

Markovnikov Regiocontrol in Hydroboration of Alkene by Trifluoromethyl Substituent

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The reactions of dichloroborane BHCl_2 with 3,3,3-trifluoroprop-1-ene (TFP), and propene have been studied using B3LYP method with 6-31G* basis set. Based on the calculations, all transition structures have parallelogram-like H-B-C four-center geometry with small deformations. The introduction of fluorine atoms changes the proportions of hydroborational products and reverses the regioselectivity.

Keywords Hydroboration, 3,3,3-trifluoroprop-1-ene, propene, DFT

The particular regioselectivity has made the hydroboration of alkenes become one of the most widely utilized reactions in modern organic synthesis.¹⁻³ The anti-Markovnikov mechanism has been verified by theoretical computations.^{4,5} Houk's RHF/3-21G calculation of the reaction between propene and BH_3 indicated that the transition state leading to the major product is 15.1 kJ/mol (3.6 kcal/mol) lower than that to the minor one. However, the Markovnikov products are far more predominant in the hydroboration of perfluoroalkylethylenes surprisingly.⁶ Especially, this kind of unusual regioselectivity is more than 97% if perfluoroalkylethylenes react with Cl_2BH or Br_2BH .

In the following paragraphs, an investigation of quantum chemistry has been performed to describe the influence of trifluoromethyl substituent upon ethylene and the role dihaloborane plays in the reaction of hydroborations. A reasonable explanation of mechanism is also expected to make a contribution to the applications in organic synthesis and biological techniques. Geometry optimizations of equilibrium and transition states, followed

by analytical frequency calculations were performed at the level of B3LYP/6-31G* using Gaussian 98 quantum chemistry software.⁷ All thermodynamic analyses were carried out at 298.15 K and 1.0 atm and corrected by corresponding scales.⁸

The hydroborations of perfluoroalkylethylene by dihaloborane are instantaneous in hexane⁶ and this phenomenon is contrary to the perhydrogen counterpart.^{1,9,10}



The equilibrium (1) between dichloroborane monomer and its dimer, which contains two H-bridge bonds, was studied at the level of B3LYP/6-31G*. The length of B—H bonds is 0.1337 nm and the angles of B—H—B are equal to 85.8° in the two H-bridge bonds. The dimer is disfavored in energy and ΔE , ΔH , ΔG , ΔS for Eq. (1) are -29.04, -26.90, -80.29 kJ/mol and 179.16 J/(K·mol) respectively. Enhanced by the preference of entropy, dichloroborane dissolves in hexane all in the form of monomer. Although the hydroboration of alkenes by borane, alkylboranes or monofluoroborane were extensively studied by theoretical methods,^{5,11,12} the attention to that of dihaloboranes by computational chemists is not parallel to experimental ones.¹³⁻¹⁵

Differing from reactions of alkenes with BH_3 , no π -complex intermediates between dichloroborane and the alkenes (TFP and propene) were found after a long time searching at various levels (B3LYP/6-31G*, B3PW91/

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6-31G* and MP2/6-31G*). Namely, the hydroboration of alkenes by dichloroborane proceeds not via a three-center intermediate followed by intramolecular hydrogen transfer process but most likely direct dimolecular reaction as shown in Scheme 1.

All of transition states involved in Scheme 1 are illustrated in Fig. 1, in which some structure parameters are also presented. The activation energies and the changes of thermodynamics of Scheme 1 are given in Table 1. Obviously, all the transition states have paral-

lelogram-like HB-B-C-C four-center geometry which is similar to the transition state for the reaction of BH₃ and propene.⁵

Scheme 1

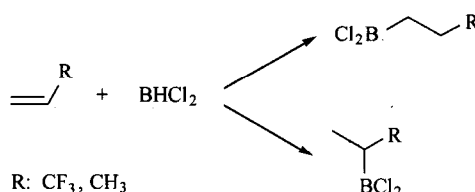


Table 1 Activation energies and thermal analyses for Scheme 1

Hydroboration		E_a^a	ΔH^\ddagger	ΔG^\ddagger	ΔS^\ddagger^b	ν_i^c	ΔE	ΔH	ΔG	ΔS
TFP	Sec	84.56	81.80	136.57	-183.72	-412.5	-120.58	-121.50	-73.72	-160.29
	Pri	87.15	84.27	138.49	-182.00	-470.2	-132.21	-133.43	-86.65	-156.90
Propene	Sec	68.70	64.81	118.70	-180.87	-544.6	-114.14	-116.06	-71.59	-149.29
	Pri	49.58	45.77	99.16	-179.08	-435.4	-109.12	-110.92	-64.22	-156.65

^a The units of E_a^a , ΔH^\ddagger , ΔG^\ddagger , ΔE , ΔH , and ΔG are kJ/mol; ^b The units of ΔS^\ddagger^b and ΔS are J/(K·mol); ^c unit is cm⁻¹;

^d Sec and Pri refer to the products: sec-alkylborane and pri-alkylborane respectively.

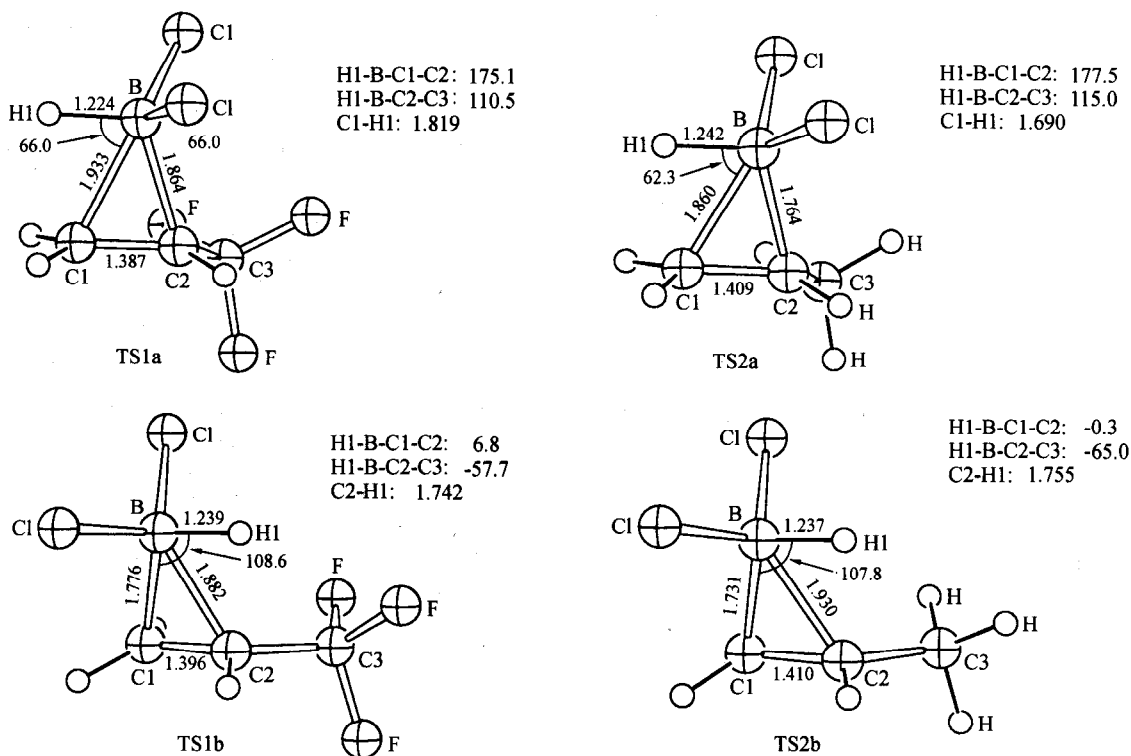


Fig. 1 Transition states of the hydroboration of BHCl₂ with TFP and propene. All distances between atoms are in 0.1 nm, all angles and dihedral angles are in degree.

In the circumstance of propene, TS2b, which leads to *n*-propylborane, is more stable than TS2a by

19.12 kJ/mol. The computational prediction keeps consistent with experimental data. A proximate datum

(15.1 kJ/mol) has been reported by Houk at the level of RHF/3-21G.⁵ However, the situation is overturned when comparing the two transition states of TFP's hydroboration. The DFT calculation predicts that the barrier leading to *anti*-alkylborane is 2.6 kJ/mol higher than that to secondary product and that keeps quite parallel to Brown's data.⁶

It is noticeable that the introduction of fluorine atoms on the methyl heightens the energy barriers on the pathway of hydroboration. Considering the frontier orbitals of the reactants, trifluoromethyl impedes the electron donation of the π orbital of alkenes (Table 2). The energy of TFP's HOMO is 1.33 eV lower than propene's. Namely, the energy gap between TFP's HOMO and BHCl_2 's LUMO is 1.33 eV larger than that between propene's and BHCl_2 's. On the other hand, compared to propene, trifluoromethyl inverts the charge distribution on olefinic carbon atoms in TFP (Fig. 2) and this might be driving force resulting in the irregular regioselectivity.

Table 2 Energies of LUMO and HOMO orbitals in TFP, propene and BHCl_2

Species	LUMO (eV)	HOMO (eV)
TFP	-0.55	-8.13
Propene	0.77	-6.80
BHCl_2	-1.83	-8.96

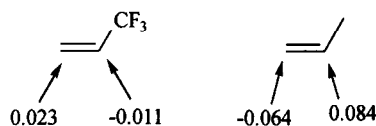


Fig. 2 Partial charges on the olefinic carbon atoms in TFP and propene. The charges of hydrogens are summed into the connected carbon atoms.

The transition states for the reaction between dichloroborane and alkenes (TFP and propene) were located by Synchronous Transit-Guided Quasi-Newton (STQN) method^{16,17} and at the level of B3LYP/6-31G*. *Anti*-Markovnikov products are preferred in the hydroboration of propene, whereas the regioselectivity is overturned when three fluorine atoms are introduced.

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