1) Propose reasonable mechanisms to account for the following transformations:

As you probably noticed, all are electrophilic aromatic substitution reactions, with varying ways of generating the active electrophile.

a) The reaction of benzene with hypobromous acid (HOBr) in the presence of sulfuric acid (H$_2$SO$_4$) to yield bromobenzene.

Clearly the electrophile here is Br$^+$. Here’s how it goes:

\[
\begin{align*}
\text{HO} &\quad \quad \text{Br} \\
\text{H} &\quad \quad \text{SO}_4\text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{HSO}_4^- &\quad \quad \text{Br}^+ \\
\text{H}_2\text{O} &\quad \quad \text{Br} \\
\end{align*}
\]

b) This one is a bit more interesting, as an S$_N$1 reaction follows the electrophilic aromatic substitution reaction. Here’s how I saw it:
c) The following are the typical conditions used to introduce the nitroso (NO) group onto a benzene ring. Propose a reasonable mechanism.

Again, just another example of an electrophilic aromatic substitution reaction with an interesting way of generating the active electrophile. Here is how I saw it:
2) Once a Diels-Alder reaction has been performed, it is sometimes possible to perform a retro-Diels-Alder (think of the lab last semester) reaction to produce not the original diene but a totally new product, which new product may be highly synthetically useful (or just fun!) Propose the structures for compounds S-V below. (N.b.: S & T are Diels-Alder products; U & V are products of a retro-Diels-Alder)

a)

Remember, in a roadmap, no mechanisms are necessary; you may draw them, of course, if it helps you see where things are going. Here is my take on S and U:
3) Starting with benzene, synthesize the following: (more than one step may be required)

I saw many good and interesting answers on the exam; the ways I had envisioned were much shorter and more direct.

a) *m*-bromobenzenesulfonic acid

Bromo is *ortho*, *para* directing, the sulfonic acid group, being electron-withdrawing, is *meta* directing. Seems like putting the sulfonic acid group on first is the ticket. Here it is:
b) *p*-bromobenzenesulfonic acid

This synthesis is just the reverse order of steps of part (a). Need the *ortho, para* directing of bromine to put the sulfonic acid group on where you want it.

\[
\begin{array}{c}
\text{CH}_2 = \text{CH}_2 \\
\text{FeBr}_3 \\
\text{Br}_2 \\
\text{H}_2\text{SO}_4 \cdot \text{SO}_3 \\
\text{SO}_3\text{H}
\end{array}
\]

c) *p*-nitrotoluene

Alkyl groups are *ortho, para* directing plus nitro is **very** deactivating (so much so that an old dictum was: you can’t Friedel-Crafts a nitro arene!). First the methyl, then the nitro. Here’s the scheme:

\[
\begin{array}{c}
\text{CH}_3 \text{Cl} \\
\text{AlCl}_3 \\
\text{CH}_3 \\
\text{HNO}_3 / \text{H}_2\text{SO}_4 \\
\text{NO}_2
\end{array}
\]

d) *p*-nitrobenzoic acid

This one follows directly from (c): just add an oxidation and you’re there. Here it is:
4) Use the molecular orbital analysis (HOMO/LUMO) analogous that that used to describe the Diels-Alder reaction to predict which of the following cycloaddition reactions would be possible (i.e. allowed):

The Diels-Alder reaction is a HOMO-LUMO interaction reaction (the HOMO of one component interacts with the LUMO of the other.) Therefore, an examination of the HOMO and LUMO of both components is necessary.

\[ \text{a) } \text{HOMO} + \text{HOMO} \rightarrow \Delta \]

Here we have the same two components. Here is the HOMO-LUMO diagram.

Because of the anti-bonding interaction indicated, this reaction will not go as written.
b) Doing the same analysis yields:

\[ \text{HOMO} \quad \text{LUMO} \]

[Diagram showing orbital interactions]

And for the same reasons, this reaction will not go as written.

\[ \text{HOMO} \quad \text{LUMO} \]

[Diagram showing orbital interactions]

c) Doing an orbital analysis one last time, we get:
Here there is “goodness” all around—all bonding interactions between the required orbitals, so this reaction will go as written.
5) Identify the reagents represented by the letters a-e in the following scheme:

A nice “provide the reagents” question. Here’s the list; note that for some, there may be other good options.

a: CH₃CH₂COCl/AlCl₃
b: NH₂NH₂, OH⁻, glyme (high-boiling solvent)
c: Br₂/FeBr₃
d: NBS, CCl₄, (PhCO₂)₂
e: (CH₃)₃CO⁺/(CH₃)₃COH