Some Answers to the 301 Final, 2003-2004

1.

(a) Compounds 2 and 3 must share the following structures:

(b) Because the OH appears where the boron is, the two boranes involved must be:

The number of times H is replaced with R depends on the steric demands of R. Now the question is which TS for borane formation is lower energy? Here are pictures:
The lower TS has delocalized charge, the upper one does not. Therefore, electronic effects predict that the major product will be the lower borane.

(c) But the NMR data do not support this analysis! The major product has a methyl triplet and the minor product has a methyl doublet. In fact, the upper TS must be the lower energy one.

methyl doublet - must be minor product

methyl triplet - must be major product
(d) The only other effect is a steric effect - that methyl group must hinder approach of the borane, and favor the electronically less stable TS.

(e) \( \Delta G = -RT \ln K \) and 75/25 is closest by far to 1 kcal/mol.

(f) Look at the picture in the answer to part (b). That methoxy group helps stabilize the TS leading to the minor product. When it’s not there, the steric effect is even more effective at out-competing the electronic effect.

2. See book, pp 220ff. right there.

There are many experiments possible, Here’s one.

![Reaction diagram](image)

Determination of the coupling constant at the substituted ring carbons would serve to distinguish the cis product from the trans product.
3. Ionization does not lead initially to a symmetrical carbocation. The leaving group, here iodide, lurks on the side from which it left, hindering the retention path.

In a more polar solvent the original ion pair lives longer than in EtOH, and the iodide can diffuse away. The two alcohols are formed through addition of water to the cation, and the stereochemical result approaches racemization as more and more achiral, free carbocation is formed.
4. 
(a) There are many ways to do the construction: Here is the result. Note that the orbitals increase in energy as the number of nodes goes up.

(b) Here are the appropriate interactions:

A $\pm 2s$
B $\pm 2p_y$
C $\pm 2p_x$
D no interactions - (remember that we have not used the $2p_z$ orbital).

The results are:
E, F, and G are bonding, and of course there remains the nonbonding $2p_z$ orbital. Order them by counting nodes, and put in the appropriate six electrons (four from H4, three from B, and one is removed to account for the plus charge):

To stabilize this system we need something with a filled $p$ orbital, so that we get a filled-empty stabilizing interaction with the empty $2p_z$. Oxygen, nitrogen, or a halogen should do the trick.

5.

(a) $\text{CH}_2\text{N}_2/h\nu$
(b) $\text{CF}_3\text{COOH}$
(c) $\text{H}_2\text{Pd/C}$
(d) $\text{KMnO}_4/\text{HO}^-$
(e) $\text{Br}_2/\text{H}_2\text{O}$

(f) Na/NH$_3$
(g) Lindlar cat/H$_2$
(h) 1. Lindlar cat 2. $\text{O}$ 3. HOOH
(i) 1. Hg(OAc)$_2$ 2. H$_2$O/H$_3$O$^+$
(j) 2 Br$_2$
6. (a) 1. Br₂  2. (CH₃)₃CO⁻/(CH₃)₃COH  3. Na/NH₃
   (b) 1. Br₂/hv (Q₂ will not work) 2. (CH₃)₃CO⁻/(CH₃)₃COH  3. D₂/Pd/C
   (c) 1. NBS/hν  2. BH₃  3. HOOH/HO⁻  4. H₂O/H₃O⁺
   (d) 1. HBr/ROOR  2. (CH₃)₃N  3. (CH₃)₃CO⁻/(CH₃)₃COH

7a. Compound (a) will show one signal in the ¹³C NMR spectrum, (b) will show five, (c) four, and (d) will show three.

7b.

(e) The acid will show a broad OH stretch in the IR at 3200-2800 cm⁻¹. The aldehyde will show Henry’s favorite pair of C-H stretching bands at 2900-2700 cm⁻¹.

(f) the cis (0°) coupling constant will be larger than the trans (~120°) coupling constant.

(g) the two hydrogens in the first compound are diastereotopic and will give two signals. The methylene hydrogens in the second compound are equivalent, and will have the same chemical shift.

8. The competition is not between an allyl cation (13) and a secondary vinyl cation. Look at the geometry of allene - protonation cannot not give the allyl cation directly, instead it must yield a simple primary carbocation, which is at least as bad as the vinyl cation. This is the “no overlap” problem again.

9. The first reasonable step is formation of either a bromonium ion or the
corresponding open carbocation (in fact it’s the open one - look at the resonance stabilization).

The reaction doesn’t go on to add bromide - the structure of the product tells you that (and we didn’t ask why). To make bromobenzene, a proton must be lost - it is just a garden-variety E1 step most easily written from the open ion, but possible from both intermediates.

Toluene can form three possible ions. Two are better stabilized by resonance than the third (note the tertiary carbocation in A and B, but not C), and the transition states leading to them will profit energetically from that stabilization. However there are steric problems in B, and the major product is the 1,4-isomer (called para).

Steric effects will favor the para isomer over the ortho isomer.

10. Ionization of the tosylate to give an ion must be the slow, rate-determining step. But
if it is a simple ionization to a secondary carbocation, followed by hydride (or deuteride) migration, the rate can’t depend on the strength of the adjacent C-H or C-D bond.

That adjacent bond must break as the tosylate leaves. Only that way can there be what is called an isotope effect.