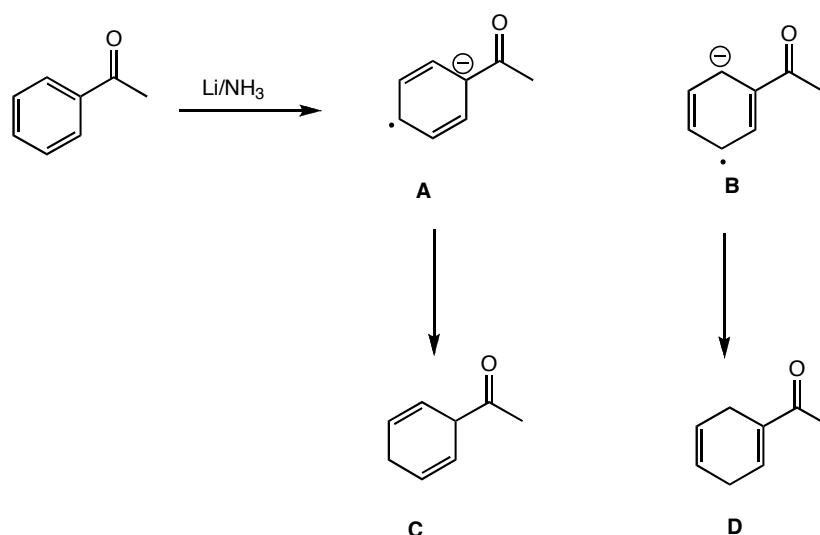


## Chemistry 218, Problem Set 8

Recommended problems from the book: 20.25, 20.29-20.30, 20.34-20.35, 20.40 (l), 20.41, 20.43 (f), 20.48 (g, j), 20.50, 20.51, 20.52(c), 20.60 (except f), 20.61-20.66

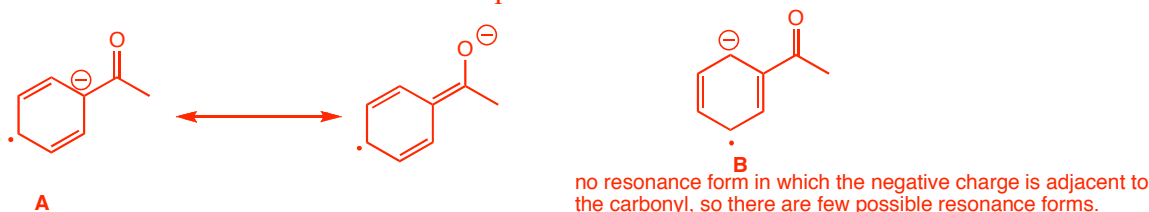
(Recommended problems from 1<sup>st</sup> ed): 20.26, 20.29-20.31, 20.34, 20.39 (l), 20.40, 20.42 (f), 20.48 (g,j), 20.49, 20.50, 20.51 (c), 20.57, 20.58 (except h), 20.59-20.62

1. In a Birch reaction, an aromatic compound is treated with  $\text{Li}/\text{NH}_3$  to give cyclohexadiene products (**C** and **D** below). One of the intermediates in the Birch reaction is a radical anion. In the example below, anisole could potentially form radical anion **A** or **B**, which go on to give **C** and **D** respectively.



(a) Is the Birch reaction an oxidation or reduction? **There is an increase in hydrogen in the product, so the reaction is a reduction.**

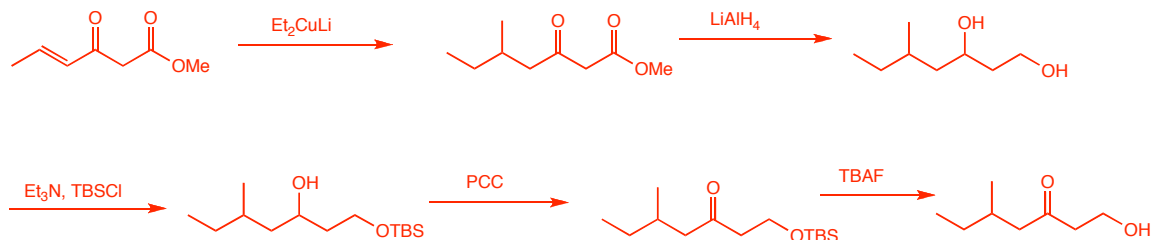
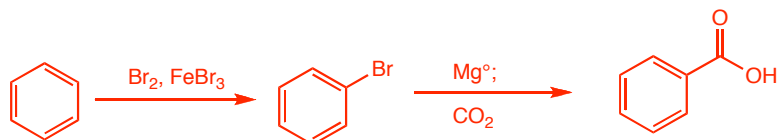
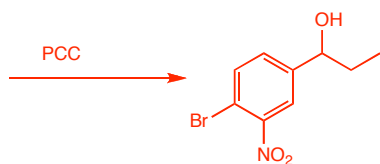
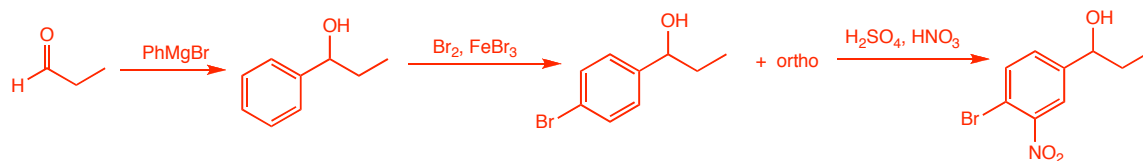
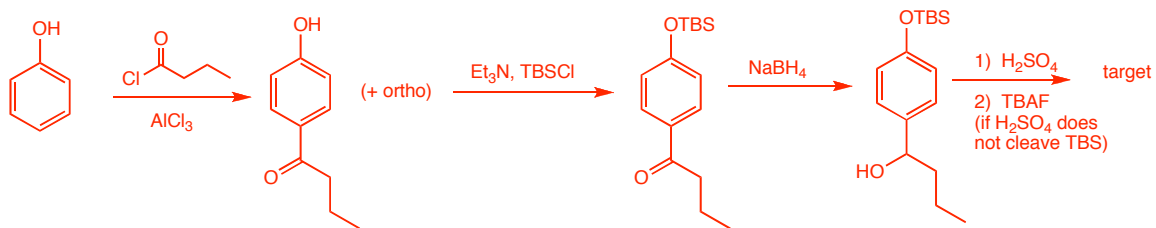
(b) Which anion is more stable, **A** or **B**? Why? **Anion **A** is more stable because there is an additional resonance form that compound **B** does not have:**



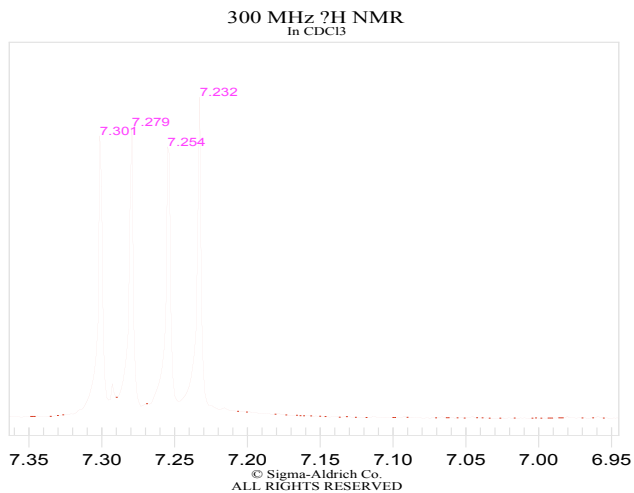
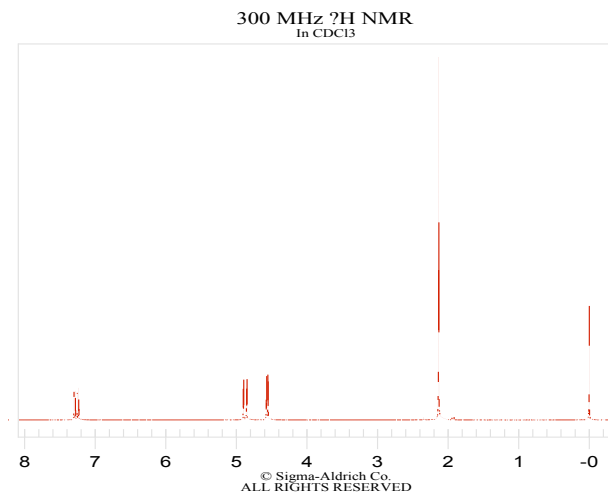
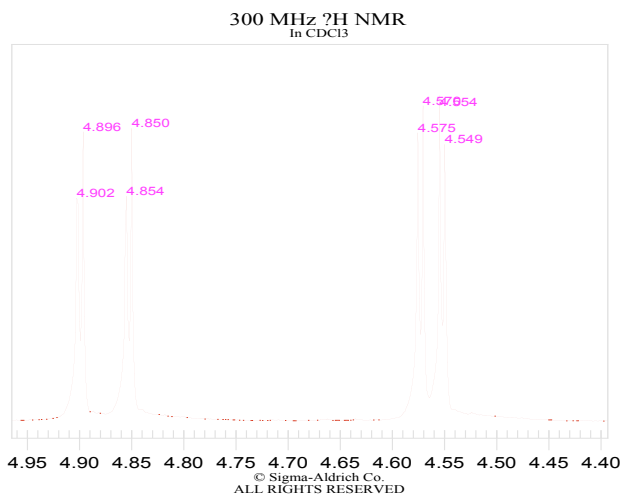
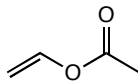
(c) For the Birch reaction, is a carbonyl group activating or deactivating?

**The carbonyl group is activating, because it is electron withdrawing, pulling electron density away from the negatively charged ring, and increasing stabilization. Note this is the opposite to EAS, because the Birch reduction involves a carbanion not a carbocation.**

2. Propose a synthesis with the following stipulations. There are also many excellent synthesis problems in the text. **There may be more than one possible answer. Here is one for each that definitely works.**



3. The  $^1\text{H}$  NMR spectrum for vinyl acetate is shown below. Assign the peaks as best you can, and explain the observed coupling patterns.



2.1 ppm, singlet:  
assignment: proton a

4.6 ppm, dd  $J=1.8$  (coupling between c/d) Hz, 14.1 (coupling with b) Hz,  
assignment: proton d or c (most likely d because the coupling constant for protons that are trans to one another is larger than the coupling constant for protons that are cis).

4.9 ppm, dd  $J=1.8$  Hz (coupling between c/d), 6.3 Hz (coupling with b)  
assignment: c or d (most likely c: see above).

7.3 ppm, dd  $J=6.6$  Hz, 14.1 Hz,

assignment: proton b (would have a higher chemical shift than c and d because it is attached to an oxygen).