THE RATES OF HYDROBORATION OF SUBSTITUTED STYRENES

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The kinetics of the reduction of cyclohexanones with diborane were studied recently[1]. We now report the rates of hydroboration of some substituted styrenes.

The hydroboration of olefins was assumed by Brown[2-4] to proceed by a four-centre transition state, in which the participating two carbon atoms of the double bond and the boron and hydrogen atoms of borane have alternate partial charges. A partial negative charge was placed on the carbon next to boron. This mechanism was a rationalization of the *cis* addition of boron and hydrogen to the double bond, of the preferential attack by boron on the terminal carbon in α-olefins and of the change of the ratio of α- and β-isomers obtained from styrenes with the change of the *para* substituent in the phenyl ring. The phenylring was considered to be able to stabilize both positive and negative charges α to it, the relative stabilization of these charged structures changing with the substituent in the ring. The ratios of isomers formed from substituted styrenes were obtained, but the rates at the respective positions and their change with the electronic properties of the substituents were unknown. Relative rates of hydroboration of a series of olefins were also measured[5] and only minor changes in reactivity were found. These studies were carried out with an excess of olefins, so that the results are an average of the reaction of diborane, alkylboranes and dialkylboranes. Relative rates of hydroboration of olefins with dialkylborane amines[6] and disiamylboranes[7] were also studied.

RESULTS

We have measured the rates of hydroboration of styrenes with excess diborane in tetrahydrofuran by a spectrophotometric method[1,8]. The results are recorded in Table 1 and an example of typical experimental curves are shown in Fig. 1 (optical density of the reaction mixture against time).

The reaction is pseudo-first order in styrene. The change of rate with change in the diborane concentration showed that the reaction is also first order in diborane or borane.

$$\frac{-d[\text{styrene}]}{dt} = k_1 [\text{styrene}]$$

$$\frac{-d[\text{styrene}]}{dt} = k_2 [\text{styrene}][\text{diborane}]_t$$

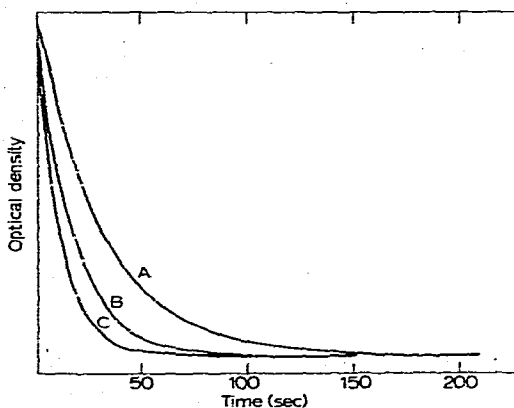The use of an excess of diborane does not permit to make a choice between the two

Fig. 1. Rates of hydroboration of styrene. Conc. of styrene was $1.25 \cdot 10^{-3}$ M. Conc. of diborane: A, 0.14 M; B, 0.28 M; C, 0.42 M.

TABLE 1

RATES OF HYDROBORATION OF STYRENES[a]

Olefin[b]	λ^c $(m\mu)$	B_2H_6 conc. (M)	Half-life τ (sec)	pseudo k_1 (l/sec)	$k_2{}^d$	k_2 average	$k_2{}^\alpha$	$k_2{}^\beta$
styrene	285	0.14	21	0.033	0.235			
		0.28	11	0.063	0.225	0.225	0.045	0.180
		0.42	7	0.099	0.215			
o-methoxy-styrene	295	0.14	19	0.036	0.258			
		0.28	9	0.077	0.275	0.269	0.027	0.242
		0.42	6	0.115	0.273			
m-methoxy-styrene	295	0.14	20	0.035	0.250			
		0.28	10	0.070	0.250	0.235	0.047	0.188
		0.42	7	0.099	0.215			
p-methoxy-styrene	295	0.14	13	0.053	0.380			
		0.28	7	0.099	0.354	0.367	0.018	0.349
		0.42	4.5	0.154	0.368			
o-chloro-styrene	295	0.14	21	0.033	0.235			
		0.28	11	0.063	0.225	0.222	0.075	0.147
		0.42	8	0.087	0.206			
m-chloro-styrene	295	0.14	27	0.026	0.186			
		0.28	13	0.053	0.189	0.186	0.071	0.115
		0.42	9	0.077	0.184			
p-chloro-styrene	295	0.14	21	0.033	0.235			
		0.28	11	0.063	0.225	0.232	0.076	0.156
		0.42	7	0.099	0.235			

[a] In tetrahydrofuran solution at 25°. [b] All solutions were $1.25 \cdot 10^{-3}$ M in olefin. [c] Wave length, at which the measurements were carried out. [d] k_2 values in $1 \cdot mole^{-1} \cdot sec^{-1}$.

possibilities. The ratio of the isomers with the boron at α- and β-positions was established by analyzing, by GLC, the alcohols obtained on oxidation of the hydroboration product of parallelly run reactions, using a solution having much higher concentration of reagents. That this change of conditions did not affect the ratio of products was tested by running reactions with a solution 0.08 M in styrene and 0.8 M in diborane. A solution 0.8 M in styrene and 0.8 M in diborane was also used. A similar ratio of isomers was obtained in all conditions. The ratio did not change also on changing the order of addition, borane to styrene or inverse. These results proved also that the reaction at both centres α and β are of the same order. The rate constants of hydroboration at the α (k_2^α) and the β positions (k_2^β) were calculated from the overall rates and the ratio of isomers, shown in Table 2. (This calculation is permissible because no isomerization occurs in the reaction conditions[9].) Addition of boron trifluoride etherate did not affect the rate of the reaction. This fact is in variance with the observed acceleration on this addition during the reduction of ketones with diborane[1].

TABLE 2

RATIO OF ALCOHOLS FROM HYDROBORATION OF $RC_6H_4CH=CH_2$

R	Procedure[a]	$RC_6H_4CH_2CH_2OH$	$RC_6H_4CH(OH)CH_3$
H	A	80%	20%
	b	80	20
o-Cl	A	66	34
	B	64	36
m-Cl	A	62	38
	B	65	35
p-Cl	A	67	33
	B	64	36
	b	65	35
o-CH$_3$O	A	90	10
	B	95	5
m-CH$_3$O	A	80	20
	B	80	20
	C	78	22
p-CH$_3$O	A	95	5
	B	96	4
	b	91	9

[a] Procedures A, B and C are described in the experimental section. [b] Results of ref. 4.

An interesting feature of this reaction was observed during the rate measurements on o-methoxystyrene. The hydroboration of this compound shows an initiation period which increases when the concentration of diborane in the reaction mixture is diminished (Fig. 2). This is due to an impurity, since the same effect, observed with a sample of m-methoxystyrene, disappeared after redistillation of the olefin. The solvent influences also the formation of the initiation period. A solution of m-methoxystyrene, which was kept for several days showed during the rate measurement a plateau larger than six half-lifes of the reaction (Fig. 3). An attempt to produce a similar plateau by addition of 1-decene or di-tert-butyl peroxide in equimolecular amounts to styrene, failed.

These results permit to evaluate the rates of hydroboration of aliphatic olefins by a comparison with the relative rates determined by Brown[5].
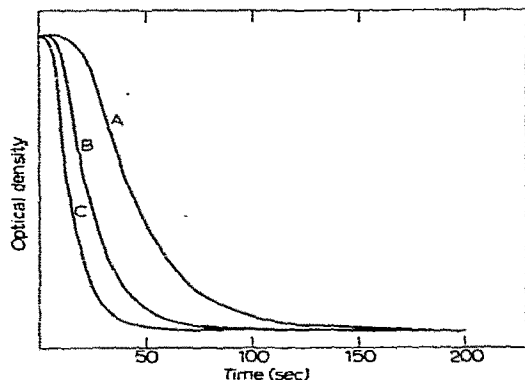

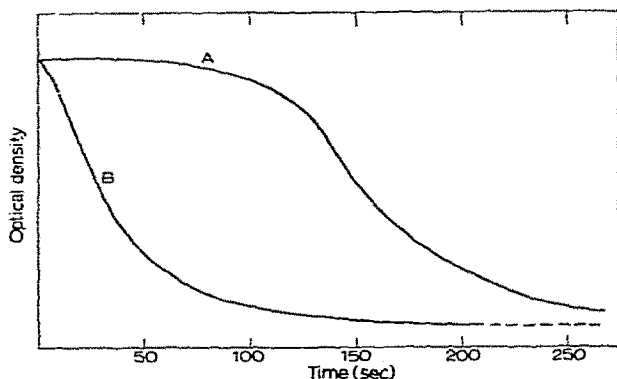Fig. 2. Rates of hydroboration of o-methoxystyrene. Conc. of styrene and diborane as in Fig. 1.

Fig. 3. Rates of reaction of m-methoxystyrene ($1.25 \cdot 10^{-3}$ M) with diborane (0.14 M). A, aged solution. B, freshly prepared solution.
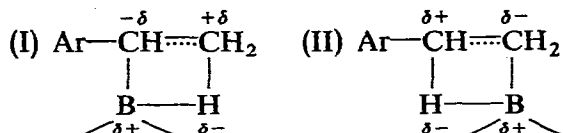
DISCUSSION

The reaction is first order in styrene and diborane (or borane). The induction period seems however to indicate the presence of an active intermediate. This intermediate cannot involve the styrene, since the initial ultraviolet absorption is the same in the cases, when a plateau appears and also when the reaction is normal. Moreover, the induction period can be longer than the time necessary to react most of the styrene. The most plausible explanation is to assume that the species that diborane forms in tetrahydrofuran, i.e., the borane/tetrahydrofuran complex[10], is not the one reacting with styrene, but it undergoes dissociation by a fast and reversible reaction to borane and a molecule of the solvent. The formed borane reacts with styrene in a slow step. If diborane is, in fact, the reactive species, the first dissociation must be followed by a fast and reversible dimerization to diborane. The possibility that diborane is the reacting species is supported by the results of Brown[7] which established that the dimer of disiamylborane is involved in the slow step of hydroboration with this agent.

When the reactive impurity is present, the rate of its reaction with borane (or diborane) is much faster than the rate of hydroboration of styrene and is comparable to the rate of formation of borane. Thus the borane formed is destroyed by the impurity and the styrene concentration remains stationary, until the whole impurity has reacted. The impurity interfering with the hydroboration must be very reactive. Since an olefin or a peroxide do not interfere, we assume that this impurity is a peroxide radical. It has been observed before that trialkylboranes react very rapidly with radicals (with an energy of activation of 3 kcal/mole[11]).

The overall rate of hydroboration of styrenes changes little with the various substituents studied. This extends the results of Brown[5] on the insensitivity of hydroboration rates to major changes in the structure of olefins to include polar effects. The rates do not follow the Hammett ρ,σ relation for the reaction either overall or when each position is considered separately. However, a trend of polar influence can be observed: electron-withdrawing substituents accelerate the reaction at the α-position and diminish the rate at the β-position. A straight line can be fitted separately for the change of log (k/k_0) at the α-position with the Hammett σ constant separately for meta substituents with ρ equal 0.5 and for para substituents with ρ 1.2. This may be a consequence of a greater interaction between the reacting centre and the para than the meta substituents. At the β-position a different trend is observed with a ρ value of approximately -0.5 for meta substituents, but no straight line could be fitted even approximately for the para substituents. The rates of the ortho substituted styrenes are very close to those of their para isomers. These seem to confirm the observation that steric effects have only a secondary influence on rates of hydroboration or may be a consequence of a balancing of polar and steric effects. The ρ values reported here are not intended to establish this parameter for the hydroboration reaction, but to show that even after dissection of all the factors according to the position of boron attack and the position of the substituents only very low values can be found for this parameter. Moreover the sign is opposite for the α- and β-positions. These results exclude an intermediate with a fully developed charge, where higher values of ρ would be expected[12]. The hydration of styrenes has a ρ value[13,14] of -4 and the bromination of styrenes in methanolic solution involving probably a carbonium ion has a ρ value[15] of -4.3. Even bromination of styrenes in acetic acid, thought to proceed by a bromonium intermediate[16] has a ρ value of -2.23.
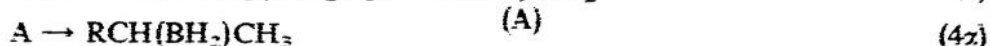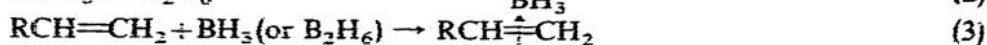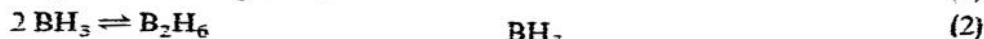
These minor polar influences exercising in opposite directions and depending on the position of attack support the mechanism postulated by Brown involving a four-centre intermediate, with partial charges on the participating atoms, and the aryl group acting in one transition state leading to one of the isomers as electron sink (I) and as electron source (II) in the transition state leading to the other isomer.

$$\text{(I)} \quad \overset{-\delta}{\text{Ar—CH}}\!\!=\!\!\overset{+\delta}{\text{CH}_2} \qquad \text{(II)} \quad \overset{\delta+}{\text{Ar—CH}}\!\!=\!\!\overset{\delta-}{\text{CH}_2}$$

$$\underset{\delta+ \qquad \delta-}{\text{B———H}} \qquad\qquad \underset{\delta- \qquad \delta+}{\text{H———B}}$$

The activation of the β-position by electron-donating substituents is not strong enough to overcome the deactivating effect of the phenyl, even in the case of the p-methoxy substituent. The inductive effect of the sp^2 carbon is therefore more important than electron delocalization.

The low sensitivity of the reaction to polar effects with a less than a twofold change in overall rate is accompanied by a more than fourfold change in rates at the α-position. Even more pronounced differences between substrate and positional selectivity were found[4,5] for non-polar linear olefins, which have a threefold range of rates of hydroboration, but a sixteenfold range between the primary and secondary positions. This effect can difficultly be attributed to steric hindrance, since introduction of a methyl on a carbon α to the double bond lowers only slightly the rate of hydroboration, and introduction of an additional methyl on the double bond of 1-butene raises the rate by 20%[5]. A calculation based on the results of Brown[4,5] shows that the secondary carbon in 2-pentene is three times as reactive as the secondary carbon in 1-butene and the secondary carbon in 2-methyl-2-butene is 8 times more reactive than the same carbon in 1-butene (although the total rate of the first member of these pairs is half of that of the second). The tertiary position in 2-methyl-2-butene is seven times less reactive than in 2,3-dimethyl-2-butene, although a more pronounced steric hindrance would be expected in the last compound and the rate of hydroboration of the last compound is seven times slower than that of the first.

An attractive although not compelling explanation for the much higher positional than intermolecular selectivity is the formation, during the reaction, of an intermediate π-complex between borane and the olefin. Similar complexes were proposed for Lewis acids with aromatic hydrocarbons[17] and assumed to be intermediates in Friedel–Crafts reactions[18]. The formation of the complex would then be insensitive to the structure of the olefin and would proceed with most of them with comparable rates. This complex rearranges by way of the transition states postulated by Brown to the products. The differences between the energies of the transition states leading to the isomers are larger than the differences in the activation energies for complex formation between borane and various olefins. A possible sequence of reactions is shown:

$$BH_3 \cdot THF \rightleftharpoons BH_3 + THF \tag{1}$$

$$2\,BH_3 \rightleftharpoons B_2H_6 \tag{2}$$

$$RCH\!=\!CH_2 + BH_3 (\text{or } B_2H_6) \longrightarrow RCH\overset{BH_3}{\overset{\vdots}{=}}CH_2 \tag{3}$$
$$(A)$$

$$A \longrightarrow RCH(BH_2)CH_3 \tag{4α}$$

$$A \longrightarrow RCH_2CH_2BH_2 \tag{4β}$$

Reaction (3) should be the slow step in the sequence, but in this case a more regular dependence of the overall rate of hydroboration on the σ values would be expected. It is possible that reactions (3) and (4) have comparable rates and energies of their transition states.

EXPERIMENTAL SECTION

Styrene (Hopkins & Williams); o-, m-, p-chlorostyrene and p-methoxystyrene (Fluka) were redistilled products.

m-Methoxystyrene was prepared by dehydration[19] of 1-(m-methoxyphenyl)-ethanol[20] with KHSO$_4$: 14 g of the carbinol were added dropwise to 40 g fused and powdered KHSO$_4$ heated to 200–220° in a Claisen flask. The product obtained was

submitted once more to the same treatment with 25 g $KHSO_4$, redistilled at 70° (1.5 mm) and yielded 4 g. (Found: C, 80.4; H, 7.5. $C_9H_{12}O$ calcd.: C, 80.6; H, 7.5%.) A similar reaction with 10 g 1-(o-methoxyphenyl)ethanol yielded 3 g of o-methoxystyrene; b.p. 70–72° (1.2 mm). (Found: C, 80.1; H, 7.3. $C_9H_{10}O$ calcd.: C, 80.6; H, 7.5%.)

Hydroboration/oxidation of styrenes

Procedure A. Styrene (0.001 mole) dissolved in 5 ml of dry tetrahydrofuran was added dropwise to 7 ml of a 1.4 M solution of diborane in the same solvent at 0°. The reaction mixture was left one hour at room temperature and the excess diborane decomposed with 5 ml of water. Sodium hydroxide solution (5 ml, 10%) was then added, followed by a dropwise addition of 1 ml H_2O_2 30%. The solution was concentrated *in vacuo*, after one hour, and then the product was extracted with ether and analyzed by GLC.

Procedure B. 14 ml. of a solution of diborane in tetrahydrofuran (14 ml, 1.4 M) was added during 5 minutes dropwise to a stirred solution of 0.02 mole styrene in 10 ml of the same solvent, cooled in an ice bath. The reaction mixture was left for one hour at room temperature and 8 ml of water were added dropwise with cooling in an ice-bath, followed by 8 ml of sodium hydroxide 10% and then, at room temperature, 8 ml of hydrogen peroxide 30%. The reaction mixture was stirred for one hour, the layers separated and the aqueous layer extracted with dichloromethane. Distillation gave 70–80% of the alcohols.

Procedure C. This procedure was similar to A, but the diborane solution was added to the olefin solution.

The isomers were separated and analyzed by GLC on a 2 m column of Ucon nonpolar 10% or on 2 m column of Versamide 900 10% on Chromosorb P acid washed.

The α-carbinols of reference were prepared by the method of Brooks[20].

Kinetic measurements

The rates of the reaction of styrenes with diborane were followed spectrophotometrically at the indicated wavelength in tetrahydrofuran solution at 25°, using an Uvispec Hilger spectrophotometer with the Gilford Absorbance Indicator (Model 220) adapted by Perlmutter-Hayman and Wolff[8] to the measurement of fast reactions. In each experiment, 0.075 ml solution of the styrene in anhydrous tetrahydrofuran were added with the aid of a rapid mixing syringe to a diborane solution in the same solvent. The total amount of solution was 3 ml. Each experiment was repeated three times in the same conditions. The half-lifes τ were found from the central portion of the curve several times for the same curve by the relation:

$$\tau = t_{(d/2)} - t_{(d)}$$

where $t_{(d)}$ and $t_{(d/2)}$ are the invervals from the beginning of the reaction, where the optical density after the second interval is half of the optical density of the first one.

SUMMARY

The rates of hydroboration of styrenes have been measured by a spectro-

photometric technique. The Hammett relationship is not followed for the overall reaction, but it is obeyed partly for the reaction at α- and β-positions. There are only slight differences in rates; but electron-withdrawing substituents activate slightly for boron attachment at the α-carbon and deactivate for attachment at the β-carbon atom.

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