Transfer Reactions Involving Boron. XV. A Kinetic Study of the Hydroboration of Olefins with Monochloroborane[1,2]

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Abstract: The rates of hydroboration of a number of representative olefins and substituted styrenes with monochloroborane in tetrahydrofuran at a variety of temperatures have been measured. The rate and product distribution data for the addition to substituted styrenes correlate best with σ. The hydrogen-deuterium isotope effect for the addition to styrene at 25° is found to be 1.92 and 1.90 for internal and terminal addition, respectively. The data support a four-centered transition state in which very little charge density is developed on the olefinic carbon atoms.

Practically no quantitative kinetic studies have been carried out involving the hydroboration reaction. Preliminary studies in our laboratories revealed that the reaction of simple olefins with borane in tetrahydrofuran is a potentially very complex reaction, these complications being a series of consecutive hydroboration steps and the occurrence of disproportionation and monomer–dimer equilibria involving the intermediate monoalkyl- and dialkylboranes.[4] We therefore decided to select a less complex hydroboration system for our initial study.

The hydroboration of olefins with monochloroborane in tetrahydrofuran appeared to be well suited for this purpose. Our earlier studies with monochloroborane[5] revealed: that monochloroborane could be prepared by the disproportionation of borane and boron trichloride in tetrahydrofuran; that the monochloroborane does not undergo disproportionation under the hydroboration conditions; that monochloroborane exists exclusively as a monomer in tetrahydrofuran solution; that the reaction with olefins proceeds practically only to the monoalkylmonochloroborane state (>94%); and that the product monoalkylmonochloroborane does not disproportionate and exists exclusively as a monomer in tetrahydrofuran solution. We therefore undertook a thorough kinetic investigation of the hydroboration of representative olefins with monochloroborane in tetrahydrofuran at a variety of temperatures.[6]

Results and Discussion

The tetrahydrofuran solutions of monochloroborane employed in this study were prepared by the slow adsorption of gaseous boron trichloride into a borane in tetrahydrofuran solution maintained at 0°. The stoichiometry of the reagent was determined by hydrogen evolution measurements on hydrolysis and titration of the hydrochloric and boric acids formed on hydrolysis. The stoichiometry of the reagent was then adjusted by the addition of either borane or boron trichloride. The reagent used in this study analyzed to better than 98% monochloroborane. Rate constants determined from different preparations of monochloroborane were within experimental error of each other.

The kinetic experiments were performed in the following manner. A solution of the desired olefin and an inert internal standard in tetrahydrofuran was mixed with a solution of monochloroborane in tetrahydrofuran under a nitrogen atmosphere maintained at a constant temperature. Aliquots were periodically removed and quenched with an excess of methanol. The quenched mixtures were then analyzed by gas–liquid partition chromatography. The area ratios of unreacted olefin to internal standard were measured and employed to calculate the rate constants. The calculations of the rate constants and thermodynamic activation parameters were carried out on a Univac 1107 computer. The product distributions formed by the addition of monochloroborane to an unsymmetrical olefin were determined by basic hydrogen peroxide oxidation followed by glpc analysis of the alcohol mixtures employing predetermined response ratios. The rate constants and product compositions (where not previously determined[5]) are tabulated in Tables I and II.

A comparison of the relative rates of hydroboration of the representative olefins with monochloroborane, borane, and disiamylborane in tetrahydrofuran is presented in Table III.[7] Comparison of the relative reactivities of the various olefins with monochloroborane and borane shows only minor differences. It would appear that the relative reactivity increases as the electron density of the olefinic center increases, but that steric effects become important with the more highly substituted olefins resulting in a decreased reactivity.

Monochloroborane has been shown to be more electrophilic than borane,[5] thus resulting in an increased sensitivity to the electron density of the olefin, and to be very highly complexed with tetrahydrofuran,[5] thus increasing its steric bulk. This rationalization is

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(1) (a) For part XIV, see D. J. Pasto and J. Hickman, *J. Am. Chem. Soc.*, **89**, 5608 (1967); (b) presented at the Symposium on Recent Advances in Organoboron Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 12, 1967; Abstract S38.

(2) Research supported by National Institutes of Health Grant CA 07194-05.

(3) Alfred P. Sloan Research Fellow, 1967–1969.

(4) D. J. Pasto and L. Balasubramaniyan, unpublished observations (see ref 1b).

(5) D. J. Pasto and P. Balasubramaniyan, *J. Am. Chem. Soc.*, **89**, 295 (1967). Note that we have made use of a method similar to the one described by H. C. Brown and P. A. Tierney, *J. Inorg. Nuclear Chem.*, **9**, 51 (1959), for the preparation of monochloroborane.

(6) Subsequent to the completion of this work, T. T. Zweifel (*J. Organometal. Chem.* (Amsterdam), **9**, 215 (1967)) published the results of a comparison of qualitative rate studies of monochloro- and dichloroboranes with several olefins against those of other substituted boranes.

(7) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **85**, 2063 (1963).

qualitatively consistent with the trend in the activation parameters determined for these reactions (see Table IV).

Table I. Rate Constants for Addition of Monochloroborane to Olefins

Olefin	Temp, °C	$k \times 10^3$, l./(mol min)^a
1-Hexene	2.5	10.6
	25.0	141
cis-3-Hexene	15.5	36.6
	25.0	94.2
trans-3-Hexene	0.0	3.5
	15.5	18.2
	25.0	41.1
2-Methyl-2-butene	25.0	104
2,3-Dimethyl-2-butene	25.0	7.4
	30.0	15.9
	42.0	53.9
Styrene	0.0 (91.8)^b	0.306
	15.0 (91.0)^b	2.27
	25.0 (90.0)^b	7.31^c
	35.0 (89.0)^b	2.31
	42.8 (88.0)^b	6.25
	45.0 (88.0)^b	7.40

[a] Most rate constants are average values taken from the data of two or more runs. The deviation of individual runs from the average value was usually less than 4%. [b] Per cent terminal addition product. [c] Values of 7.42, 7.22, 7.28, and 7.37 $\times 10^{-3}$ l./(mol min) were obtained, representing results from two different preparations of monochloroborane.

Table II. Rate Constants and Product Composition Data for the Addition of Monochloroborane to Substituted Styrenes (25°)

Substituent	% terminal product	$k \times 10^3$, l./(mol min)
H	90.0^a	7.31
4-CH_3	92.0	12.2
4-*i*-Pr	92.0	8.96
4-F	89.0	5.06
4-Cl	87.0	3.30
4-Br	88.0	4.98
4-CH_3O	93.3	27.8^b
4-C_2H_5O	92.5	23.9^b
4-NO_2^{c}	67.0^d	3.24
3-NO_2^{c}	75.0^d	5.48

[a] Previous values from our laboratories reported 89.8 and 90.2%.[5] [b] The initial rate of reaction up to approximately 25–30% completion was very fast; the rate constants cited here are for the region beyond 30% reaction which provided a good second-order plot. Glpc analysis of the two starting materials revealed no impurities after repeated vacuum fractional distillation; however, the same highly erratic behavior was exhibited by the highly purified samples. [c] No reduction of the nitro group was observed. [d] Accurate values could not be obtained. These values were estimated from glpc and nmr data of the crude alcohol mixture.

Table III. Comparison of Olefin Relative Reactivities with Monochloroborane and Borane in Tetrahydrofuran (25°)

Olefin	BH_2Cl	BH_3^{a}	Rel reactivities of disiamylborane^a
1-Hexene	100	100	100
cis-3-Hexene	67		2
trans-3-Hexene	29		0.2
2-Pentene		34^b	2,^{c} 0.3^d
2-Methyl-2-butene	74	50	
2,3-Dimethyl-2-butene	5.2	7^e	
Styrene	52	19	

[a] Taken from ref 7. [b] Geometrical isomer not specified. [c] *cis* isomer. [d] *trans* isomer. [e] Calculated from the relative reactivity *vs.* cyclopentene.

Table IV. Activation Parameters for the Hydroboration of Olefins with Monochloroborane in Tetrahydrofuran

Olefin	$\Delta H^{\ddagger}$, kcal/mol^a	$\Delta S^{\ddagger}$, eu^b
1-Hexene	18.8	−7.2
Styrene, internal addition	23.1	−3.3
terminal addition	21.6	−4.2
cis-2-Hexene	16.6	−15.6
trans-3-Hexene	16.0	−19.4
2,3-Dimethyl-2-butene	21.4	−4.5

[a] Estimated ±1 kcal/mol. [b] Standard state of l./(mol sec) at 25° with an estimated ±2.0 eu.

In order to evaluate the electronic demands in the transition state we determined the rates of hydroboration of several substituted styrenes with monochloroborane (see Table II). Assuming that the formation of the internal and terminal addition products occur *via* two competitive, nonreversible reactions (the latter is readily demonstrated to be true under the conditions of the experiments), the total rate for the hydroboration of the substituted styrenes can be subdivided into the rates for internal and terminal product formation. Plots of log k *vs.* σ and σ^+ indicated that the best linear correlation is obtained with σ, giving ρ values of -0.65 and -1.43 for internal and terminal addition, respectively. However, a considerable scatter of the points is noted, making a clear-cut distinction impossible. A more revealing method of analysis of the data is provided by plotting the log of the ratio of terminal product to internal product *vs.* σ and σ^+ (Figures 1 and 2, respectively). In these plots it is obvious that the best correlation is obtained with σ, giving a ρ value of -0.65.

The observation that the rate and product distribution data correlate best with σ is somewhat surprising. Brown[8] and Klein[9] and their coworkers have studied the hydroboration of substituted styrenes with borane in tetrahydrofuran. Brown and Sharp[8] observed that the log of the product distribution *vs.* σ^+ gives a reasonably good straight line with a ρ value of approximately -0.7. Klein and coworkers[9] observed that the rates of hydroboration of substituted styrenes do not follow the Hammett ρ,σ relationship either over-all or when each position is considered separately. These authors did find linear correlations of log (k/k_0) at the α position with σ for *meta* substituents with a ρ value of 0.5 and for *para* substituents with a ρ value of 1.2, whereas for the β position a linear correlation is observed with *meta* substituents (ρ -0.5) but apparently no reasonable correlation for the *para* substituents.[9]

Monochloroborane would be expected to be considerably more electrophilic than borane, and hence possibly correlate with σ^+, giving larger ρ values than obtained with borane. However, a considerable number of differences are apparent between the two reactions. The reaction of borane in tetrahydrofuran with olefins is complicated by the fact that the second

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(8) H. C. Brown and R. L. Sharp, *J. Am. Chem. Soc.*, **88**, 5851 (1966).

(9) J. Klein, E. Dunkelblum, and M. A. Wolff, *J. Organometal. Chem.* (Amsterdam), 7, 377 (1967).

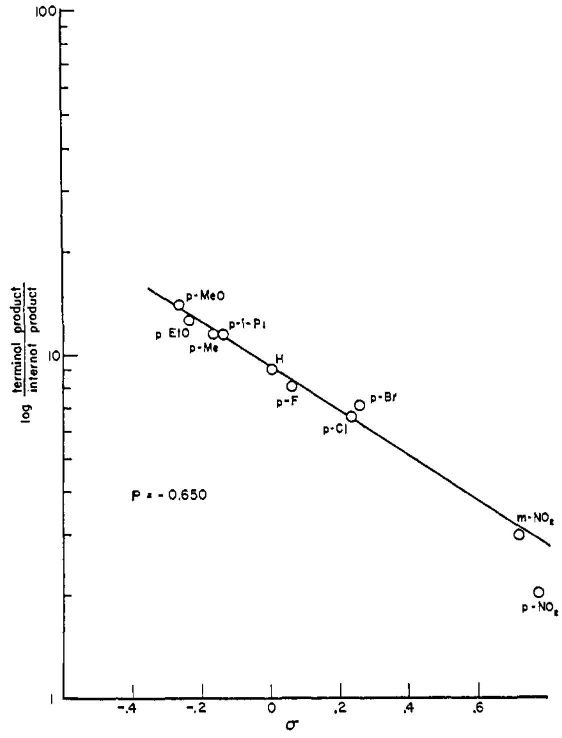

Figure 1.

hydroboration step competes with the first addition step and a number of monomer–dimer equilibria exist in solution. The effect of these factors on the type of correlation derived cannot be anticipated and must await further experimental study. Furthermore, it has been pointed out that monochloroborane is strongly complexed with tetrahydrofuran.[5] Such complexing would be expected to reduce the electrophilic properties of monochloroborane.[10] Thus, it is believed that the tetrahydrofuran complex of monochloroborane is involved in the reaction, thus reducing the electronic demands on the substrate in the transition state, giving relative low ρ values.

Further information regarding the nature and structure of the transition state can be derived from hydrogen–deuterium kinetic isotope effects (see Tables V and VI). Brown[11] originally proposed that the hydroboration reaction "involves a simple four-center transition state." Recently, Streitwieser,[12] in an effort to rationalize the stereochemistry of the optically active 1-deuterio-1-butanol derived from the hydroboration of *cis*-1-deuterio-1-butene with diisopinocampheylborane, proposed that "the olefin–borane complex is a triangular π complex and that the transition state involves a relatively small perturbation from this triangular structure." Distinction between these possibilities should be possible on the basis of isotope effects, the former exhibiting a primary H–D isotope effect and the latter a secondary H–D isotope effect (a matter of a few per cent). The hydrogen–deuterium isotope effect values observed in this work (see Table VI) support Brown's[11] four-center transition state for the hydroboration of olefins with monochloroborane. This evidence does not preclude a possible pretransition-state π complex in the hydroboration reaction. Furthermore, our present studies with monochloroborane should not be extrapolated to hydroboration reactions involving other substituted boranes.[13]

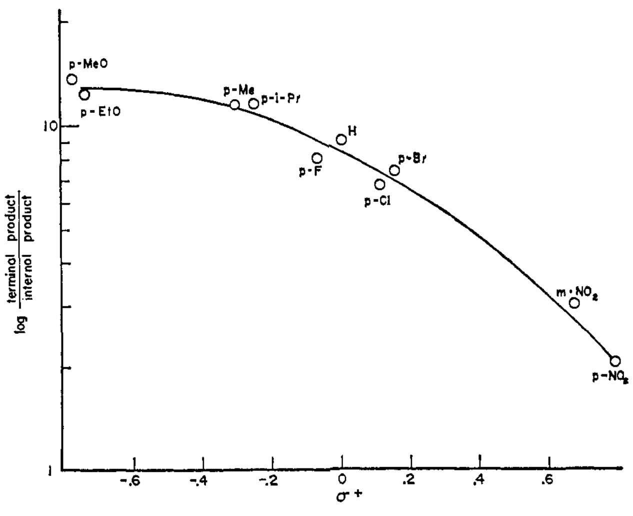

Figure 2.

Table V. Rate Data for the Deuterioboration of 1-Hexene and Styrene with Dideuteriomonochloroborane in Tetrahydrofuran

Olefin	Temp, °C	$k \times 10^3$, l./(mol min)
1-Hexene	25.0	58.9
Styrene	25.0 (89.5)[a]	3.93
	35.0 (88.8)[a]	13.8

[a] Per cent terminal addition product.

Table VI. Hydrogen–Deuterium Kinetic Isotope Effects

Olefin	k_H/k_D
1-Hexene	2.4[a]
Styrene (25°), internal addition	1.78
terminal addition	1.87
(35°), internal addition	1.56
terminal addition	1.68

[a] Over-all addition isotope effect.

The near identity of the internal and terminal isotope effects for the addition to styrene indicates that the transition states for the two modes of addition have developed to nearly the same extent of bonding. This result is consistent with the Hammett ρ values, which are quite similar, which also indicate that the two transitions states demand similar electronic stabilization and do not involve extensive charge buildup on either carbon atom of the double bond.[14]

In summary, all of the data presented here supports the proposal of a four-centered transition state as

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(10) A similar viewpoint has been expressed by Zweifel (see ref 6).

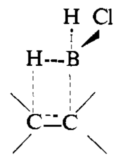
(11) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p 13.

(12) A. Streitwieser, Jr., L. Verbit, and R. Bittman, *J. Org. Chem.*, 32, 1530 (1967).

(13) Hydrogen–tritium isotope effect studies initiated in our laboratories on the reaction of diisopinocampheylborane with 2-pentene reveal a substantial isotope effect for both the borane addition to β-pinene and the addition of diisopinocampheylborane to 2-pentene (D. J. Pasto and J. Hickman, unpublished observation; see ref 1b).

(14) A similar view has been expressed by Klein and coworkers[9] concerning the transition state for the addition of borane to the substituted styrenes.

illustrated below, with extensive solvent interaction



and stabilization.

Experimental Section

Preparation of Monochloroborane. Tetrahydrofuran solutions of monochloroborane were prepared by the slow adsorption of gaseous boron trichloride into a borane in tetrahydrofuran solution maintained at −10–0° as described previously.[5]

Dideuteriomonochloroborane was prepared similarly.

Standardization of the Monochloroborane Solutions. An aliquot (2.00 ml) of the solution was hydrolyzed with 10 ml of water at room temperature, the volume of hydrogen evolved being carefully measured. The aqueous solution was transferred to a beaker and titrated to the first end point (neutralization of the hydrochloric acid formed on hydrolysis of the monochloroborane) with standardized 1 *N* sodium hydroxide employing a Beckman research pH meter. Mannitol (approximately 2.5 g) was then added to the solution, and the titration was continued to the end point for the neutralization of boric acid. The analytical data were converted into equivalents of available "hydride," boron, and chloride. When the solution analyzed for less than 98% monochloroborane, calculated amounts of additional boron trichloride or borane in tetrahydrofuran were added and the standardization procedure was repeated. Concentrations of monochloroborane in tetrahydrofuran employed in the kinetic experiments ranged from approximately 0.2 to 1.0 *M*.

Kinetic Measurements. Carefully weighed quantities of the olefin and an inert internal standard (for glpc analytical purposes) were dissolved in 25.0 ml of dry tetrahydrofuran. A 20.0-ml aliquot of this solution was added to 20.0 ml of standardized monochloroborane solution in a thermostated vessel sealed with a rubber septum under a nitrogen atmosphere. Aliquots were periodically removed, by means of a syringe through the rubber septum, and immediately quenched by injection into an excess of methanol. The quenched reaction mixtures were then analyzed by glpc on 10-ft Carbowax 20M columns at appropriate temperatures. The olefin : internal standard area ratios, corrected for response ratio differences, were employed to calculate the second-order rate constants employing the Univac 1107 computer.

Product Analysis. Reaction mixtures of monochloborane and olefin were allowed to proceed to completion under conditions of the kinetic experiments. The reaction mixtures were hydrolyzed by the addition of excess 20% sodium hydroxide and oxidized by the addition of an excess of 30% hydrogen peroxide. The oxidized reaction mixtures were extracted several times with ether. The extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated under reduced pressure. The residues were analyzed by glpc on Carbowax 20M columns at appropriate temperatures, the per cent compositions being calculated employing predetermined response ratios.[15]

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(15) Not all of the products from the substituted styrenes were characterized. It was found that the response ratios of substituted α- to β-phenylethanols (H, 4-Me, 4-Cl) did not vary substantially, and thus this response ratio was employed for the analysis of the other systems.

The Reactions of Ambident Anions with an Ambident Electrophile

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Abstract: It has been found that the reaction of sodiodipivaloylmethane with triphenylmethyl chloride gives nearly 90% yields of the carbon-arylated diketone **6**. Although not isolable, the trityl enol ether **17** is the only other identifiable primary product of this reaction. No evidence for normal C-tritylation or for abnormal O-arylation could be found. The reaction with triphenylmethyl bromide gives increased yields of **17** at the expense of **6**. The arylation reaction is a carbonium ion process. When the trityl halides are replaced by triphenylmethyl fluoroborate, the intermediate cross-conjugated triene **14** can be isolated. Rearrangement of **14** to **6** occurs smoothly, and to some extent intramolecularly, in basic media. The reaction with triphenylcarbonium ion has been extended to 14 other enolate systems. Among those derived from β-diketones, appreciable C-arylation was observable only with the highly hindered dipivaloylmethane. In the β-diester series, however, this reaction is more general. Even diethyl malonate undergoes C-arylation to the extent of 20%, and from two other β-diesters the intermediate trienes **18** and **19** could be isolated. *para* substitution in the trityl system serves to block the arylation reaction completely.

In connection with a spectrophotometric study of enolate ions,[1] the synthesis of several monosubstituted dipivaloylmethanes was undertaken. Alkylation of sodiodipivaloylmethane with benzyl and benzhydryl chlorides gave the expected products **1** and **2** in poor yields (6 and 3%, respectively).

$$\mathrm{RX} + \mathrm{Na}^+\,\bar{\mathrm{C}}\mathrm{H}[\mathrm{COC}(\mathrm{CH}_3)_3]_2 \longrightarrow \mathrm{RCH}[\mathrm{COC}(\mathrm{CH}_3)_3]_2$$

1, R = $C_6H_5CH_2$
2, R = $(C_6H_5)_2CH$
3, R = $(C_6H_5)_3C$
4, R = $(p\text{-}BrC_6H_4)_3C$
5, R = $(p\text{-}CH_3C_6H_4)_3C$

Surprisingly, the bulkiest member of the series, trityl chloride, led to an alkylation product in yields ap-

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(1) H. E. Zaugg and A. D. Schaefer, *J. Amer. Chem. Soc.*, **87**, 1857 (1965).