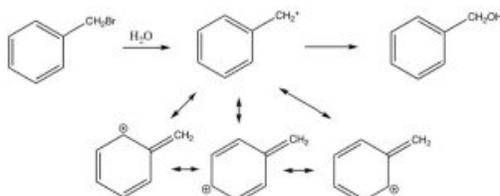
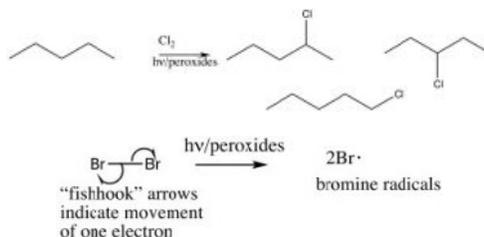


8.1: Reactions of Substituted Benzenes- Reaction at the Benzylic Position

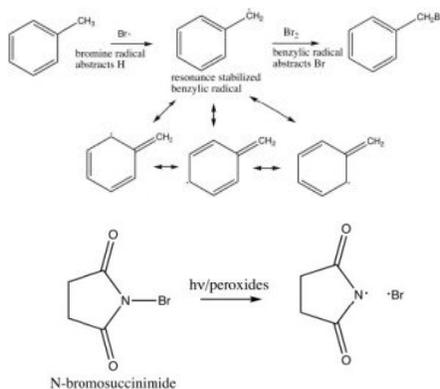
The position next to the benzene ring is special because reactive species such as carbanions, carbocations, or radicals at that site can be conjugated (and therefore stabilized) with the benzene pi system. For example, we have already seen that phenol (C_6H_5OH , $pK_a \sim 10$) is much more acidic than a typical alcohol ($pK_a \sim 16$) because the negative charge can be stabilized in the aromatic ring. Similarly, benzyl halides (e.e. $C_6H_5CH_2Br$) undergo nucleophilic substitution under S_N1 conditions, even though these compounds appear to be primary halides, a carbocation next to the ring can be stabilized.



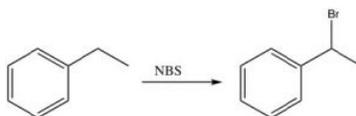
The position next to the ring is called the benzylic position, and is particularly reactive because of the ability to stabilize any intermediate in the aromatic ring. For example, it is possible to selectively introduce a bromine at the benzylic position via a reaction in which radicals are generated. We have spent little time on the reactions of organic compounds with radicals^[9], because, generally, these reactions are very difficult to control. For example, an alkane will react with halogens in the presence of light or peroxides (which initiate the reaction by forming a radical), but the reaction is not synthetically useful and typically the halogen can end up in all the possible positions.



However, we can selectively introduce a bromine atom at a benzylic position, because the intermediate benzylic radical is most stable, and will have a lower activation energy to formation. The reaction begins by producing a bromine radical from Br_2 by breaking the bond with light to give two Br radicals. The Br radical abstracts (removes) an H from the benzylic position to give the resonance-stabilized benzylic radical which then abstracts a Br from bromine (Br_2).



In practice, we use a source of bromine radicals that is easier to handle than elemental bromine, *N*-bromosuccinimide (NBS), which has a weak $N - Br$ bond that will break homolytically (i.e. to give two radicals) in the presence of light or peroxides. NBS will react with alkyl benzenes to introduce a bromine specifically at the benzylic position.



Another unique reaction of benzylic positions is that they can be oxidized by reagents such as KMnO_4 to give the corresponding carboxylic acid; any other carbons in the side chain are removed in the process.



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