## In-Class Solutions: Proton-Mediated S<sub>N</sub>1 Mechanisms

$$H_3C$$
 $H_3C$ 
 $H_3C$ 

$$H_3C$$
 $H_3C$ 
 $H_3C$ 

Here, I've used Br as the base in the second step. I could also have used methanol as the base. Which is better? The conjugate acids of Br and  $CH_3OH$  (HBr and  $CH_3OH_2^+$ ) have very similar pKa values. So we'd expect the two bases would have very similar basicities.

One incorrect mechanism that students sometimes draw is to deprotonate methanol first (with either methanol or bromide serving as the base), and then have methoxide attack as the nucleophile. There is no way that this would happen, because making a methoxide and a protonated methanol from two methanol molecules would be pretty endothermic (kind of like making  $OH^-$  and  $H_3O^+$  from two water molecules is), and wouldn't occur to any significant extent.

$$CH_3$$
 $HBr$ 
 $H_2SO_4$ 
 $CH_3$ 

One alternative here would have been to make  $OH^-$  leave first, have it deprotonate HBr, and then follow with  $Br^-$  attack. But  $OH^-$  is a horrible leaving group, and it would never ever exist in strong acid like  $H_2SO_4/HBr$ . Given that, the better approach outlined here is to go back and protonate the oxygen first (to make  $-OH_2^+$ , a fantastic leaving group), so that  $OH^-$  doesn't have to be invoked in the first place.