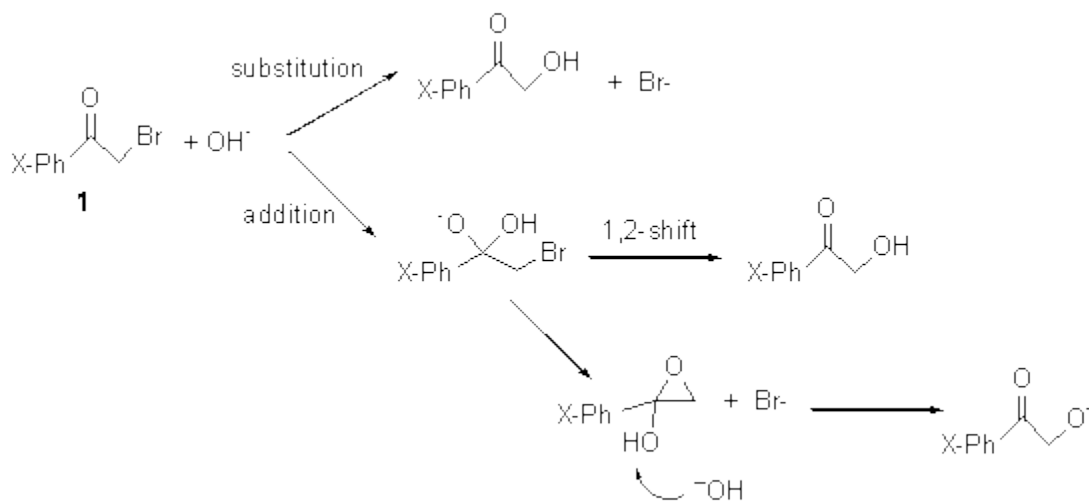


SUBSTITUTION VS. ADDITION: DYNAMIC EFFECTS

Reactions whose outcomes depend on dynamic processes is a major theme of my book. The recent study of the reaction of a nucleophile (hydroxide) with bromoacetophenones adds yet another case for post-transition state product determination.

Itoh and Yamataka have examined the reaction of hydroxide with substituted α -bromoacetophenones **1**.¹ The nucleophile can attack at the carbonyl carbon or the α -carbon, though both lead ultimately to the same product, as shown in Scheme 1.

Scheme 1



B3LYP/6-31+G* computations of the reaction surface with a variety of different substituents on the phenyl ring of **1** located in all cases a single transition state for the two different reactions (addition and substitution). This TS is shown in Figure 1 for the parent case (X=H).

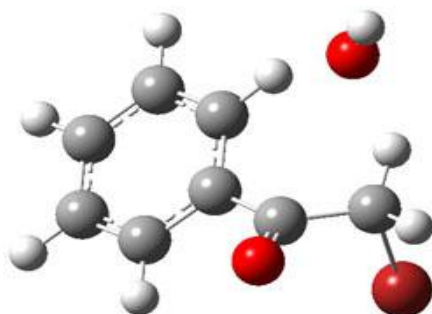


Figure 1. The single transition state for the addition and substitution reaction of **1** and hydroxide.

Tracing the IRC forward leads to either the carbonyl addition product or the substitution product, and which path is traced depends to some extent on the nature of the substituent. Most intriguing is that trajectories initiated at the transition state lead to both products. So once again, we see a case where a single transition state leads to two products, and product selectivity is determined by the dynamics – the initial conditions at the TS dictate which of the two products is eventually obtained.

Source: <http://comporgchem.com/blog/?p=1871>