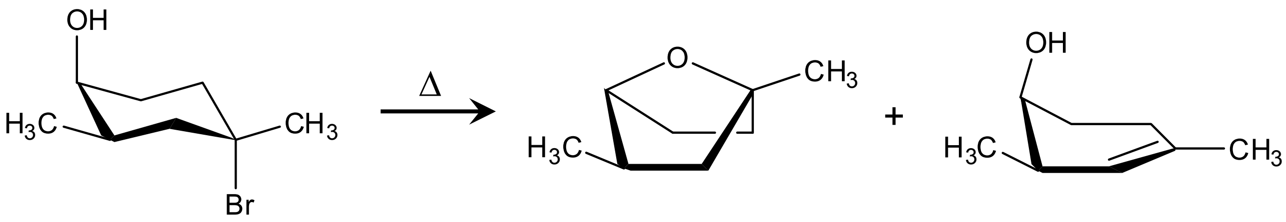
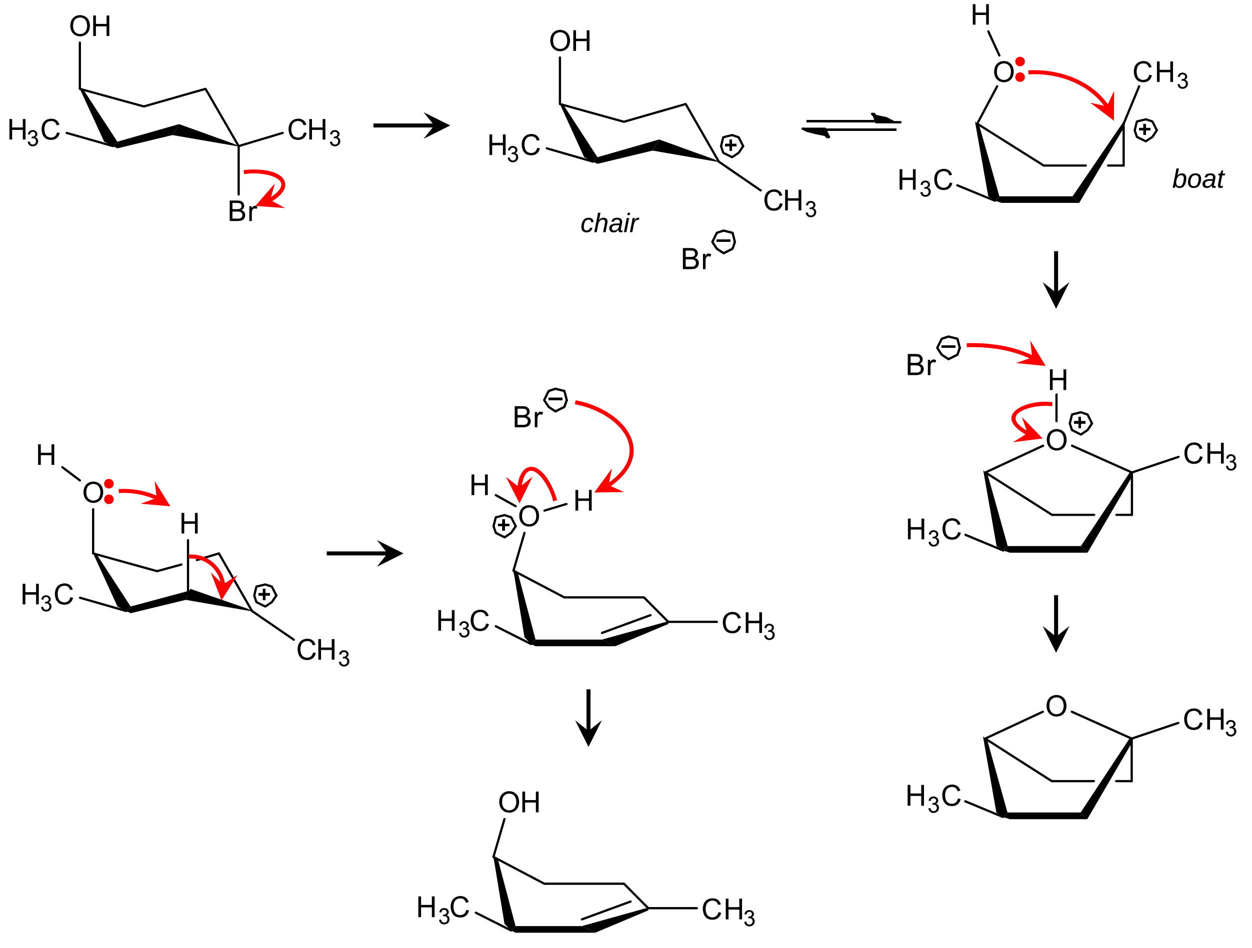
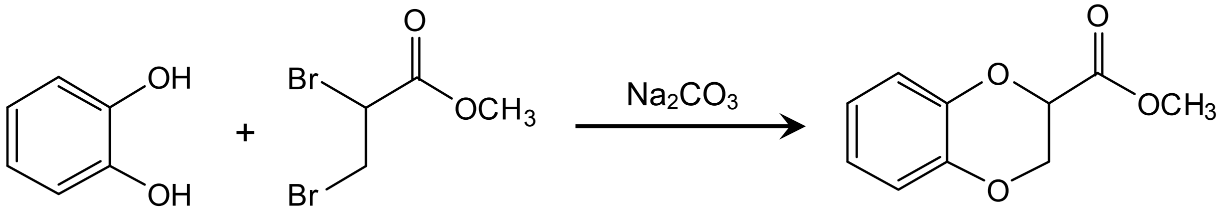
Chemistry 2301

At-Home Solutions:
Mechanism Practice Problems

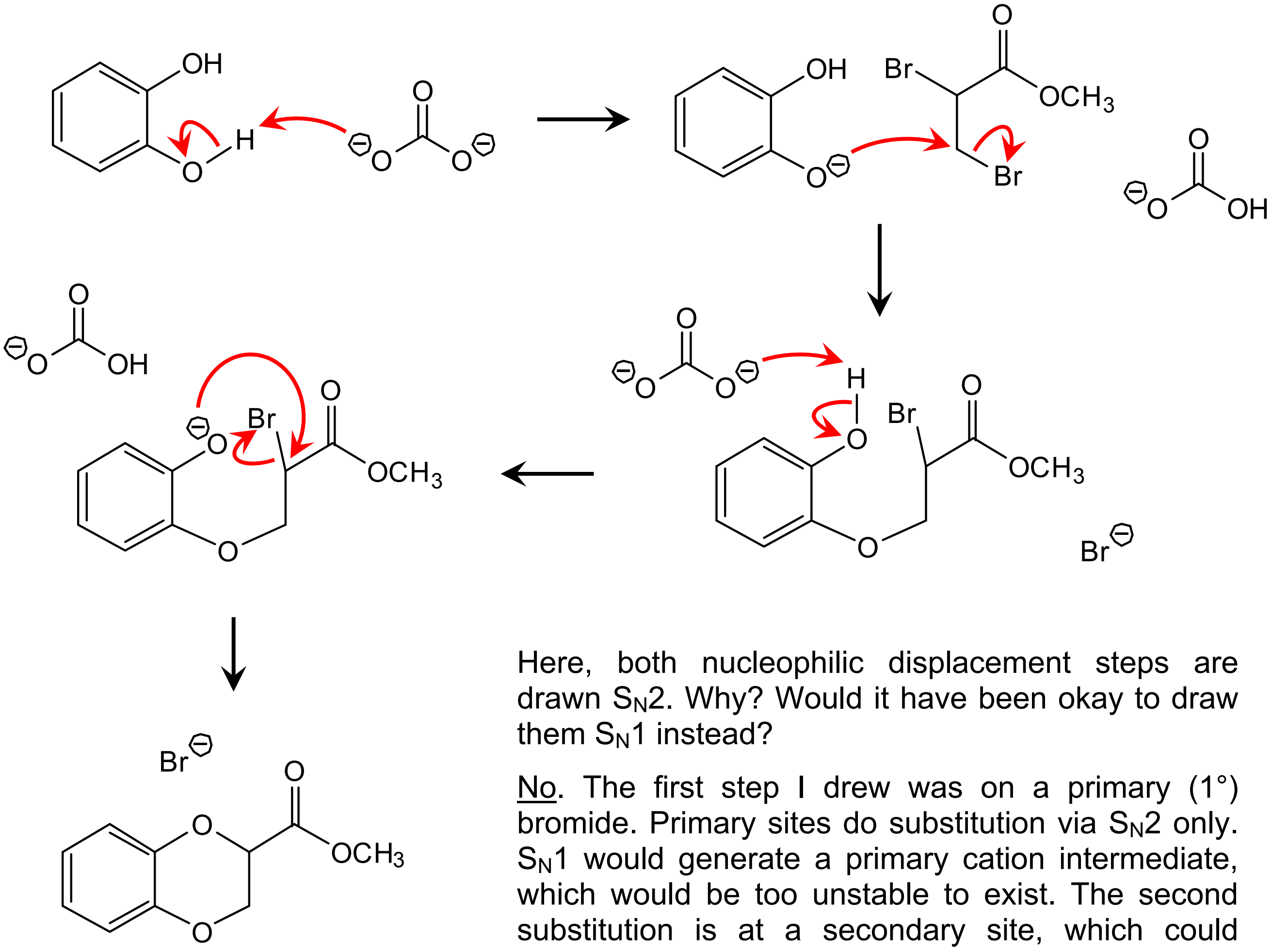


The heat (Δ) is a tip that we can start with E1/S$_N$1's first step: making a carbocation.



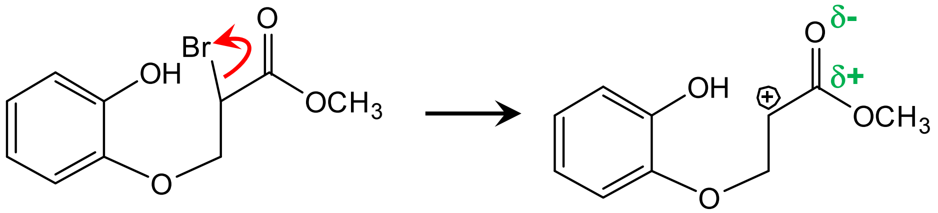


The sodium carbonate base is strong enough to deprotonate the alcohol starting material; that wouldn't happen with an alcohol like ethanol (pK_a = 16), but it's possible in this case because of resonance stabilization of the conjugate base:



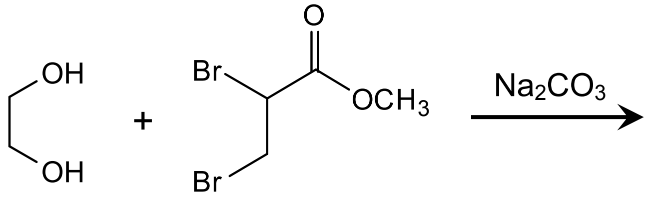
Here, both nucleophilic displacement steps are drawn S$_\text{N}$2. Why? Would it have been okay to draw them S$_\text{N}$1 instead?

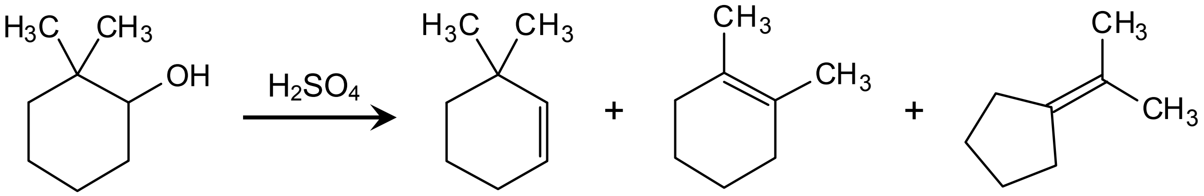
<u>No</u>. The first step I drew was on a primary (1°) bromide. Primary sites do substitution via S$_\text{N}$2 only. S$_\text{N}$1 would generate a primary cation intermediate, which would be too unstable to exist. The second substitution is at a secondary site, which could generate a secondary carbocation, but I don't like that carbocation very much (next page):

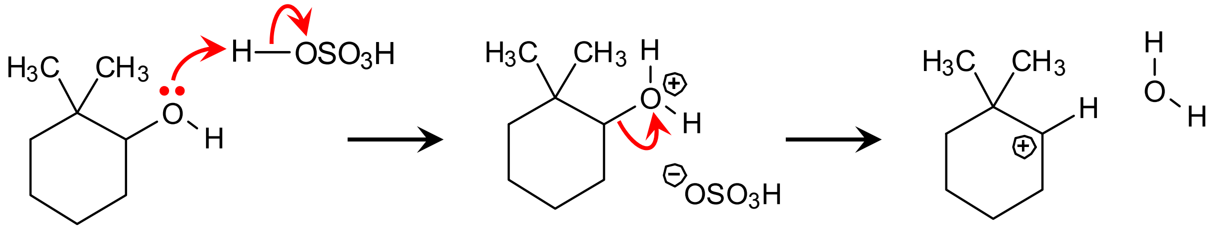


The carbocation ends up next to a partial positive charge from the carbonyl—**not good**. This wouldn't happen.

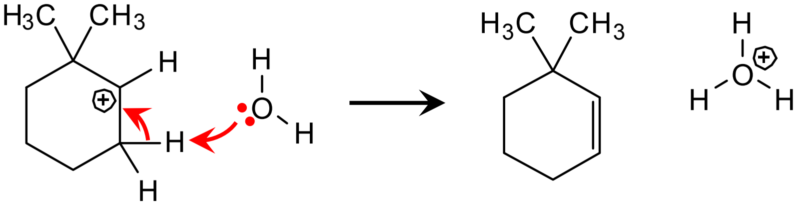
So, a bonus question—how might this mechanism be different if ethylene glycol (pK_a = 16) was used as the diol instead of catechol? (Answer at the end of this answer key.)

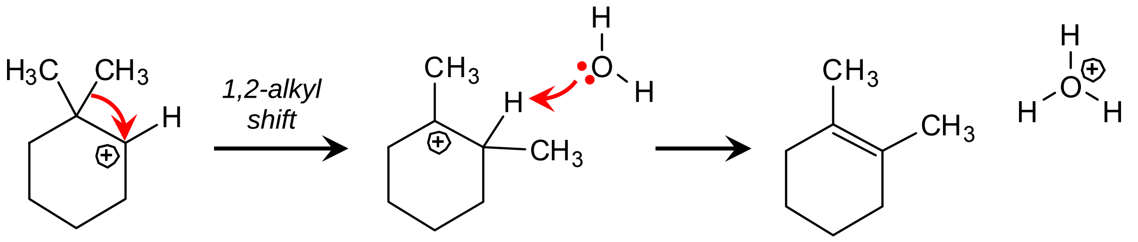




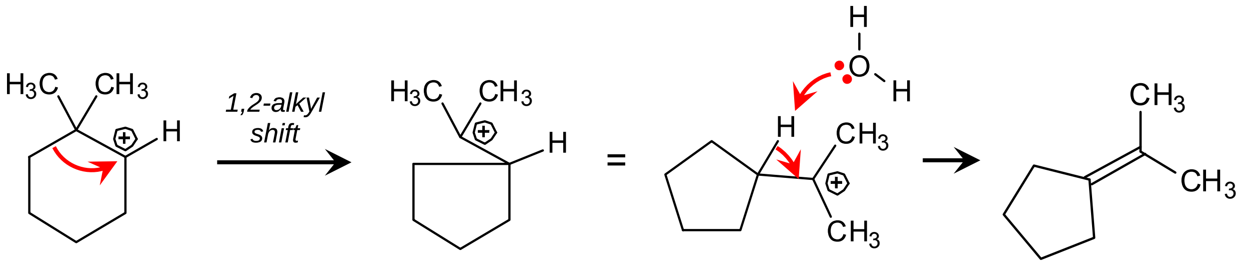


a common intermediate for all three products

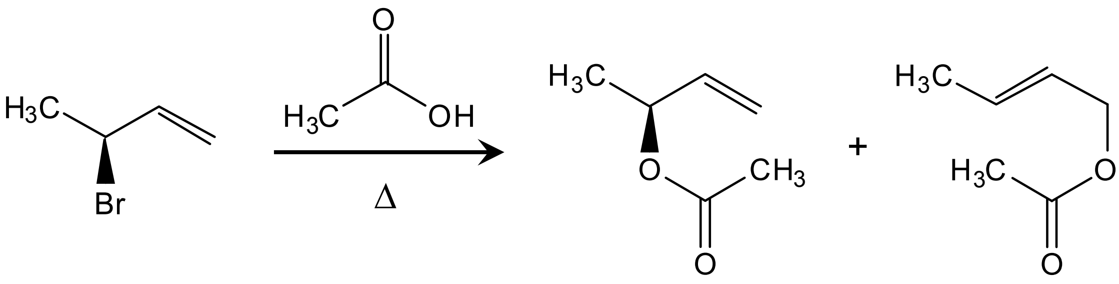




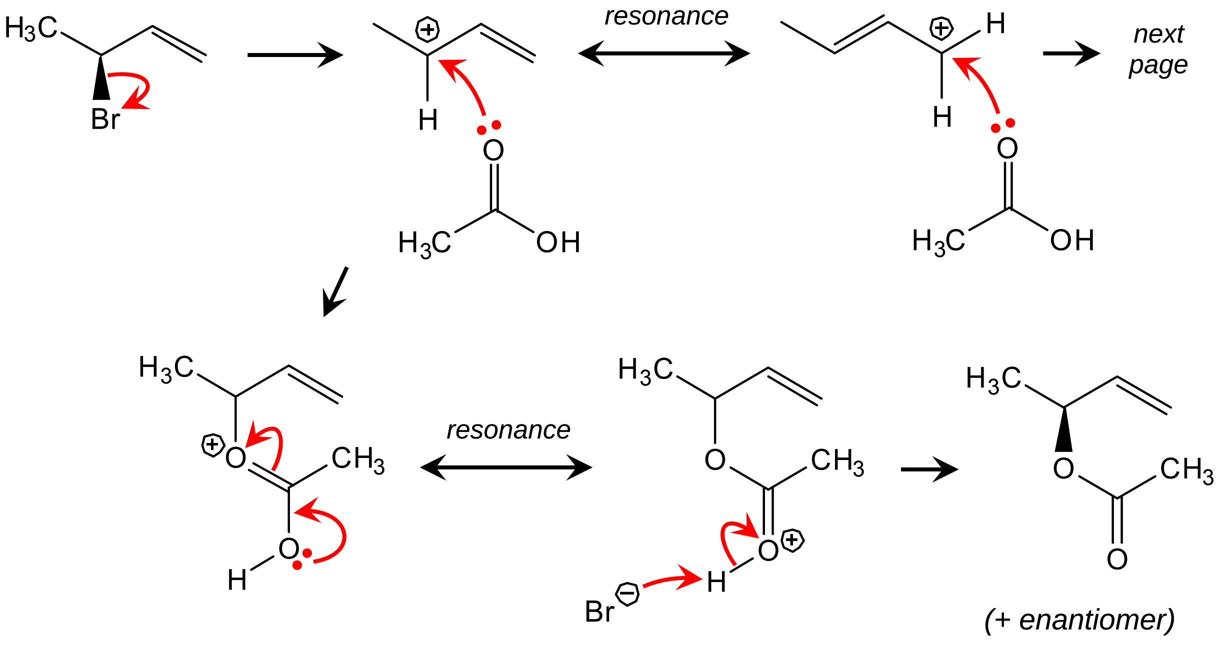
1,2-alkyl shift



1,2-alkyl shift

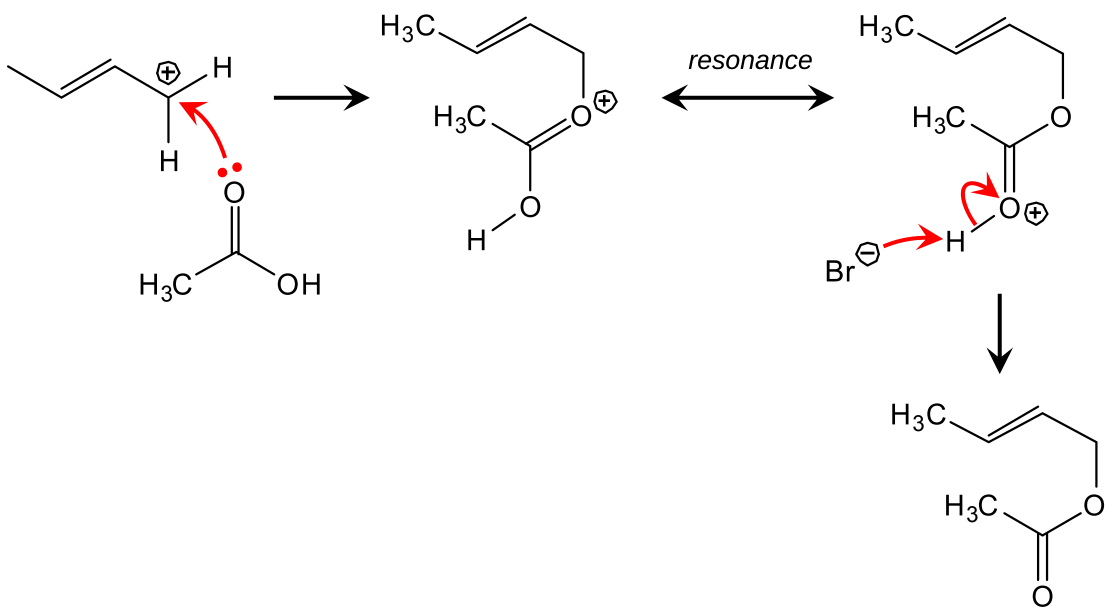


Δ

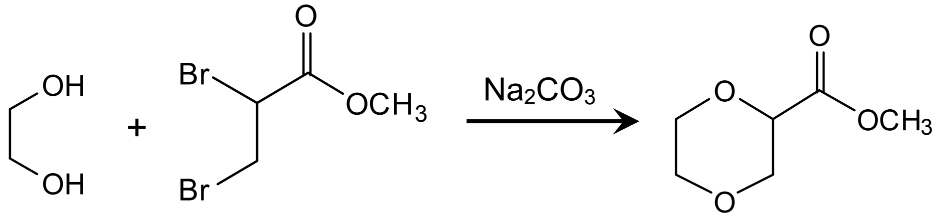


resonance
next page
resonance
(+ enantiomer)

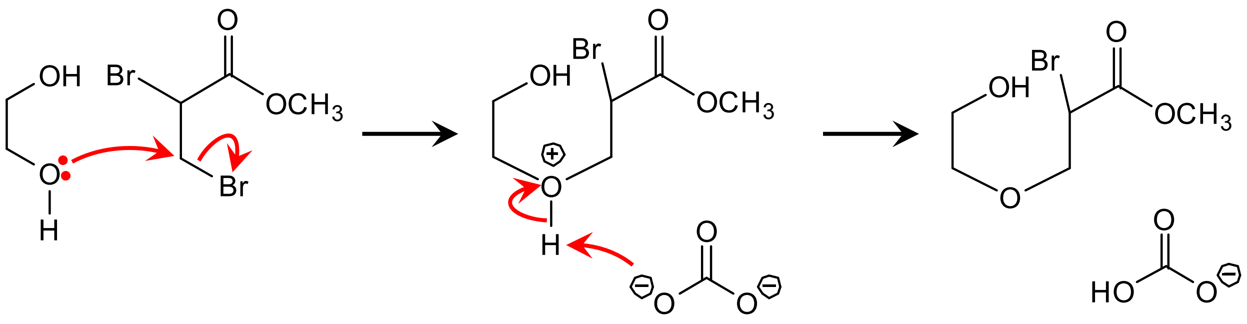
Same process with the other resonance adduct…

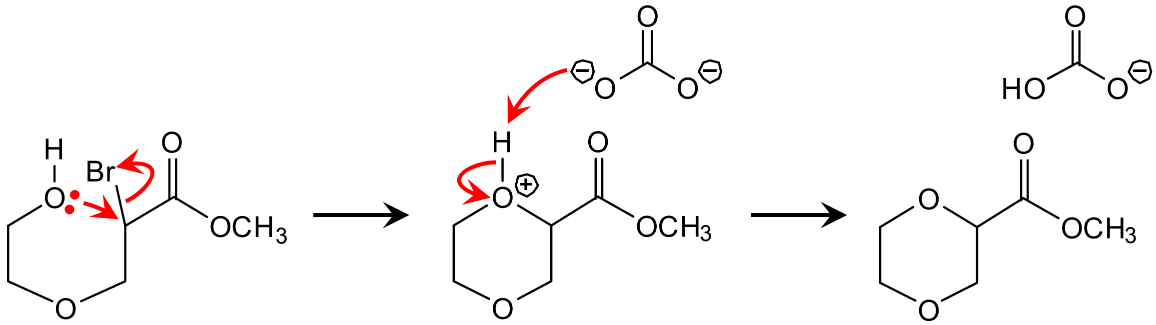


So earlier in this answer key I asked—how would ethylene glycol react differently from catechol in the second problem?



Sodium carbonate isn't basic enough to deprotonate ethylene glycol, so nucleophilic attack comes first:





H
Br
O
OCH3
O
H
O
OCH3
O
O
O
O
O
OCH3
O
O
HO
O