QUESTION 1

Give the product of the following reaction sequence with the starting material shown:

1. Excess LiAlH₄
2. H₃O⁺
3. Na₂Cr₂O₇/H₂SO₄/H₂O
4. NaOH
5. MeI (hint, SN₂ reaction)

A

CHM 234, Spring 2016
QUIZ #5 ANSWER KEY
(hit the RETURN Button to return to the Main Quiz Page)
QUESTION 2

MC29o

Which is the WEAKEST Bronsted acid?

A

\[ \text{B} \quad \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \quad \text{OH} \]

B

\[ \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \quad \text{OH} \]

C

\[ \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \quad \text{OH} \]

D

\[ \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \quad \text{OH} \]

Bronsted acids donate a proton, so first we must identify the hydrogen atom that is most likely to be lost as a proton, i.e. the most acidic hydrogen atom on the molecule. The proton attached to the oxygen will leave behind a negative charge on oxygen, whereas all other protons will leave behind a negative charge on carbon, the charge on oxygen is preferred because oxygen is more electronegative. An extra pair of non-bonding electrons are lower in energy on a more electronegative element, the electrons are lower in energy, the anion is most stabilized, the anion is easiest to form energetically.

\[ \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \quad \text{OH} \quad \rightarrow \quad \begin{array}{c}
\text{F} \\
\text{F}
\end{array} \quad \text{OH}^{-} \quad \text{H}^{+}
\]

The anion formed upon deprotonation at oxygen in all of these alcohols is further stabilized by the very electronegative fluorine due to the INDUCTIVE effect. The inductive effect "pulls" electrons through sigma bonds towards electronegative elements. The electrons are "pulled" towards electronegative elements because in doing so their energy is lowered as a consequence of the concentrated positive charge at the nucleus.

The INDUCTIVE effect decreases rapidly with distance. In D, the fluorine is farthest away from the negative charge on the oxygen, thus it stabilizes the charge the least, making the non-bonding electrons in anion from D highest in energy, this anion is thus hardest to form, its alcohol is thus the weakest Bronsted acid.
QUESTION 3

MC29t

Identify the following reaction as indicated (stereochemistry is ignored)

A addition and neither oxidation or reduction
B elimination and neither oxidation or reduction
C addition and reduction
D elimination and oxidation

\[ \text{OH} \quad \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \quad ??? \]

A. This is an OXIDATION of the alcohol, 2 H atoms are REMOVED.

\[ \text{OH} \quad \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \quad \text{O} \]

B. This is also clearly an ELIMINATION reaction, the 2 H atoms indicated in GREEN were REMOVED to form the C=O bond.

\[ \text{OH} \quad \xrightarrow{\text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O}} \quad \text{O} \]
QUESTION 4

MC29u

give the product of the following reaction sequence

1. PBr₃
2. Na⁺⁺C≡CH
3. Siₐ₂BH·THF
4. -OH/H₂O₂
5. Na₂Cr₂O₇/H₂SO₄/H₂O

A

B

C

D
QUESTION 5
MC29u
Give the reagents/conditions to perform the following reaction

\[
\begin{align*}
\text{H-} & \text{C} & \text{H} & \text{H} & \text{OH} \\
\text{A} & \quad \text{B} & \quad \text{C} & \quad \text{D}
\end{align*}
\]

1. NaNH₂
2. \(\text{O}\)
3. H₃O⁺
QUESTION 6
MC29w

rank the following in order of DECREASING Bronsted acidity

I \( \text{H}_2\text{N}-\text{OH} \)

II \( \text{H}_3\text{C}-\text{OH} \)

III \( \text{CHO}-\text{OH} \)

IV \( \text{H}-\text{OH} \)

A  \( \text{III} > \text{IV} > \text{II} > \text{I} \)
B  \( \text{IV} > \text{II} > \text{III} > \text{I} \)
C  \( \text{IV} > \text{III} > \text{I} > \text{II} \)
D  \( \text{I} > \text{II} > \text{IV} > \text{III} \)

strong donating group

\( \text{H}_2\text{N}-\text{OH} \) \( -\text{H}^+ \rightarrow \text{H}^+ \text{N}=\text{O} \)

weakest acid
anion very DESTabilized by strong electron donating group

weak donating group

\( \text{H}_3\text{C}-\text{OH} \) \( -\text{H}^+ \rightarrow \text{H}^+ \text{C}=\text{O} \)

2nd weakest acid
anion somewhat DESTabilized by weak electron donating group

Withdrawing

\( \text{CHO}-\text{OH} \) \( = \text{O}^+ \text{C}=\text{O} \) \( -\text{H}^+ \rightarrow \text{O}^+ \text{C}=\text{O} \)

strongest acid
anion stabilized by electron withdrawing group
QUESTION 7

Which is the product of the following reaction sequence?

1. Br₂
2. Excess NaNH₂
3. HgSO₄/H₂SO₄/H₂O

\[ \text{standard synthesis of an alkyne from a dihalide except that water is NOT added in a second work-up step, and so the Na}^+ \text{ salt of the acetylide is the final product} \]
QUESTION 8
MC28n

Which are the best synthons for disconnection of the bond indicated by the dashed line?

Retrosynthetic analysis involves disconnection to two fragments (break the bond under consideration). Consider the two atoms that used to be bonded in the two fragments. One of these must carry the pair of electrons that will be used to "make" the bond again, going "backwards". The electron pair is best located on the atom where they will be most stable, since this fragment will be most easy to convert into a real reagent that isn't too different from the synthon. In this case, put the electrons on the sp hybridized carbon, and not on the other carbon, which is sp3 hybridized and is also adjacent to a negatively charged oxygen.