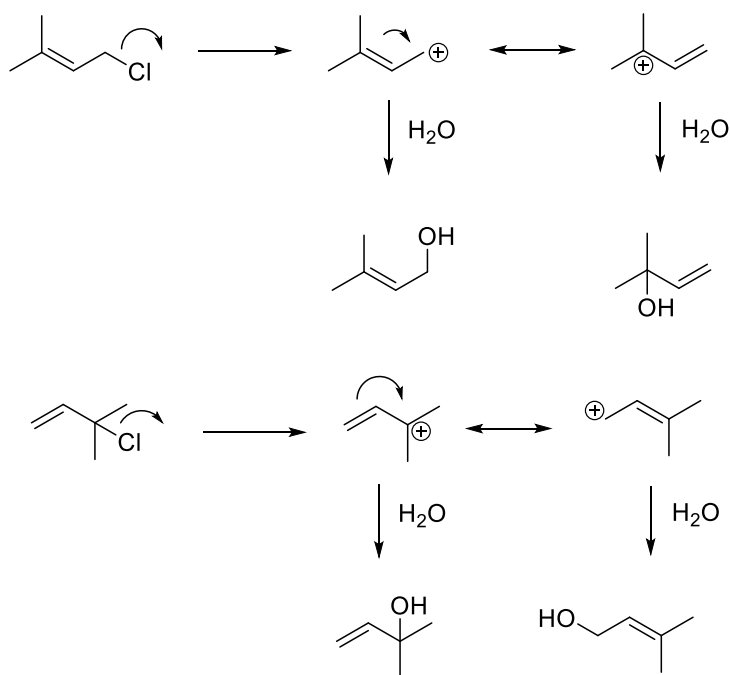


Chem 436 – Spring 2024

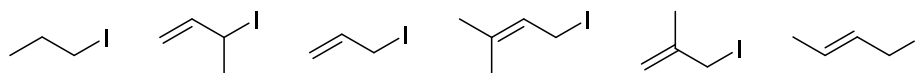
Assignment #1 Answer Key

1. When treated under S_N1 conditions, the two chlorides below give the same pair of alcohols in the same ratio. Provide structures for the two alcohols and explain mechanistically.

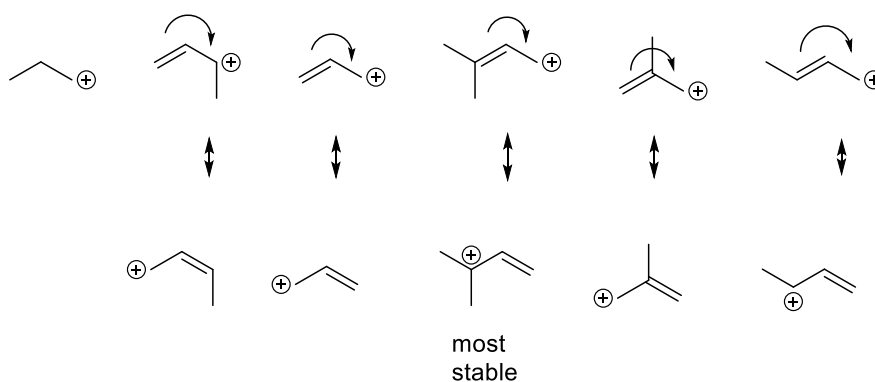


In both instances, the same carbocations are formed which then react with water to form the alcohol products.

2. Rank the relative rates of S_N2 reactions for the six alkyl and allyl iodides below when they are subjected to ethoxide in ethanol at 45 C. For the compound that you have identified to be the fastest, explain why.

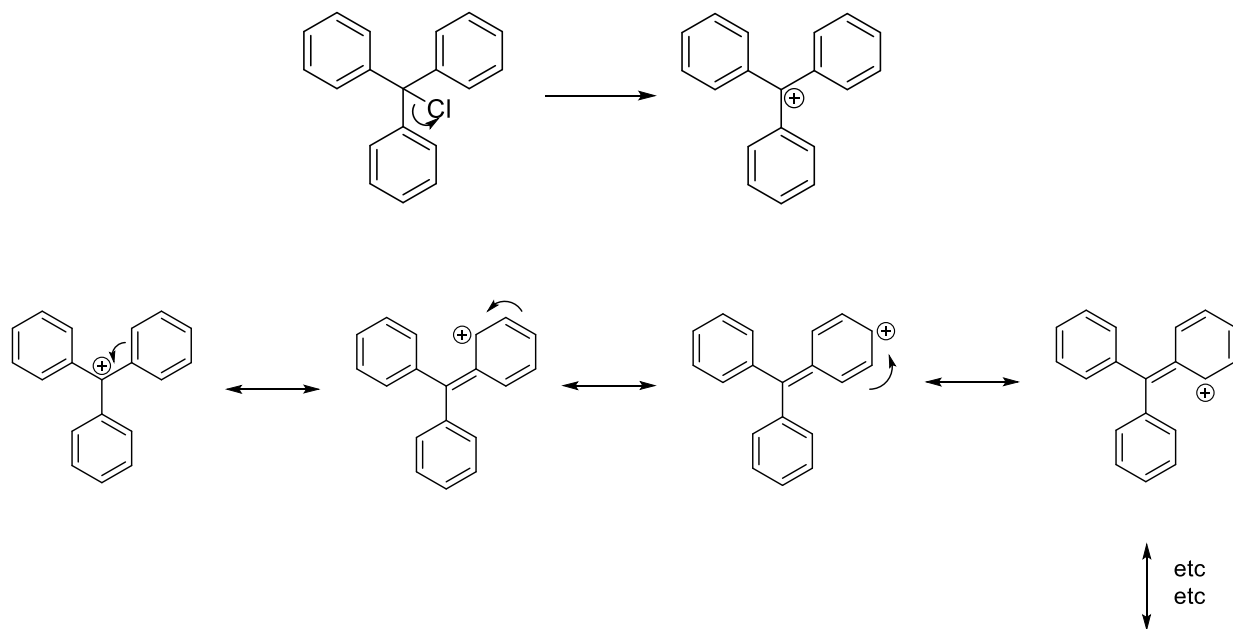


Despite the fact that this is an S_N2 question, stabilization of the partial positive charge will still accelerate the reaction. Therefore, one way to answer this question is to look at the stability of the cations that can potentially form. After this, consider resonance and stability. Lastly you should also consider steric hindrance. 1 will react faster with 2.



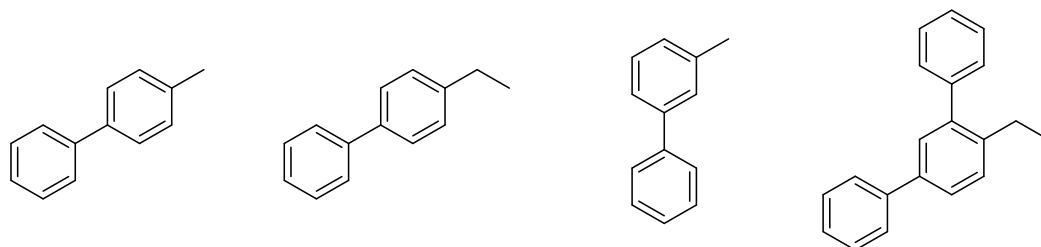
This is the fastest because it is not hindered and the positive charge character is most stabilized.

3. Departure of the chloride forms a carbocation. Use arrows to draw ALL resonance structures.

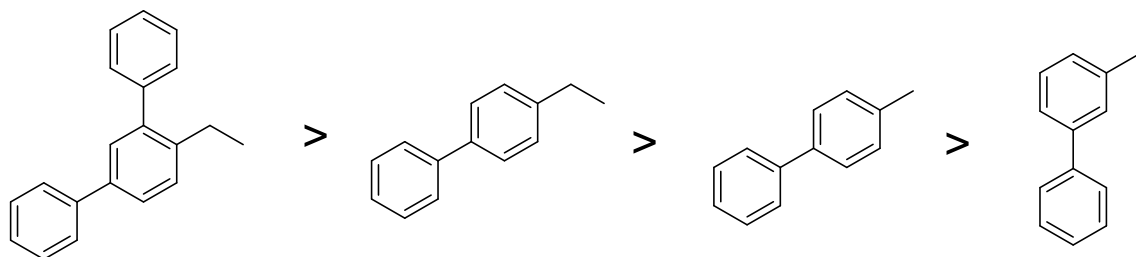


Many other possibilities, make sure the charge goes to every ring.

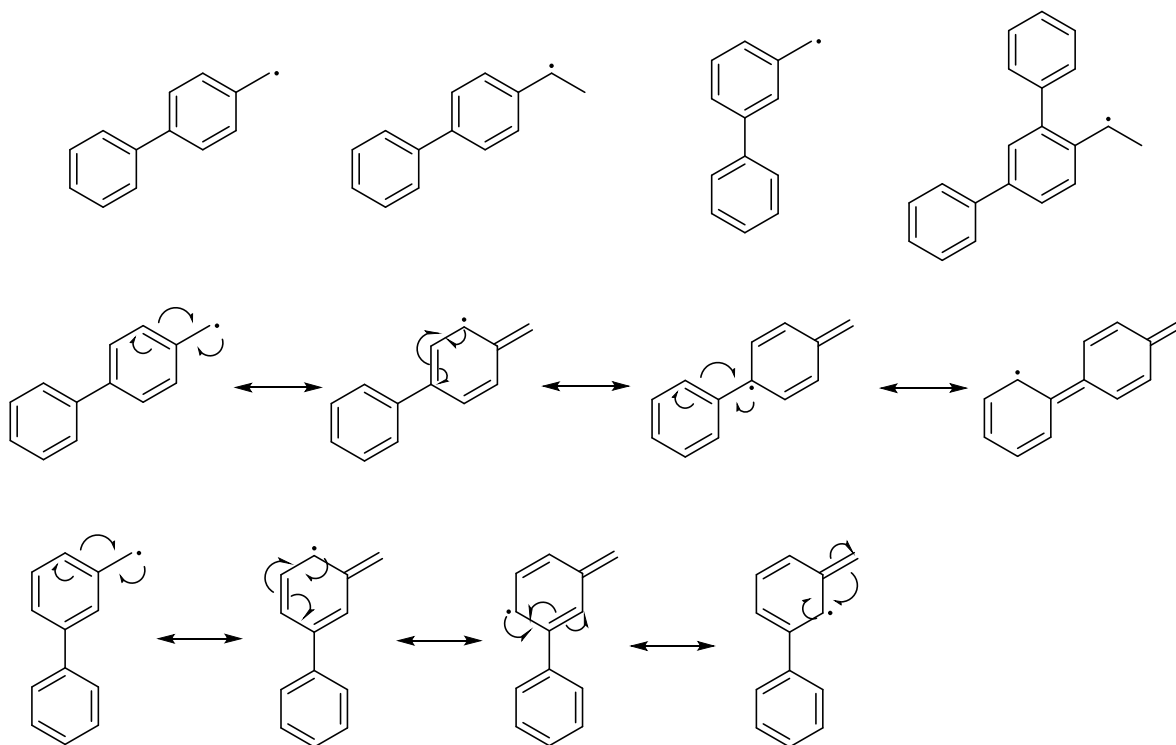
4. Each of the following compounds are treated with Br_2 and light ($h\nu$). Rank in order of reactivity and explain why.



Answer:

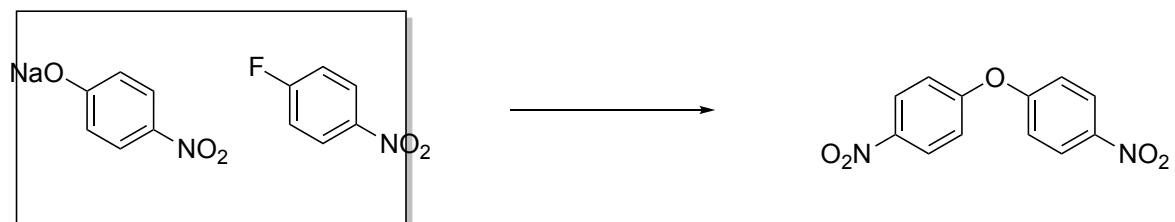
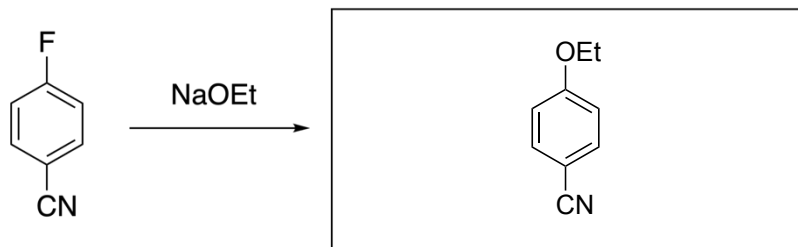


This is a typical radical reaction. The goal is to have the most stable radical. Based on organic chemistry I, the radicals should be at the following positions.

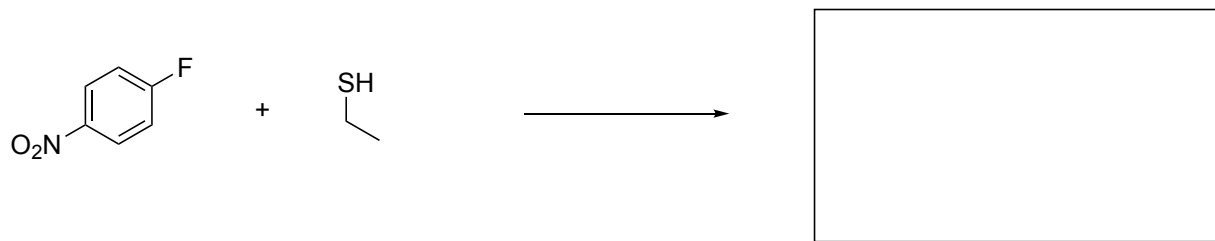


The extra benzene rings in 1, 2, and 4 can help stabilize the radicals (see the resonance structures one the lecture notes). But the one in 3 cannot since it is not involved in the resonance structures. The methyl group makes 2 more stable than 1.

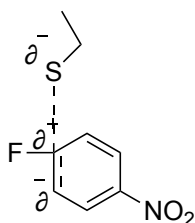
5. Fill in the reagents or predict the product. (4 pts each)



6.

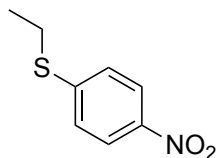


a. Draw the transition state structure for the above S_NAr reaction.



Key features include a partial bond forming between sulfur and the carbon. Partial positive charge on the carbon being attacked. And partial negative charge on the carbon at the adjacent position.

b. Indicate the major product formed.



c. Predict what would happen to the rate of the reaction if the solvent was switched from DMSO to THF. All conditions such as concentration and temperature will remain the same.

The reaction rate would slow significantly in THF because it is less polar than DMSO and therefore cannot stabilize the transition state structure shown above as effectively. This raises the energy of the TS, making it more difficult to cross the activation barrier to yield product.

d. If the nitro group was switched to a $-\text{CN}$ or $-\text{OMe}$, what would happen to the rate of the reaction?

If the nitro group was switched to a $-\text{CN}$, the rate of the reaction would be slower but would still yield product as $-\text{CN}$ is electron withdrawing and can stabilize charge via resonance. On the other hand, if the nitro group was replaced with $-\text{OMe}$, an electron donating group, the reaction would not proceed to yield product.