and reflux condenser. Borane/tetrahydrofuran (1.36 ml of 1.84 *M* solution, 2.5 mmol) was added and the mixture stirred at 50° for 22 h. After the mixture had cooled to room temperature 2 ml of methanol was added and the product was carefully distilled: b.p. 38–39°C/9.12 mmHg; NMR ($CDCl_3$) δ 1.11 (t, 3, –$C\underline{H}_3$), 1.58 (m, 9, ring hydrogens), 3.37 (m, 1, $C\underline{H}O$–), 3.73 (m, 2, –$C\underline{H}_2CH_3$), and 3.90 ppm (s, 4, –$OC\underline{H}_2$).

Diphenyl trans-2-ethoxycyclohexaneboronate (IV)

A solution of 1-ethoxycyclohexene (12.6 g, 0.10 mol) in 15 ml of tetrahydrofuran was added over a period of 2 h to 60.0 ml of 1.84 *M* borane/tetrahydrofuran maintained at −5°C in a 500 ml 3-neck flask equipped with condenser, nitrogen inlet, and a side-arm equilibrating addition funnel. After completion of the addition the reaction mixture was allowed to stir an additional 10 min and a solution of phenol (23.5 g, 0.25 mol) in 50 ml of tetrahydrofuran was added dropwise. The reaction mixture was then allowed to stir at room temperature until hydrogen evolution ceased. The solvent was removed by distillation and the residue was distilled giving diphenyl *trans*-2-ethoxycyclohexaneboronate (42%): b.p. 127–129°C/0.16 mmHg; NMR ($CDCl_3$) δ 1.25 (t, 3, –$C\underline{H}_3$), 1.53 (m, 9, ring hydrogens), 3.53 (m, 1, –$C\underline{H}O$–), 4.30 (m, 2, –$C\underline{H}_2$-CH_3), and 7.15 ppm (m, 10 aromatic ring hydrogens). (Found: C, 73.87; H, 7.63; B, 3.53. $C_{20}H_{25}BO_3$ calcd.: C, 74.09; H, 7.77; B, 3.33%.)

n-Butyl trans-2-ethoxycyclohexanemethaneborinate (V)

To a solution of 20.8 mmol of (II) in 30 ml of ether at −78°C contained in a 3-neck, round-bottom flask equipped with a reflux condenser, drying tube, and addition funnel with nitrogen inlet was added slowly (1 h) 40.0 mmol of methylmagnesium iodide in 20 ml of ether. The reaction mixture was stirred for 9 h at −78°C. The temperature of the reaction mixture was then allowed to rise to 0°C and 25 ml of 1 *N* hydrochloric acid was added with vigorous stirring. The entire reaction mixture was transferred to a separatory funnel and was extracted with two 25 ml portions of 1/1 1-butanol/ether. The combined extract was dried ($MgSO_4$) and fractionally distilled (71–73°C/10 mmHg giving a mixture of (V) (^{11}B NMR, −56.4 ppm) and dibutyl *trans*-2-ethoxycyclohexaneboronate (^{11}B NMR, −32.8 ppm) which could not be further separated.

Preparation of Lewis acid–solvent complexes

Boron trifluoride–ethyl etherate. Boron trifluoride–diethyl ether was purchased from Matheson, Coleman and Bell and was purified for use by the method described by Brown and Tierney[18].

Boron trifluoride–tetrahydrofuranate. Into a flame-dried 250 ml 3-neck flask fitted with a reflux condenser, thermometer, and gas bubbling tube was placed 75.0 ml of freshly dried and distilled tetrahydrofuran. The reaction vessel was vented from the top of the condenser first through a dry trap and then into a trap containing water to prevent boron trifluoride gas from escaping. The temperature of the tetrahydrofuran was maintained at 20°C and boron trifluoride was bubbled through the solution until absorption of boron trifluoride ceased. The product was purified by distillation under a nitrogen atmosphere; b.p. 50–51°C/0.25 mmHg.

Boron trifluoride–tetrahydropyranate. Into a 16 × 105 mm tube equipped with a ground glass jointed gas bubbling tube and side arm vent was placed 5.0 ml of freshly distilled tetrahydropyran (Aldrich Chemical Co.). The vessel was immersed in a water bath maintained at 20°C and boron trifluoride gas was bubbled slowly through the tetrahydropyran until no further absorption occurred. The complex was twice distilled under a nitrogen atmosphere (b.p. 108°C/28 mmHg) and was stored under nitrogen in a sealed vial in the freezer.

Boron trifluoride–di-n-propyl etherate. Boron trifluoride–n-propyl etherate was prepared using the procedure and apparatus described for boron trifluoride–tetrahydropyranate: b.p. 56°C/20 mmHg.

Boron trifluoride–di-n-butyl etherate. Boron trifluoride–di-n-butyl etherate was prepared using the procedure and apparatus described for boron trifluoride–tetrahydropyranate: b.p. 70°C/20 mmHg.

Boron trifluoride–isopropyl etherate solution. Isopropyl ether was purified by distillation and drying over molecular sieves (3A) for 48 h. The dried ether (4 ml) was then placed into the gas bubbling apparatus used for the preparation of boron trifluoride–tetrahydropyranate. The apparatus was cooled to 0°C in an ice bath and boron trifluoride gas was slowly passed into the ether until a small amount of white crystals had formed. An additional 4 ml of isopropyl ether was added to dissolve the crystals. The resultant solution was transferred by means of a syringe to a 10 ml septum-sealed flask and stored in a freezer.

The method of Deters[19] utilizing the proton NMR chemical shift changes of the ether protons of the complex in solution was used to determine the strength of the solution. The solution was indicated to contain 6.6% boron trifluoride.

Aluminum chloride–tetrahydrofuranate solution. Aluminum chloride–tetrahydrofuranate was prepared by the method described by Deters *et al.*[10]. A solution of aluminum chloride–tetrahydrofuranate in tetrahydrofuran was prepared under a dry nitrogen atmosphere by dissolving 1.1538 g of aluminum chloride–tetrahydrofuranate in tetrahydrofuran followed by dilution to 10.0 ml in a volumetric flask. The solution was sealed in a black painted flask and stored at −5°C. The resultant solution was 0.5602 *M* in aluminum chloride–tetrahydrofuran complex.

Aluminum chloride–ethyl etherate. Aluminum chloride–ethyl etherate was prepared by the method of Deters[19]. Distillation gave a clear white liquid; b.p. 142°C/5.5 mmHg [lit.[19] b.p. 100°C/1.0 mmHg].

Boron trichloride–ethyl etherate. In the gas bubbling apparatus described for the preparation of boron trifluoride–tetrahydropyranate was placed 4.0 ml of anhydrous diethyl ether. Boron trichloride (Matheson, Coleman, and Bell) was slowly bubbled through the ether until a slurry of white crystals had formed. The slurry was transferred to a vacuum sublimator under a dry nitrogen atmosphere. Excess ether was removed under reduced pressure and the boron trichloride–ethyl etherate was sublimed at 45°C/0.5 mmHg. A solution of the complex in diethyl ether was prepared under a dry nitrogen atmosphere by dissolving 1.1107 g (5.806 mol) of the sublimed complex in diethyl ether in a 10.0 ml volumetric flask sealed with a rubber septum. The complex was dissolved and brought to 10.0 ml of volume by the addition of anhydrous diethyl ether.

Antimony trichloride–tetrahydrofuranate solution. In a dry box 4.0101 g (17.57 mmol) of antimony trichloride (Baker Chemical Co.) was placed into a 10.0 ml volumetric flask and sealed with a rubber septum. The antimony trichloride was dissolved in tetrahydrofuran and diluted to 10.0 ml producing a pale yellow solution. NMR analysis showed no detectable tetrahydrofuran ring cleavage.

Procedure for kinetic measurements

Standard solutions of the substrate in the appropriate solvent were prepared in the following manner. A 10 ml volumetric flask was thoroughly dried for 24 h at 110°C, sealed with a rubber septum, and flushed with a dry nitrogen prior to use. With the aid of a syringe, approximately 4.0 mmol of substrate was placed in the tared flask and weighed. Approximately 8.0 mmol of an internal reference standard, such as chloroform, was added and the flask again weighed. Solvent was then added and the solution was brought to 10.0 ml. All solutions were tightly stoppered and stored in a refrigator.

A 0.500 ml aliquot of the solution containing the substrate and reference in the appropriate solvent was placed in a dry septum-sealed NMR tube by means of a syringe. The NMR tube was then cooled to below −5°C by means of an ice/salt bath and a measured amount of the appropriate Lewis acid was added by means of a microsyringe. The outside of the NMR tube was then quickly dried and the tube was placed in the probe of a Varian A-60A spectrometer and allowed to come to temperature. The intensities of the appropriate hydrogens of the reference compound (e.g. $C\underline{H}Cl_3$) and the vinylic protons of the elimination product (cyclohexene) were periodically recorded by electronic integration. The reaction temperature was assumed to be the same as the NMR probe temperature and was measured before and after each kinetic run.

In several systems the rate of elimination under pseudo-first order conditions was too slow for convenient measurement by allowing the reaction to proceed in the NMR probe. In such cases the NMR tubes were maintained in a constant temperature bath at the appropriate temperature. The tubes were periodically removed from the bath and the appropriate resonance signals were integrated.

A control sample of the standard solution without catalyst was subjected to the identical conditions that the kinetic solutions were maintained in each experiment of this type. In each case no elimination was observed.

Procedure for detecting possible redistribution reactions

A solution containing 1.0 ml of methyl borate (Centron Corp.) and 1.0 ml of the appropriate Lewis acid in the appropriate solvent was prepared in a 10 ml septum-sealed flask. The solutions were thoroughly mixed and kept at room temperature. Periodically, 0.50 ml aliquots were withdrawn by syringe and placed into a NMR tube, along with a boron trifluoride–ethyl etherate reference capillary. The NMR tube was cooled in a Dry-Ice/acetone bath and sealed. The ^{11}B NMR spectrum was then recorded on a Varian HR-60 spectrometer at 19.28 MHz.

In certain cases it was desirable to mix methyl borate and the Lewis acid complex in the absence of solvent to increase the intensity of the ^{11}B NMR spectrum. This was accomplished by using a syringe to transfer each Lewis acid complex directly into a NMR tube containing methyl borate and a boron trifluoride–ethyl etherate reference capillary. The tube was then cooled, sealed, and its ^{11}B NMR spectrum was periodically recorded. The Lewis acids used in this study did not undergo redistribution with trimethylborate.

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