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AN EXPERIMENTAL AND THEORETICAL INVESTIGATION OF THE INFLUENCE OF ALKENE HOMO ENERGY LEVEL UPON THE HYDROBORATION REACTION. ADDITIONAL EVIDENCE SUPPORTING AN EARLY TRANSITION STATE WHICH HAS RETENTION OF ALKENE CHARACTER.

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The effects of some substituents upon the hydroboration with 9-BBN of alkenes were examined. The ordering of the energy levels of the pi MO's correlates with that of the relative reactivities of the alkenes toward hydroboration: a higher MO energy level corresponds to a higher relative reactivity. The regioselectivity of boron-carbon bond formation correlates with a.o. coefficient size in the alkene HOMO.

Since 1948, the mechanism of hydroboration has been a subject of interest.[1-7] Experimental evidence from hydroboration with borane in THF, such as entropy data[7a-b] and isotope effects,[7c] implicates an early transition state and significant loss of the boron-hydrogen bond in the rate-determining step. However, there has been no experimental investigation of the change in character of the C=C moiety in the transition state.

We have determined the effects of various substituents upon the rates of hydroboration at 25°C in THF solvent using 9-borabicyclo[3.3.1]nonane (9-BBN). Rates relative to 1-hexene for allyl and for vinyl derivatives are given in Tables I and II, respectively. This separation facilitates the comparison of electronic effects in sterically similar molecules. The compounds in Table I undergo hydroboration to form the boron-carbon bond >97% gamma to the substituent.[8] Those in Table II undergo hydroboration >97% beta to the substituent,[8b,8d-f,9] except for X=BR_2. In the last compound, the boron-carbon bond is formed exclusively alpha to the boryl substituent.[9] Silyl and boryl substituents in the allyl position and alkoxy substituents in the vinyl position have rate-increasing effects. The other substituents studied have rate-decreasing effects.

An examination of various electronic properties of the alkenes, calculated using MNDO,[10] reveals a correlation between the ordering of the MNDO HOMO energy levels, corresponding to the pi bonds of the allyl and vinyl compounds, and the ordering of the relative rates of hydroboration of these alkenes. However, the borylalkene in Table I and the boryl-, bromo-, and chloroalkenes in Table II are disubstituted alkenes, have larger steric effects upon the reaction rate, and do not have the same ordering correlation as the monosubstituted alkenes. Separate mono- and disubstituted alkene series would display

Table I. Relative Rates of Hydroboration, MO Energy Levels, and Table I. Relative Rates of Hydroboration, MO Energy Levels, and Ionization Potentials of Allyl Compounds.

$H_2C{=}CHCH_2X$ X	relative reactivities	HOMO energy level (eV)	IP
$SiMe_3$	300.	-9.63	-8.85
Pr	100.	-9.96	-9.45
SMe	26.1	-10.10[c]	-9.95[c]
OAc	21.9	-10.37	
OMe	20.1	-10.17	-9.44
I	7.1[b]	-10.17	-9.75
CN	5.93	-10.51	-10.18
Br	4.5[b]	-10.32	-10.18
Cl	4.0[b]	-10.48	-10.34
BBN[c]	3.71[b]	-9.58	

[a]The HOMO corresponds to a lone pair on sulfur, so the data given is for the Next Highest Molecular Orbital (NHMO) which corresponds to the pi electrons. [b]Ref. 8. [c]Data for *B*-(*trans*-2-butenyl)-9-borabicyclo[3.3.1]nonane.

improved correlations. As a check on the theoretical data, we tabulated the pertinent experimental IP's,[11] which also show a good correlation with the relative reactivities. This correlation is best explained by invoking in the transition state an interaction between the alkene HOMO and the low-energy empty orbital on boron in 9-BBN. The alkenes which possess higher HOMO energy levels are fastest-reacting. Thus, the interaction is more favorable with HOMO energy levels which are closer to the 9-BBN LUMO energy level. These data support the concept that the transition state in the rate-determining step is an early one in which much of the pi-bond character is retained. Although it is not necessary that the experimental results for 9-BBN and BH_3·THF agree because of their different steric requirements and LUMO energies, the above conclusion for 9-BBN agrees with the interpretation of the entropy data for BH_3·THF.[7a,b] However, our results only give information concerning the change in character of the alkene moiety in the transition state and do not enable a differentiation between the various possible mechanisms with early transition states.[4]

A second demonstration of the alkene HOMO influence is the regiospecific carbon-boron bond formation at the carbon atom possessing the larger a.o coefficient in the alkene HOMO. For example, in vinyl chloride, the terminal carbon atom has the higher a.o. coefficient in the HOMO. Hydroboration of

Table II. Relative Rates of Hydroboration, MO Energy Levels, and Ionization Potentials of Vinyl Compounds.

$H_2C=CHX$ X	relative reactivities	HOMO energy level (eV)	IP
OBu	928.	-9.92	-9.07
Bu	100.	-9.96	-9.45
OAc	22.8	-10.03	-9.85
$SiMe_3$	22.8	-10.04	-9.82
BBN[a]	7.97	-9.76	
SPh	2.71	-10.39[c]	-10.5[c]
Br	0.0105[b]	-10.05	-9.82
Cl	0.0031[b]	-10.16	-10.00

[a]Data for B-(trans-1-hexenyl)-9-borabicyclo[3.3.1]nonane. [b]Data for the trans-butenyl compounds. [c]NHMO.

alkenyl chlorides gives carbon-boron bond formation exclusively at the terminal carbon.[8] Similarly, vinylborane has a higher a.o. coefficient at the internal carbon atom, and hydroboration of alkenylboranes produces only gem-diboryl compounds.[5c]

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