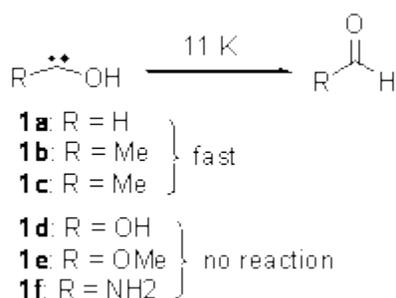# CYCLOPROPYLHYDROXYCARBENE

Schreiner has observed tunneling in hydroxycarbenes that is either very rapid (**1a-c**) or not at all (**1d-f**).[1-4] In a recent paper his group investigates whether cyclopropylhydroxycarbene **2** might have an intermediate lifetime due to the π-donating effect of the three-member ring.[5]

Schreiner makes this carbene in his usual manner: flash pyrolysis of the cyclopropylglyoxylic acid. Let's now consider three possible rearrangements of carbene **2**. The hydrogen can migrate (Scheme 1, path a) to give cyclopropylcarboxyaldehyde **3** similar to what was observed with the related hydroxycarbenes. Carbon can migrate (Scheme 1, path b), opening up the three-member ring to give the cyclobutenol **4**. This ring could open to the diene **5** and tautomerize to the ketone **6**. Lastly, a hydrogen migration from carbon (Scheme 1, path c) would lead to **7**. The relative energies of these species computed at CCSD(T)//cc-pVTZ//M06-2x//6-311++G(d,p) are shown in Scheme 1.

Scheme 1. Relative energies in kcal mol^{-1}.
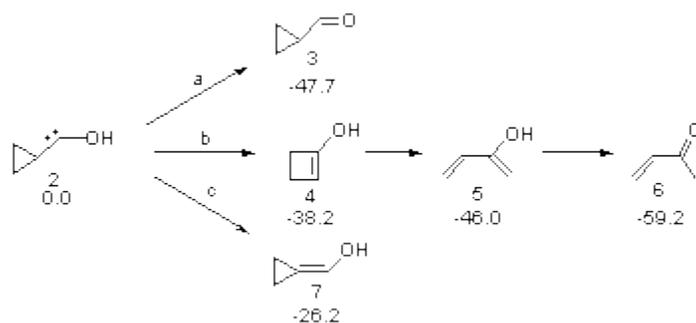
The computed barriers for the initial step of each pathway is +30.4 kcal mol^{-1} for path a, +21.9 kcal mol^{-1} for path b and +35.8 kcal mol^{-1} for path c. Thus, one might expect to see only the reaction along path b at low temperature and mostly along b at high temperature with some small percent along path a. So what actually occurs?

After capturing the flash pyrolysis product in an Ar matrix, besides the unreacted cyclopropylglyoxylic acid, **6**, **3**, and **2** are observed in an approximate 8:5:1 ratio. **2** is identified on the basis of the nice agreement between the experimental and computed IR frequencies. Irradiation of **2** in the matrix leads to clean conversion to **4**, also identified by comparison of the observed and computed IR frequencies. This is all consistent with the computed activation barriers. In the pyrolysis, at high T, **6** is the major product and **3** is the minor product. At very low T (11 K), irradiation of **2** produces **4** (crossing only the lowest barrier) and not continuing further along the rearrangement path to **6**.

What is perhaps most exciting is that **2** disappears slowly in the dark at both 11 K and 20 K, converting at the same rate to **3**. The half life is 17.7 h, much longer than for the alkyl and aryl substituted hydroxycarbenes **1a-c**. This confirms the stabilization effect of the cyclopropyl group, as does its large singlet-triplet gap. The computed tunneling half-life using the WKB approach is 16.6 h, in excellent agreement with experiment. And as expected for a tunneling phenomenon, the dueterated analog has a much longer half-life, computed to be 10^5 years. Experimentally, **2-d** persists with no conversion to **3-d** observed.

As with methylhydroxycarbene, we see here an example of tunneling control vs kinetic control. At high T, the reaction crosses the lowest barrier (shown in Figure 1a), proceeding to **4** and subsequent rearrangement products. At low T, the reaction crosses a *higher barrier* (shown in Figure 1b), but this path involves tunneling of the very light hydrogen atom only, producing **3**.

TS 2 → 3   TS 2 → 4
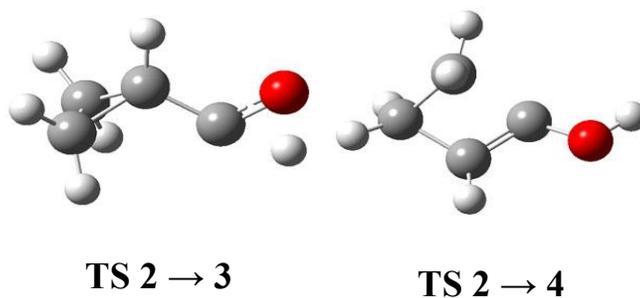
Figure 1. M06-2X/6-311++G(d,p) optimized geometry of the transition states connecting **2** to (a) **3** and (b) **4**.