QUESTION 1
Which is the strongest Bronsted acid?

A

B

C

D

as in most Bronsted acid questions, write the acid/base equation, and look for the most stable conjugate base, in this case carboxylate anion

the stronger acid of these two has the more stable conjugate base anion

H–A \rightarrow H^+ + A^–  \quad \text{the more stable anion of these is the conjugate base of the stronger acid}

A

the only resonance structures that can be drawn that involve the ring and maintain the octet rule for all atoms are both unreasonable and result in DONATION of electrons from the benzene ring, the ring does NOT stabilize the negative charge, it is a WEAK donating group to the carboxylate anion π-system

B

the fluorines weakly stabilize the negative charge, weak stabilization because the inductive effect diminishes rapidly with distance from the carboxylate anion

C

same as A, the alkene DESTABILIZES the anion by resonance, it is a weak DONATING group, weak because the resonance contributor is unreasonable

D

the oxygen in the –OMe group is withdrawing inductively, thus is stabilizing, but not as strongly as the –CF2. It is NOT donating since it can not conjugate to a pi-system.
QUESTION 2
MC35b

Which is the strongest Bronsted acid?

A

B

C

D

as in most Bronsted acid questions, write the acid/base equation, and look for the most stable conjugate base, in this case carboxylate anion

the stronger acid of these two has the more stable conjugate base anion

H–A → H⁺ + A⁻ the more stable anion of these is the conjugate base of the stronger acid

in this position, β with respect to the carbonyl carbon of the carboxylate group (-CO₂⁻), the oxygen is a weak INDUCTIVE WITHDRAWING GROUP, since it is more electronegative than carbon. The oxygen can NOT donate electrons in a resonance sense to the carboxylate π-system (see below), since there is an sp³ carbon in the α position between the oxygen and the π-system of the carboxylate anion. The more inductive withdrawing groups (2 in C), the more stable the carboxylate anion, the stronger the conjugate acid.

resonance DONATION to the π-system of the carboxylate anion is IMPOSSIBLE due to the intermediacy of the sp³ hybridized α-carbon, the -OMe groups are ONLY inductively withdrawing in this case
QUESTION 3
MC39e

Which represents a possible synthesis of the anhydride shown from ethyl benzoate?

ethyl benzoate $\rightarrow$ ???

1. SOCl₂
2. ethanoic acid
3. ethanoic acid

A

1. $\text{H}_3\text{O}^+$
2. SOCl₂
3. propanoic acid

B

1. $\text{H}_3\text{O}^+$
2. SOCl₂
3. propanoic acid only reagent

C

propanoic acid only reagent)

D

ethyl benzoate = ethyl ester of benzoic acid = $\text{C}O\text{O}_{\text{Et}}$

ethanoic acid = $\text{H}_3\text{C}^{-}\text{C}^{-}\text{OH} = \text{CH}_3\text{CO}_2\text{H}$

ethanoic acid = $\text{H}_3\text{C}^{-}\text{CH}_2^{-}\text{C}^{-}\text{OH} = \text{CH}_3\text{CH}_2\text{CO}_2\text{H}$

A

ethyl benzoate $\xrightarrow{\text{SOCl}_2}$ no reaction

B

ethyl benzoate $\xrightarrow{\text{H}_3\text{O}^+}$ ethanoic acid $\xrightarrow{\text{SOCl}_2}$ incorrect compound

C

ethyl benzoate $\xrightarrow{\text{H}_3\text{O}^+}$ ethanoic acid $\xrightarrow{\text{SOCl}_2}$ ethanoic acid $\xrightarrow{\text{CH}_3\text{CH}_2\text{CO}_2\text{H}}$

D

no reaction, can’t directly make a more reactive derivative from a less reactive derivative
**QUESTION 4**

MC35d

Which synthetic method can be used to make the provided carboxylic acid?

A

\[
\begin{align*}
&\text{1. Mg.THF} \\
&\text{2. CO}_2 \\
&\text{3. H}_3\text{O}^+ \\
\end{align*}
\]

can't use a Grignard in the presence of an -OH bond

B

\[
\begin{align*}
&\text{1. NaCN} \\
&\text{2. H}_3\text{O}^+/\text{heat} \\
\end{align*}
\]

1. \( \text{EtO} \quad \text{OEt} \)

\[
\text{adds 2 carbons}
\]

C

\[
\begin{align*}
&\text{1. NaOH} \\
&\text{2. } \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O} \\
\end{align*}
\]

doesn't add a carbon

D

\[
\begin{align*}
&\text{1. Mg.THF} \\
&\text{2. CO}_2 \\
&\text{3. H}_3\text{O}^+ \\
\end{align*}
\]

can't use a Grignard in the presence of an -OH bond

\[
\begin{align*}
&\text{1. NaCN} \\
&\text{2. H}_3\text{O}^+/\text{heat} \\
\end{align*}
\]

1. \( \text{EtO} \quad \text{OEt} \)

\[
\text{adds 2 carbons}
\]

\[
\begin{align*}
&\text{1. NaOH} \\
&\text{2. } \text{Na}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4/\text{H}_2\text{O} \\
\end{align*}
\]

doesn't add a carbon
**QUESTION 5**

**MC39d**

Which represents the best synthesis of ethyl benzoate from bromobenzene?

\[ \text{Br} \xrightarrow{???} \text{CO}_2\text{Et} \]

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Na(^+) – CN</td>
<td>Mg.THF</td>
<td>Mg.THF</td>
<td>Na(^+) – CN</td>
</tr>
<tr>
<td>2.</td>
<td>H(_3)O(^+)</td>
<td>CO(_2)</td>
<td>CO(_2)</td>
<td>H(_3)O(^+)</td>
</tr>
<tr>
<td>3.</td>
<td>SOCl(_2)</td>
<td>H(_3)O(^+)</td>
<td>H(_3)O(^+)</td>
<td>SOCl(_2)</td>
</tr>
<tr>
<td>4.</td>
<td>EtOH</td>
<td>EtOH/HCl</td>
<td>EtOH/HCl</td>
<td>EtOH</td>
</tr>
</tbody>
</table>

1. Mg.THF
2. CO\(_2\)
3. Na\(^+\) – CN
4. EtOH/HCl
5. EtOH

A: cannot do an SN2 at an sp\(_2\) hybridized carbon

B: reversible, not a good way to make an ester

C: cannot do an SN2 at an sp\(_2\) hybridized carbon

D: Mg.THF
1. CO\(_2\)
2. H\(_3\)O\(^+\)
3. SOCl\(_2\)
4. EtOH

---
QUESTION 6
MC39c

Which represents a viable synthesis of the following anhydride?

\[ \text{benzyl acetic acid} \rightarrow \text{anhydride} \]

1. \( \text{CH}_3\text{CO}_2\text{H} \)
2. \( \text{H}_3\text{O}^+ \)
3. \( \text{SOCl}_2 \)

A  B  C  D

1. \( \text{H}_3\text{O}^+ \)
2. \( \text{CH}_3\text{CO}_2\text{H} \)
3. \( \text{SOCl}_2 \)

A  B  C  D

\[
\begin{align*}
\text{A} & \quad \text{no reaction} \\
\text{B} & \quad \text{no reaction} \\
\text{C} & \quad \text{no reaction} \\
\text{D} & \quad \text{no reaction}
\end{align*}
\]
QUESTION 7

MC39a

Which is the product of COMPLETE hydrolysis, using boiling aqueous acid, of the following structure?

\[
\text{H}_3\text{O}^+ / \text{boil}
\]

A \quad HO\text{-C}-\text{CH}_2\text{-OH} \quad \text{B} \quad \text{HO}_2\text{C}-\text{C}-\text{OH} \quad \text{C} \quad \text{HO}\text{-CH}_2\text{-OH} \quad \text{D} \quad \text{HO}_2\text{C}-\text{C}-\text{CO}_2\text{H}

\[
\text{H}_3\text{O}^+ / \text{boil}
\]

\[
\text{HO}\text{-C}-\text{C}-\text{CO}_2\text{H} = \text{HO}_2\text{C}-\text{C}-\text{OH}
\]
**QUESTION 8**

MC35n

Which has the largest pKa?

A

B

C

D

---

**pKa is defined as follows.....**

\[
\text{pKa} = -\log_{10} \frac{[H_3O^+][A^-]}{[H^+ A^-]}
\]

the acid with the largest pKa is thus the least
dissociated in water, it is the weakest Bronsted acid

as in most Bronsted acid questions, write the
acid/base equation, and look for the most stable
conjugate base, in this case carboxylate anion

the stronger acid

of these two has

the more stable

conjugate base anion

the more stable

anion of these is

the conjugate base

of the stronger acid

in this problem, we are comparing anion stabilities

for the different substituents

the trifluoromethyl group (in B) is very electron

withdrawing when connected to a simple \(\pi\)-system such

as the carboxylate anion as a consequence of the

inductive effect, thus stabilizing the carboxylate

anion conjugate base, increasing the acidity of B

the methyl group (in D) is weakly donating when connected
to a simple \(\pi\)-system such as the carboxylate anion due to
the hiperconjugation effect, which destabilizes the anion,
decreasing the acidity of D, which in this series is thus
the weakest acid and thus has the largest pKa