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Reaction Mechanism of Hydroboration. Ab Initio MO Study on the $C_2H_4 + BH_3$ Reaction

Sir:

Despite its great synthetic usefulness and applicability, the detailed mechanism of the hydroboration reaction[1] has been a matter of a considerable dispute. Brown[2] originally proposed a simple four-center transition-state mechanism. On stereochemical grounds, Seyferth[3] and Streitwieser et al.[4] have suggested an intermediate triangular π complex prior to a three-center-like transition state. These possible mechanisms have been argued by Pasto and Kang[5] on the basis of kinetic isotope effects.

Four molecular orbital studies,[6-9] at the semiempirical and the ab initio minimal basis set levels, have appeared within the last year to elucidate the mechanism of a prototype reaction of C_2H_4 with BH_3. The results, however, are very divergent. A CNDO/2 result of Dasgupta et al.[6] preferred a three-center transition state. In a MNDO study, Dewar and McKee[7] have found that a loose π complex is formed with an energy barrier of 7.6 kcal/mol, this being the rate-determining step for the overall reaction. In contrast to this, an ab initio study with a very limited geometry optimization with the minimal basis set by Clark and Schleyer[8] has found that the formation of the π complex, located at a late stage of reaction, requires no energy barrier. The resultant three-center π complex transforms into the final products through a transition state which resembles the π complex closely in structure and in energy, the reaction proceeding without an overall energy barrier. Finally, Lipscomb et al.[9] very recently have reported a PRDDO study which mostly concurs with that of Clark and Schleyer, though there seem to be some differences in transition-state geometries.

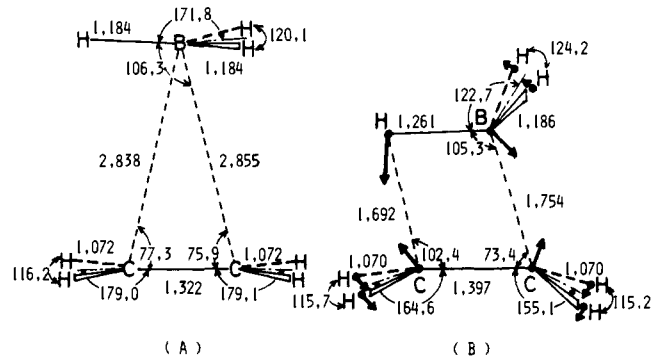

Figure 1. Optimized geometries (in angströms and degrees) for the intermediate π complex (A) and the transition state (B) at the 4-31G SCF level. The arrows in B indicate the displacement vector of the reaction coordinate (the normal coordinate with an imaginary frequency) at the transition state.

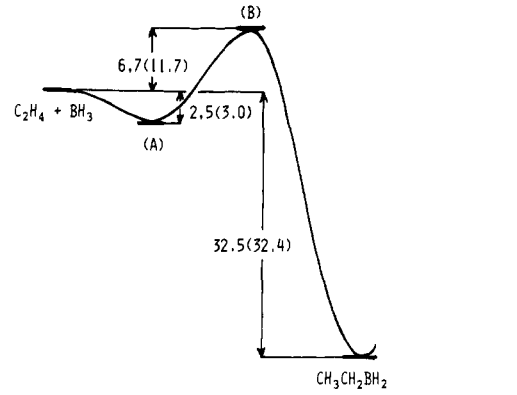

Figure 2. The energy profile (kilocalories/mole) for the reaction of C_2H_4 with BH_3 at the 4-31G (in parentheses) and 6-31G** SCF levels. Geometries used are optimized at the 4-31G SCF level. A and B are the π complex and the transition state, respectively.

To resolve the discrepancies and to determine the reaction mechanism, we have searched carefully for the stationary points on the potential energy surface of the title reaction with the ab initio SCF energy gradient method[10] at the split-valence 4-31G level.[11] The stationary points were identified as the equilibrium or the saddle point by examining the calculated normal vibrational frequencies. At the 4-31G SCF optimized stationary points, energies were also calculated with the 6-31G** basis set[12] which includes polarization functions needed for a better estimate of the energy differences involved. The barrier height for the reaction was further refined with the direct configuration interaction (CI) method.[13]

Upon going from the reactant, $C_2H_4 + BH_3$, to the final product, ethylborane, with a C_s symmetry constraint, we found two stationary points, an intermediate π complex and a transition state (saddle point), as shown in Figure 1. The π complex is in a fairly early stage of reaction and is held together by a three-center bond. The transition state, having *a four-center-like structure*, involves the concerted formation of the C—H and the C—B bond and cleavage of the B—H and the C=C bond, as shown by the reaction coordinate vector in Figure 1.

The energy profile at the SCF level is given in Figure 2. There exists no energy barrier to the formation of the π complex. The predicted exothermicities of 32.4 (4-31G) and 32.5 (6-31G**) kcal/mol agree well with an estimated value[14] of ~33 kcal/mol, while the previous studies provided 38.8 (MNDO),[6] 63.1 (STO-3G),[7] and 70.7 (PRDDO)[8] kcal/mol, respectively. Interestingly the polarization functions have little effect on the exothermicity.

An important point to notice in Figure 2 is that the π com-

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Table I. Overall Barrier Height (ΔE) for the $C_2H_4 + BH_3$ Reaction

method[a]	ΔE, kcal/mol	method[a]	ΔE, kcal/mol
4-31G	11.7	4-31G + CI (S + D + Q)	5.6
4-31G + CI (S + D)	9.7	exp[b]	2 ± 3
6-31G**	6.7		

[a] S = single excitation, D = double excitation, and Q = quadruple excitation. [b] Reference 15.

plex has to pass over a substantial energy barrier to complete the reaction, and this should be the rate-determining step for the overall reaction. The calculated SCF overall barriers of 11.7 (4-31G) and 6.7 (6-31G**) kcal/mol are, as expected, too large, compared with a gas-phase experimental estimate (2 ± 3 kcal/mol)[15] determined indirectly from an Arrhenius plot of the relative peak areas of mass spectra. We have carried out CI calculations including all the single and double excitations relative to the SCF reference configuration, except that the core orbitals are frozen. The unlinked quadruple-excitation contribution to the correlation energy was estimated further with the Davidson method.[16] The results are summarized in Table I. Though not actually carried out, the best calculation, an S + D + Q CI with the 6-31G** basis set, is expected to give a barrier of ~4 kcal/mol which is in reasonable agreement with the experimental estimate.

In conclusion, the hydroboration reaction proceeds through a two-step process. First, a loose three-center π complex is formed in the early stage without an energy barrier, and then it is transformed to the product via a four-center transition state, this process being the rate-determing step. The overall mechanism proposed is significantly different from any previous study, though it in part supports some of previous findings. Details of the study will be published elsewhere.

Acknowledgment. The authors are grateful to Dr. Kimihiko Hirao for the use of his direct CI program. N.K.R. acknowledges the Indian National Science Academy and the Japan Society for the Promotion of Science for their Scientist Exchange Program. The numerical calculations have been carried out at the Computer Center of IMS.

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Peptide Synthesis Using Unprotected Amino Acids and Novel Imidoyl Halide Reagents

Sir:

We report herein the synthesis and use of new imidoyl halide reagents for condensation reactions (including peptide synthesis). The reagents have the important advantage that (a) it is not necessary to protect amino acids using blocking agents, (b) racemization is minimal, (c) reaction conditions are particularly mild, and (d) competing reactions (such as intramolecular O → N acyl group migration) are suppressed.

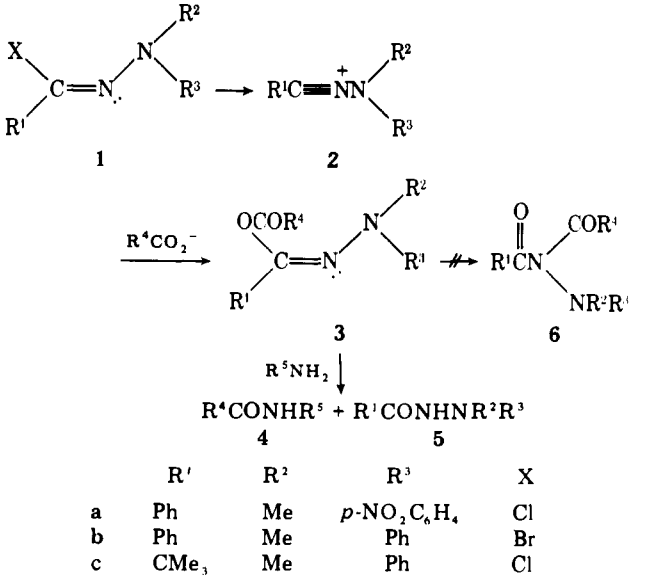
Imidoyl halides **1** on dissolution in polar solvents undergo rapid unimolecular ionization to give the nitrilium ions **2** (Scheme I). These ions are highly selective (as shown by large common ion effects) and undergo stereospecific reaction at carbon with nucleophiles.[1,2] Thus only the isomer (e.g., **3**) in which the incoming nucleophile and forming lone pair on nitrogen are trans is formed.

We have now found that nitrilium ions are unusual in that they react more rapidly with carboxylate ions than with simple amines.[3] Scheme II summarizes some typical rate data for imidoyl halide **1a**. It is clear that, when acetate and the amine (morpholine) are present in equal concentrations, the major product formed is still the *O*-acylisoamide **8** rather than the amidine **9**. This competition can be further altered in favor of the isoamide **8** by pH control. For example, when trapping of the nitrilium ion is carried out at pH 6 (>2 pH units below the pK_a of the amine), >99% of the trapped product formed is the isoamide **8** (in the presence of equal concentrations of acetate and morpholine). However the nitrilium ion discriminates between H_2O and AcO^- (see Scheme II); thus the trapping reactions can be carried out in aqueous solution.[4]

The *O*-acylisoamide **3**, once formed by selective trapping, shows the normal reactivity expected from an activated ester. Thus the rate of reaction of **3** with carboxylate ion is negligible in basic solution when compared with its reactivity toward amines (yielding the amide **4**). The formation of the amides (or peptides) **4** can therefore be carried out by adding the halide **1** to a solution containing both amine (R^5NH_2) and carboxylate ($R^4CO_2^-$). The initial reaction (formation of the adduct **3**) is best carried out at pH ~6; when the pH is adjusted to ~8, formation of the amide **4** is rapid and complete.

A vital feature of the reagent **1** is that the intermediates **3** are stable toward O → N acyl group rearrangement (to give

Scheme I



	R¹	R²	R³	X
a	Ph	Me	*p*-$NO_2C_6H_4$	Cl
b	Ph	Me	Ph	Br
c	CMe_3	Me	Ph	Cl

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