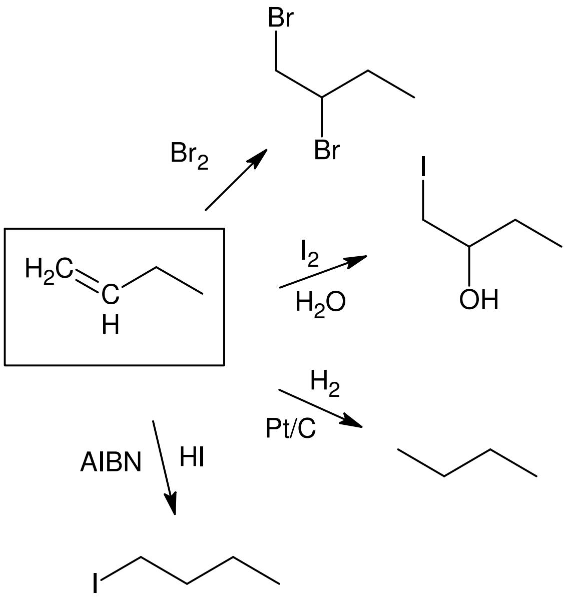
Chem 201, 2009
HW #4, due Th, Oct 8, 12 PM

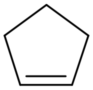
ANSWERS

Loudon problems from chapter 5: 28AGHO 30ABG, 32H, 42, 45AB, 48DF, 50

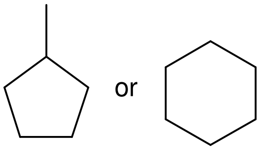
28AGHO (Note: I'm surprised that HI adds in a radical chain reaction. I had persuaded myself that this wouldn't happen. I'm not sure I trust Loudon on this.)



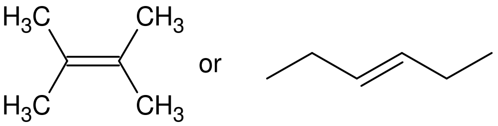
30ABG



a "5-C alkene" that gives the same pdt w/ HBr regardless of peroxide contamination



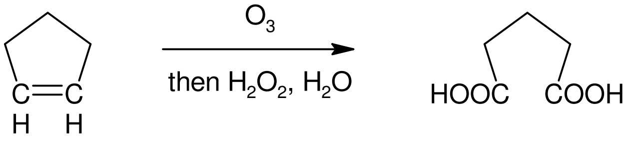
a "C_6H_{12}" that refuses to react w/ ozone (b/c no C=C); **other ring answers are OK too**



a "C_6H_{12}" that gives same (**identical**) alcohol with oxymercuration or hydroboration, **cis-3-hexene OK too**

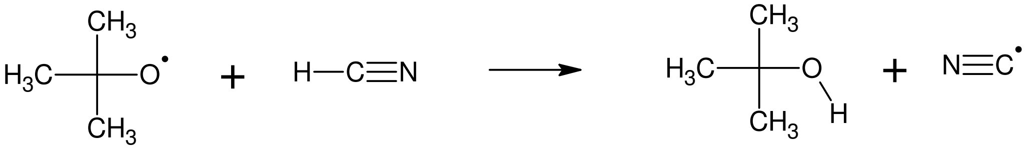
* with these tools, the order in which you select atoms is important

32H You can make this diacid in one synthetic step from cyclopentene. Do not draw a mechanism, intermediates. Just draw the recipe as shown below.

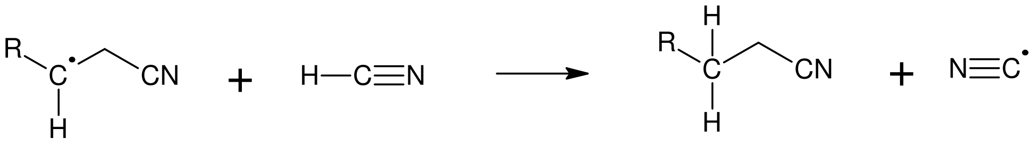


42

a. Relevant reaction shown below. BDE are RO—H (438) v. H—CN (528) and est'd ΔH_{rxn} = +90 kJ/mol. Endothermic ☹.

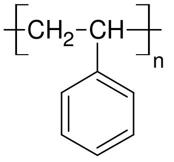


b. Relevant reaction shown below. BDE are H—CN (528) v. H—CHR_2 (412) and est'd ΔH_{rxn} = +116 kJ/mol. Endothermic ☹.

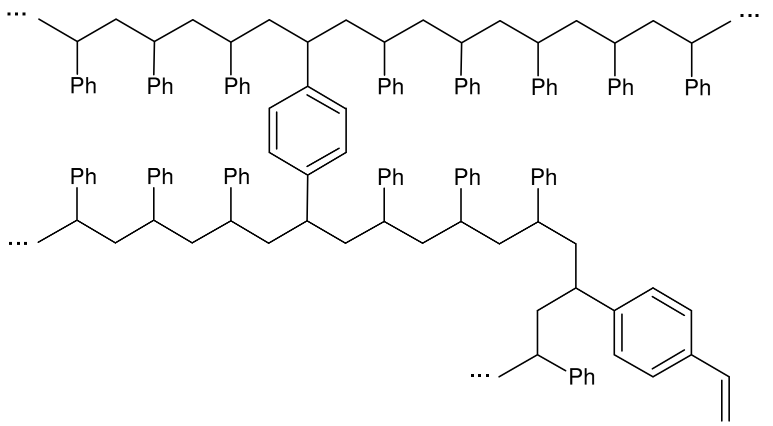


45

Polystyrene can be drawn most easily using the "bracket" notation. When polystyrene is polymerized with 1,4-divinylbenzene (DVB), each vinyl group can participate in a chain-growing reaction so that two chains become "cross-linked". Cross-linking usually makes polymers stiffer. The formula shows one DVB cross-linking two chains and another DVB incorporated into one chain, but not yet cross-linked.

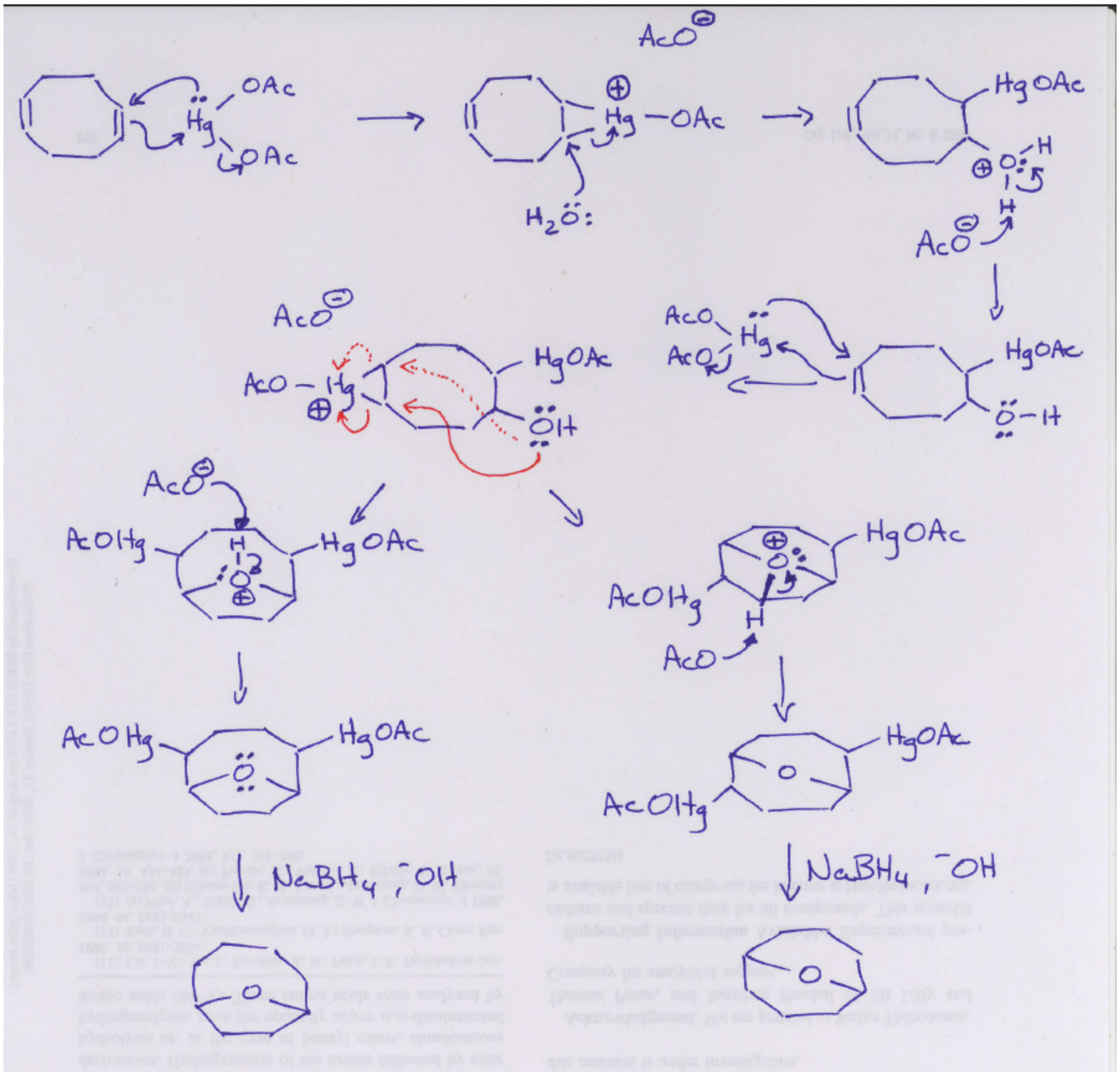


polystyrene



* with these tools, the order in which you select atoms is important

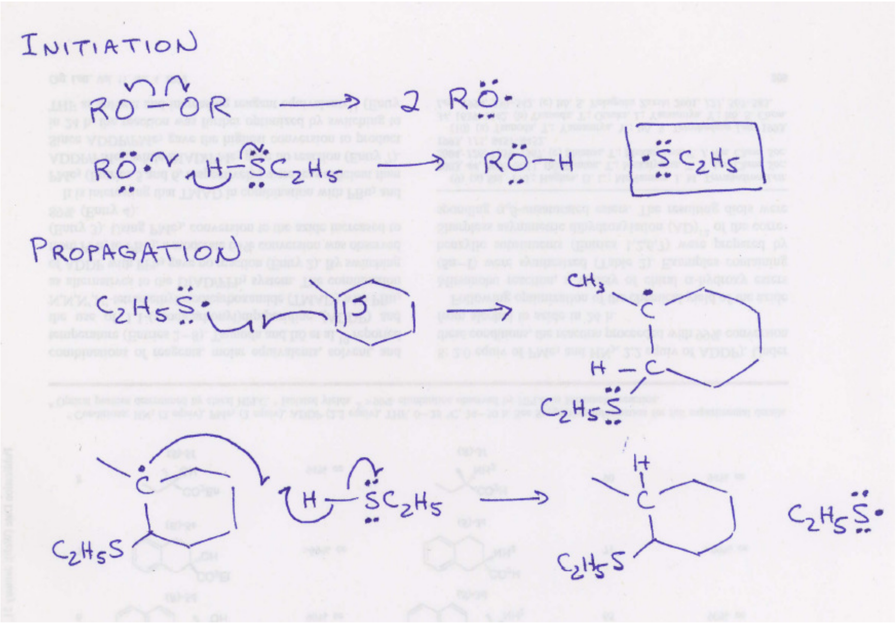
48D The drawing covers a lot of real estate, but you should read it carefully to make sure you understand it. *Every* step is drawn just as it appears in a standard oxymercuration-demercuration mechanism. The only *strange* step is the one with red curved arrows. Here, a neutral O nucleophile intercepts the positively charged intermediate before a water molecule can (note: water is also a neutral O nucleophile). This is not too surprising because an *intra*molecular reaction (a reaction where both the electrophile and nucleophile are part of the same molecule) is going to have two advantages over an *inter*molecular reaction: no entropy penalty (the reactants are already connected), no waiting for a collision.



48F This mechanism looks just like HBr/peroxide addition. RS addition is favorable because a “weak” CC pi bond (BDE 243) is replaced by a “strong” CS sigma bond (BDE ~295). H abstraction from RSH is also favorable because a “weak” HS bond (366) is replaced by a “strong” HC bond (404).

* with these tools, the order in which you select atoms is important

The addition should be regioselective in the *anti*-Markovnikov manner because creation of the tertiary free radical is likely to be faster than creation of a secondary free radical, however we are following a dangerous line of reasoning here (I have avoided mentioning this danger until now and you might want to skip the rest of this paragraph). Recall that our discussion of HBr addition to alkenes included the statement “tertiary carbocations form more rapidly than secondary carbocations because *tertiary cations are more stable*.” If we apply this same reasoning to radicals, we would say, “tertiary radicals form more rapidly than secondary radicals because *tertiary radicals are more stable*.” This is probably true, but it’s harder to justify. Carbocations form in *endo*thermic reactions and the Hammond postulate pushes us to say that transition state energies and carbocation energies are correlated. Radicals like Br and RS, on the other hand, add to alkenes in *exo*thermic reactions. The Hammond postulate now pushes us to say that the transition states are *reactant*-like, i.e., like the alkene + free radical (Br, RS). The transition state energies do not have to be correlated with the energies of the “products”. Gotcha.



50

Hydroboration of highly substituted alkenes is possible, but it is rarely possible to have a single BH_3 unit add to *three* alkenes. Instead, a single addition occurs to give an alkylborane, or two additions to yield a dialkylborane. Steric repulsion between the alkyl groups attached to boron and the approaching alkene prevent further addition.

You can find evidence for this steric repulsion in several ways. For example, I compared C-C-B bond angles in the alkyl, dialkyl, and trialkylboranes. The results varied from one C-C bond to the next, and they also varied with the conformations of the alkyl groups, but I saw the following trend: the C-C-B angle was always smallest in the alkylborane (alkyl groups bent slightly *towards* B) and largest in the trialkylborane (alkyl groups bent *away* from B). Clearly, as more alkyl groups get loaded onto boron, they struggle to find adequate room.

---

* with these tools, the order in which you select atoms is important

Chem 201, 2009
HW #4, due Th, Oct 8, 12 PM

Another sign of steric repulsion: my models of the trialkylboranes often showed several “space-filling” hydrogens in strong overlap. This could be confirmed by measuring the distances between these hydrogens which were much less than the *sum* of the hydrogen van der Waals radii. The trialkylboranes are sterically crowded and unstable.

* with these tools, the order in which you select atoms is important