Fritsch–Buttenberg–Wiechell (FBW) Reaction of 1-Halovinyllithium Carbenoids: A Computational Study

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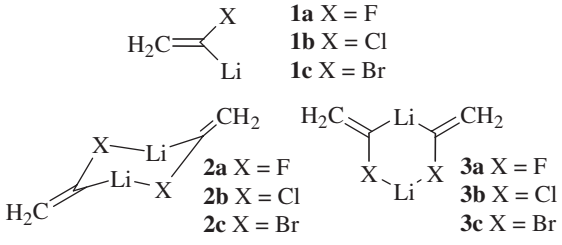
1-Halovinyllithium carbenoids can undergo the Fritsch–Buttenberg–Wiechell (FBW) rearrangement to form alkynes. This reaction is quite facile when a hydrogen atom is present on carbon 2. The gas-phase reaction mechanism may consist of a single-step or several steps, depending on the aggregation state of the carbenoid. We examined the FBW reaction of 1-fluoro, chloro-, and bromovinyllithium in the monomer and two isomeric dimers. The migratory aptitude of the hydrogen atoms is dependent on the halogen and the aggregation state.

1-Halovinyllithiums are an important class of carbenoid intermediate. Although some bond insertions and reactions with nucleophiles are known,[1,2] typical carbenoid insertion reactions are relatively uncommon with these compounds. This may be due, in part, to the facile rearrangement reaction described in detail below. The FBW reaction involves the migration of a hydrogen atom or an alkyl group from carbon 2 to carbon 1, forming an alkyne with the elimination of lithium halide. This reaction has been used extensively in the synthesis of functionalized alkynes and polyynes that are difficult to synthesize by other methods.[3–8]

Modern computational methods are able to provide significant insight into reaction mechanisms, particularly those which are difficult to elucidate experimentally. The choice of computational method is critical, however.[9,10] We have recently shown that while the popular B3LYP density functional theory (DFT) method generates good optimized geometries for halomethyllithium carbenoids in the gas-phase, it is a poor method for 1-halovinyllithiums.[11] In contrast, MP2 generated geometries and relative energies in good agreement with the high level G3MP2 method. Therefore, the MP2 method with the 6-31+G(d) basis set was used for all calculations in this work.

Hydrogen migration was examined via the carbenoid monomer **1a**–**1c**, via the two isomeric dimers **2a**–**2c** and **3a**–**3c** (Scheme 1); and the dimerization energies are given in the Supporting Information.[12] Activation free energies were calculated for migration of the hydrogen atom syn and anti to the halogen atom. These are designated as the syn and anti migrations below.



Scheme 1. Carbenoid monomers and dimers.

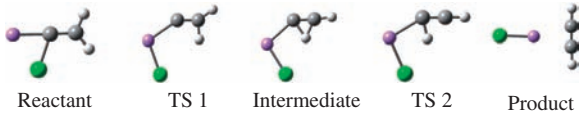


Figure 1. Syn hydrogen migration in **1b**. Reaction of **1c** is similar. Grey: C; white: H; violet: Li; green: Cl.

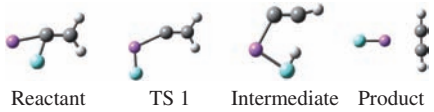


Figure 2. Syn hydrogen migration in **1a**. Grey: C; white: H; violet: Li; light blue: F.

Table 1. Free energies (kcal/mol) along the reaction path for syn hydrogen migration via $H_2C{=}CLiX$ monomer **1** at 158 K

X	React.	TS 1	Int.	TS 2	Prod.
F	0	10.6	−3.17	N/A	−33.6
Cl	0	7.07	4.42	6.06	−35.5
Br	0	8.16	6.42	6.88	−34.2

Syn hydrogen migration via monomer **1b** and **1c** occurred by a two-step mechanism, as illustrated in Figure 1. The anticipated transition state was actually a "stable" intermediate, as determined by the absence of any imaginary vibrational frequencies. This was flanked on either side by a transition state, designated as TS 1 and TS 2 in Figure 1. The syn migration of the 1-fluorovinyllithium monomer (**1a**) occurred by a different pathway, as illustrated in Figure 2. The first transition state resulted from cleavage of the C–F bond. The intermediate was formed not by the hydrogen atom bridging the two carbon atoms, but by hydrogen migration to the basic fluorine atom, with some coordination to the alkene double bond. A smooth pathway from the intermediate to product could not be located, although an acid–base reaction seems likely, and may involve a second carbenoid unit. The reaction and activation free energies are shown in Table 1.

The anti hydrogen migration was similar for all three 1-halovinyllithium carbenoids. All attempts to find a transition structure similar to that of the syn migration failed. Instead, the halogen dissociated via TS 1 to a symmetrical intermediate in which the syn and anti hydrogens became equivalent. Hydrogen migrated from this intermediate via TS 2 to a bridged intermediate, then via TS 3 to the product, as illustrated in Figure 3. The energies of the transition states and intermediates are given in Table 2. Both the syn and anti migration take place with

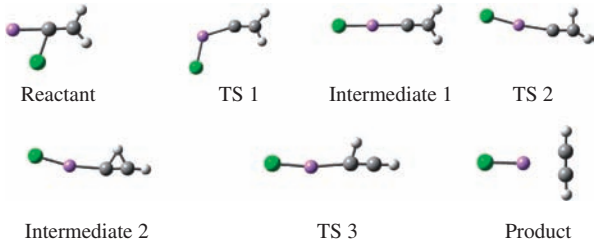


Figure 3. Anti hydrogen migration in monomer **1**. Grey: C; white: H; violet: Li; green: Cl.

Table 2. Free energies (kcal/mol) along the reaction path for anti hydrogen migration via $H_2C{=}CLiX$ monomer **1** at 158 K

X	React.	TS 1	Int 1	TS 2	Int 2	TS 3	Prod.
F	0	10.6	8.81	9.09	7.57	9.20	−33.6
Cl	0	7.50	5.86	6.06	4.36	6.07	−35.5
Br	0	8.75	7.24	7.47	5.75	7.43	−34.2

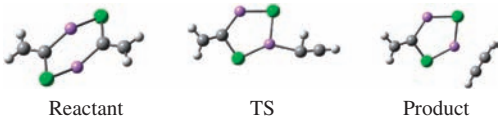


Figure 4. Syn hydrogen migration in dimer **2**.

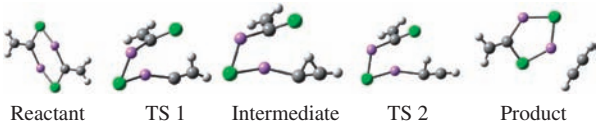


Figure 5. Anti hydrogen migration in dimer **2**.

Table 3. Free energies (kcal/mol) along the reaction path for syn and anti hydrogen migration via $H_2C{=}CLiX$ dimer **2** at 158 K

X	React.	TS 1	Int.	TS 2	Prod.
F syn	0	1.69	N/A	N/A	−42.3
Cl syn	0	6.55	N/A	N/A	−37.3
Br syn	0	9.03	N/A	N/A	−34.5
F anti	0	8.20	4.93	6.68	−42.3
Cl anti	0	7.29	4.75	6.63	−37.3
Br anti	0	6.36	4.17	6.03	−34.5

similar activation energies, with the first step being rate determining.

We investigated syn and anti hydrogen migration in the two isomeric dimers **2** and **3**. The syn hydrogen migration in dimer **2** took place in a single-step. The mechanism is illustrated in Figure 4. In contrast, the anti migration occurred in a two-step mechanism, shown in Figure 5. The migrating hydrogen atom appears to be coordinated to the halogen atom in the neighboring monomer unit in the bridged intermediate and both transition states. The energies along the syn and anti migration pathways are shown in Table 3. Comparison of these activation energies shows that the syn pathway is favored for the fluoro and chloro carbenoids, but the anti pathway is favored for the bromo carbenoid.

In dimer **3b** and **3c**, both the syn and anti hydrogen migrations occurred by a two-step mechanism which is illustrated in the Supporting Information. Syn migration of **3a** occurred in a single-step with a very small activation barrier. The anti hydrogen migration, also illustrated in the Supporting Information, was similar for the chloro and bromo carbenoids **3b** and **3c**, but the mechanism was different for the fluoro carbenoid **3a**. A similar bridged intermediate was formed, but it underwent a proton-transfer reaction to the neighboring monomer unit, leading to a different product. The energies along the reaction path are shown in Table 4.

Table 4. Free energies (kcal/mol) along the reaction path for syn and anti hydrogen migration via $H_2C{=}CLiX$ dimer **3** at 158 K

X	React.	TS 1	Int.	TS 2	Prod.
F syn	0	0.208	N/A	N/A	−42.8
Cl syn	0	4.51	2.70	4.55	−38.0
Br syn	0	6.11	5.51	5.95	−34.7
F anti	0	3.60	2.06	2.29	−54.6
Cl anti	0	5.09	3.61	5.29	−38.0
Br anti	0	6.18	3.98	6.98	−34.7

The calculations show that the most facile FBW pathways occur in aggregated species. We are currently investigating hydrogen migration via the carbenoid tetramer, and preliminary results indicate that the mechanisms are similar to those in the dimers. The FBW reaction is normally performed in a non-polar solvent,[7] and the gas-phase calculations provide a reasonable approximation for these conditions, in which carbenoid aggregates are highly favored over monomers. Preliminary results also indicate that alkyl group migration occurs in a single-step mechanism, and that activation energies are several kcal/mol higher than for hydrogen migration.

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12 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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