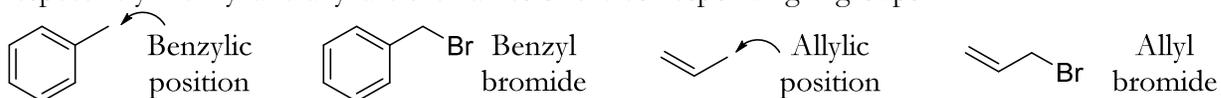# Loudon Chapter 17 Review: Allylic/Benzylic Reactivity
### Jacquie Richardson, CU Boulder – Last updated 2/7/2020

Chapter 17 is all about reactions that happen at the position one away from an aromatic ring, or one away from a double bond. These are called the benzylic and allylic positions respectively. Benzyl and allyl are the names of the corresponding R groups.

The most important thing about both these positions is that they're great at stabilizing any sort of charge or radical, through resonance. The allyl group has two resonance forms:
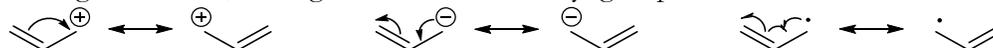

The benzyl group has four resonance forms (or possibly more, if there are any functional groups attached to the ring):
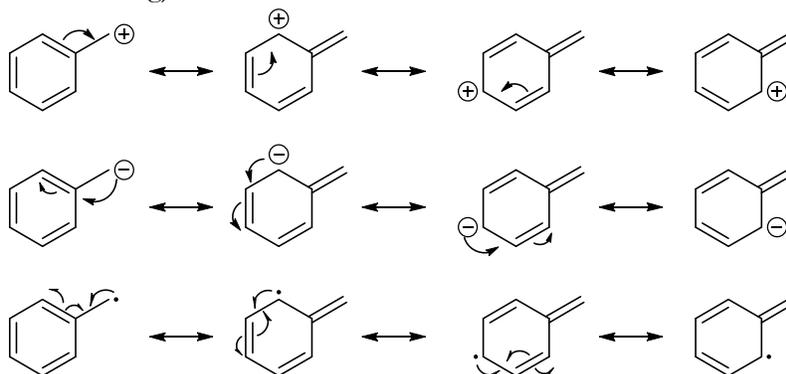

What this means is that any reaction that involves a charge or a partial charge forming at the allylic or benzylic position happens much more easily than it would for a regular R group. This includes S_N1, S_N2, E1, and E2, along with other reactions that we've seen in the past.

Reactions with Carbocations
The biggest two in this category are S_N1 and E1. Here are the mechanisms for benzylic only, but they look similar for allylic. None of the resonance forms are shown for the benzylic cation but they are responsible for its stability.

S_N1 at benzylic position


E1 at benzylic position
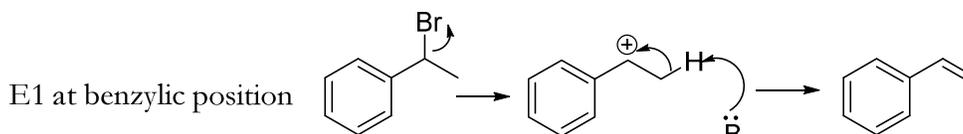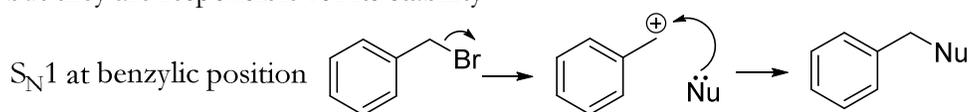
In both cases, the reaction goes much faster because the high-energy intermediate is stabilized. The reaction is usually a few hundred times faster than it would be on a saturated alkyl halide. This effect can become even greater if there are groups on the ring that stabilize the positive charge.
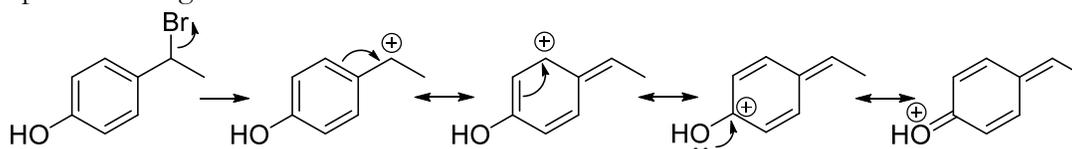
The intermediates here look somewhat similar to the intermediates for EAS reactions in Ch. 16. Since we're forming a carbocation, just like in EAS, it's not surprising that the same rules will apply for activating/deactivating groups. Also, a group will have a much stronger effect if it's ortho or para to where the benzylic carbon is attached. In the example above, the hydroxyl (OH) group is para to the benzylic carbon and so it's capable of putting the charge directly onto the oxygen. To rank some examples by how fast they react at $S_N1/E1$:

Slowest   Fastest
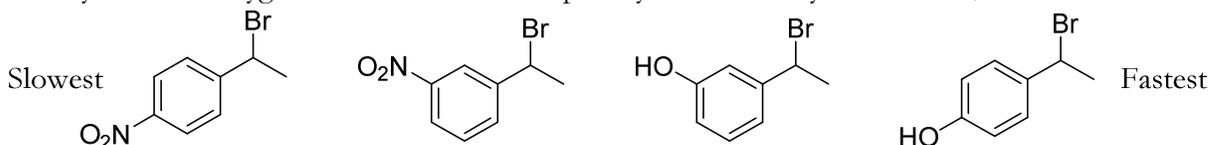
One more complication of resonance stabilization: if you make a carbocation at the allylic position, you can theoretically get two different products. This is a lot like the 1,2 vs. 1,4 additions from Ch. 15 – at some point, there are two different resonance forms to react with. Which one gives the major product depends on where the charge is most stable – here, the second product is the major one because the 3° carbocation is the major resonance form.
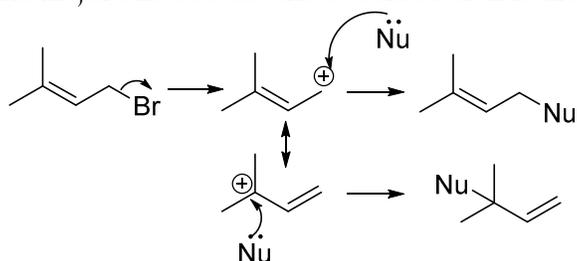
This is not the case, however, for reactions at the benzylic position. There's only one resonance form that's actually aromatic, so that's the only one that leads to product.

Reactions with Radicals

The allylic and benzylic positions stabilize radicals just as well as carbocations. We saw radical halogenation in Ch. 9, which uses $Br_2/h\nu$ to replace an H with a Br. This happens almost exclusively at the carbon that can best stabilize a radical. In alkanes this was only on the most substituted carbon (usually 3°), but the allylic and benzylic positions are even better.
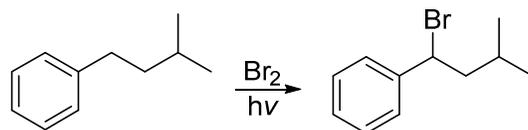
In this case, even though there's a 3° carbon at the right end of the molecule, the benzylic position is still preferred. There's a problem if we try to do this reaction on the allylic position, though. Br_2 can add straight to the alkene if it doesn't go by a radical mechanism.

If it goes by radical mechanism   If it ignores hν and goes by regular addition mechanism
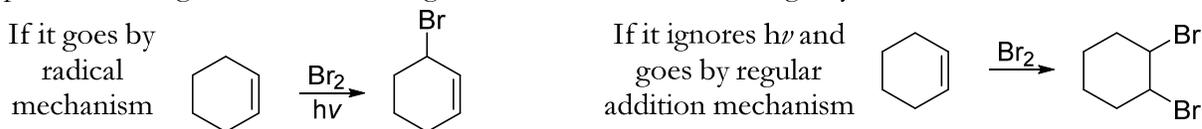
Usually we can favor the radical mechanism by using a lot of light, heat, and a polar solvent, and we can favor the addition mechanism by the opposite conditions. There are some problems in the book that say "Br_2/dark", for instance, avoiding radical formation.

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There's a new reagent that shows up here: N-bromosuccinimide, or NBS. (There are also NCS and NIS, for chlorine and iodine respectively, though NBS works best.)
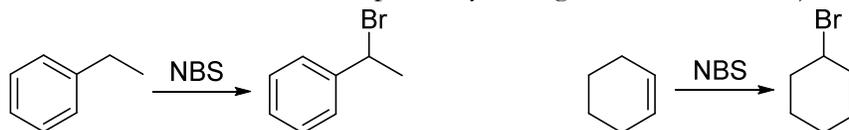
It works as a source of Br radicals without ever adding two Br atoms to the molecule the way that Br_2 would. Also unlike Br_2, it goes only for the benzylic/allylic position, and doesn't react significantly with tertiary carbons. Again, if we do this reaction at the allylic position, a mixture of products is possible based on different resonance forms.

Reactions with Carbanions
Again, a negative charge at the allylic or benzylic position is much more stable than it would be in a lot of other positions. We've seen carbanions before in the form of Grignards or organolithiums. In those cases, we could show the carbon-metal bond as either covalent or as an ionic pair – both are acceptable. Here, the charge can move around to become what looks like a different structure, though it's all just different depictions of the same thing.
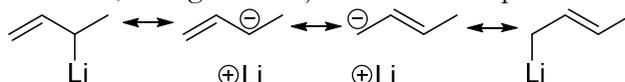
The molecule can attack from either carbanion, so if we react it with something that takes away its charge and resonance it can be trapped in either form.
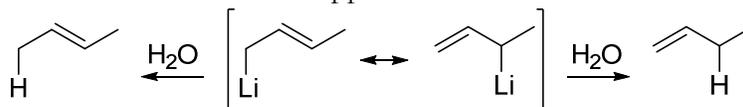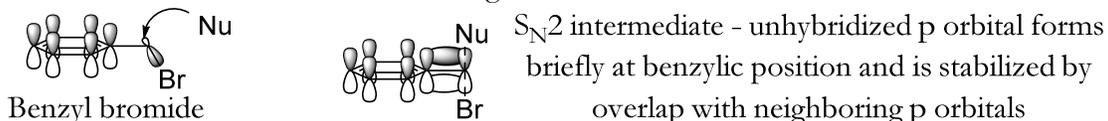
Reactions without Formal Charges
Even if there's no official positive or negative charge, reactions at this position can still have stabilized partial charges. S_N2 and E2 fit this description. In the reaction below, you'd expect, given the combination of strong base/good nucleophile/primary alkyl halide, to see S_N2 as the major pathway. But it turns out to be E2 instead.

E2 gives partial
negative charge
at benzylic position:
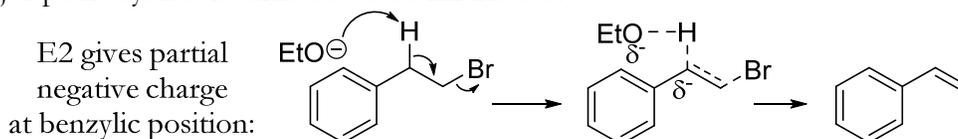
This is because E2 creates a slight negative charge at the benzylic position, which stabilizes the reaction quite a lot and allows it to happen faster. If the mechanism were S_N2, the benzylic position wouldn't be involved at all.

If the halogen itself is located at the benzylic/allylic position instead of one carbon away from it, though, then S_N2 becomes extremely favored. For allylic, it gets sped up by a couple of orders of magnitude, but for benzylic it gets sped up by about five orders of magnitude. This has less to do with charge stabilization and more to do with stabilization of the sp^2-hybridized intermediate. The p orbitals of the atom doing the reaction can overlap with the p orbitals of the double bond/aromatic ring.

Benzyl bromide

S_N2 intermediate - unhybridized p orbital forms briefly at benzylic position and is stabilized by overlap with neighboring p orbitals

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# Loudon Chapter 17 Review: Allylic/Benzylic Reactivity
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Allylic & Benzylic Oxidations

We're used to seeing alcohols getting oxidized by PCC or strong oxidizers like CrO_3/H_2SO_4:

1° alcohols:
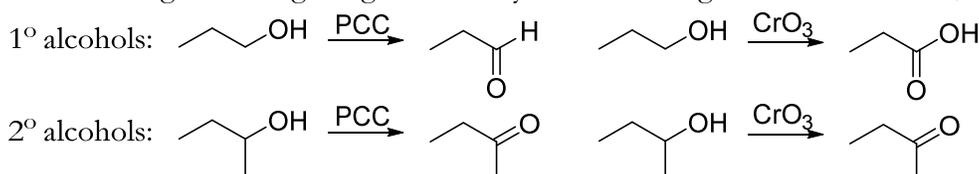
2° alcohols:

These will always do predictable things to an alcohol depending on whether it's 1°, 2°, or 3°, regardless of what the attached R groups actually are. In this chapter we start looking at reagents that specifically target alcohols in the allylic or benzylic positions, without touching other alcohol groups.

allylic/benzylic alcohols:

all other alcohols:
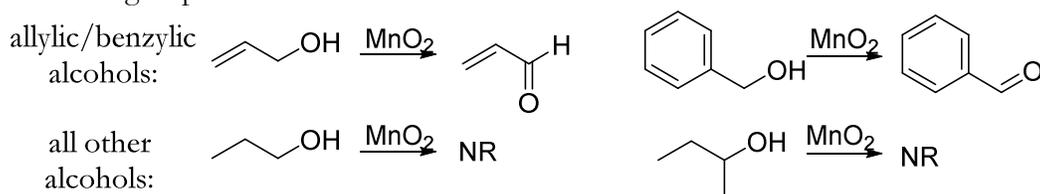
Note that if we start with a primary allylic/benzylic alcohol, it still maxes out at two bonds to oxygen (the aldehyde/ketone oxidation level) without going all the way to three bonds to oxygen (the carboxylic acid oxidation level). For this reason, we can think of MnO_2 as being kind of like a version of PCC that only goes after allylic/benzylic alcohols.

Another oxidation reaction that specifically targets these locations doesn't start with an alcohol at all. You can use either $KMnO_4$, CrO_3, or $Na_2Cr_2O_7$, but they need vigorous conditions – heat and strong acid – to work.
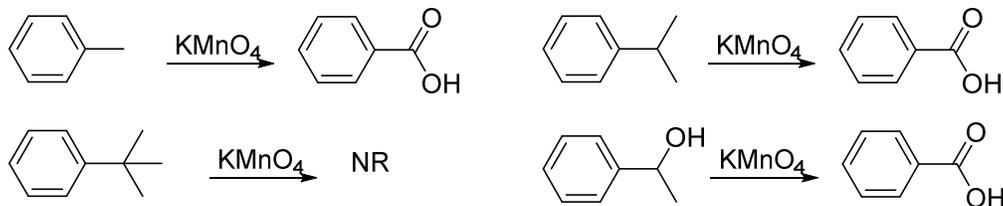
The general idea here is that if we have a carbon attached to an aromatic ring, and that carbon has at least one hydrogen or OH group on it, it will be oxidized all the way to a carboxylic acid – *even if that means losing bonds to carbons that it's attached to.* This is not something that we've seen oxidizers do before. They've mostly left carbon-carbon bonds intact until now (except ozone or HIO_4), but $KMnO_4$ is a very powerful oxidizer and the benzylic position is pretty reactive.

Ch. 17 Synthesis Practice

Let's use these reactions for a synthesis.
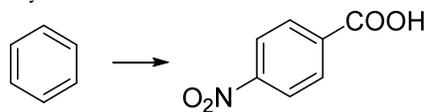
Both of the groups are meta-directing, which makes it impossible to get the para product directly. However, we can make the carboxylic acid group from an o/p-directing group.