## 4.4 Electrophilic Addition Reactions of Weak Brønsted Acids

## A. Observed Outcomes: The Need for a Strong Acid Catalyst

The first step of the electrophilic addition mechanism of Brønsted acids is protonation of a pi bond, and there is an experimentally determined threshold value for the strength of an acid that can be predicted to carry out this reaction, and a p $K_a$  above which the protonation reaction is not favorable. Although there is no reason for a clean line of demarcation, the common value of p $K_a = 5$  is used as a guideline. Naturally, there may be acids above this value that are observed to participate in the reaction, and there may be those below the value that do not. And there may be pi **bonds** that are more or less reactive in ways that influences the strength of the acids they react with. The threshold of p $K_a = 5$  for Brønsted acids that can predictably protonate pi bonds is a general guideline that can be used without other experimental infor-mation or guidance.

Quite emphatically: No predictive model is perfect. When experimental information contradicts any general guideline, then you always follow the experimental results.

Weaker Brønsted acids ( $pK_a > 5$ ) are typically not strong enough to protonate a pi bond, and so the addition reaction is not observed upon simply mixing the two reagents together (Figure 0439).

## Figure 0439

Addition reactions of weak Brønsted acids are not observed under the same reaction conditions as strong Brønsted acids.

H-OH
$$pK_{a} = -9$$

$$H-OH$$

$$pK_{a} = 15.7$$
No reaction
$$PK_{a} = -7$$

$$H_{3}C$$

The most common experimental strategies for trying to get a slow or sluggish reaction to proceed are (a) raising the temperature, (b) increasing the concentration, (c) changing the solvent, and (d) finding a catalyst.



