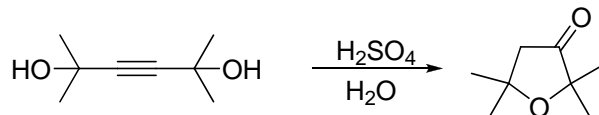
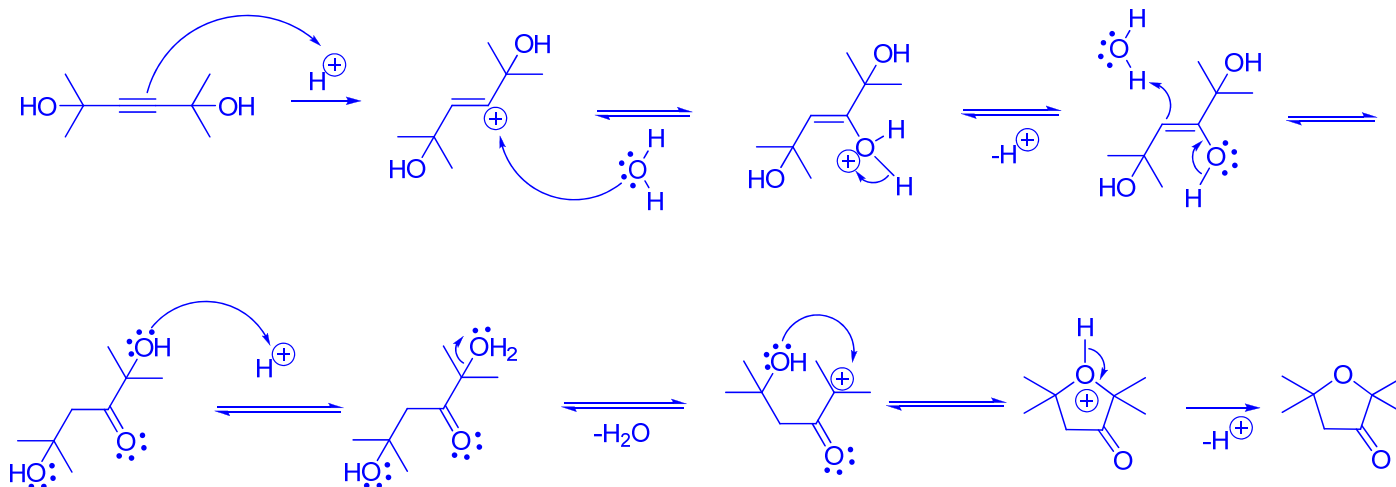


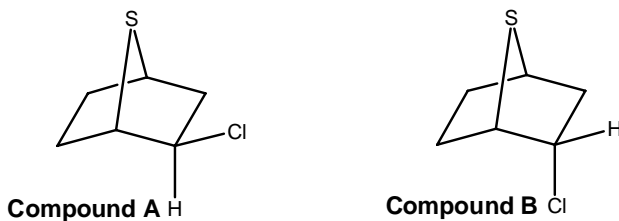
1. Draw a detailed mechanism for this transformation. _____/10



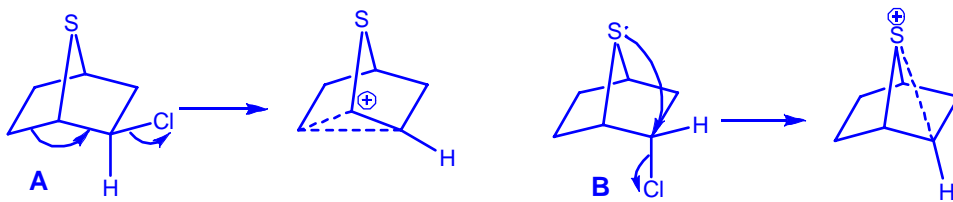
Answer:



2. Which compound reacts faster (A/B) in a solvolytic type reaction and why? Give mechanistic explanation. _____/10



Answer: Compound A reacts 4.7×10^9 times faster than B.



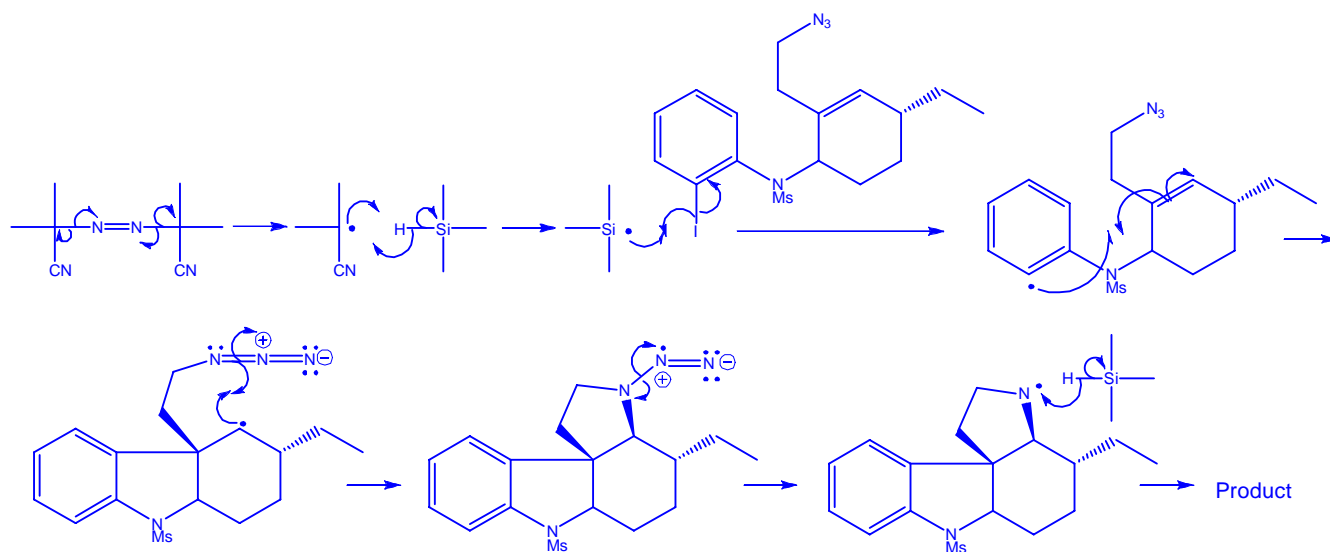
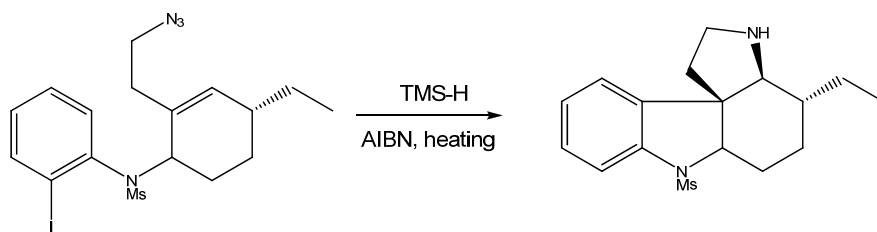
Solvolytic reaction implies that the mechanism has prominent features of S_N1 , i.e. the rate limiting step is the substrate ionization (or at least strong substrate polarization). However, this process proceeds with participation.

In the case of A : for the interaction between σ_{C-C} and σ_{C-Cl}^* helps L.G. departure. This geometric arrangement between σ_{C-C} and σ_{C-Cl}^* is quite favorable.

In the case of B : the unshared e-pair on sulfur participates somewhat in the L.G. departure. However, the spatial arrangement between the electron pair of sulfur and the σ_{C-Cl}^* is not entirely favorable, which results in slow rate in the rate-limiting step.

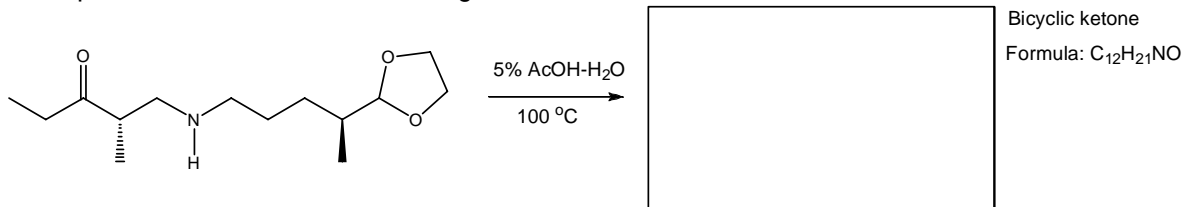
3. Propose mechanism for the following reaction:

_____ /20

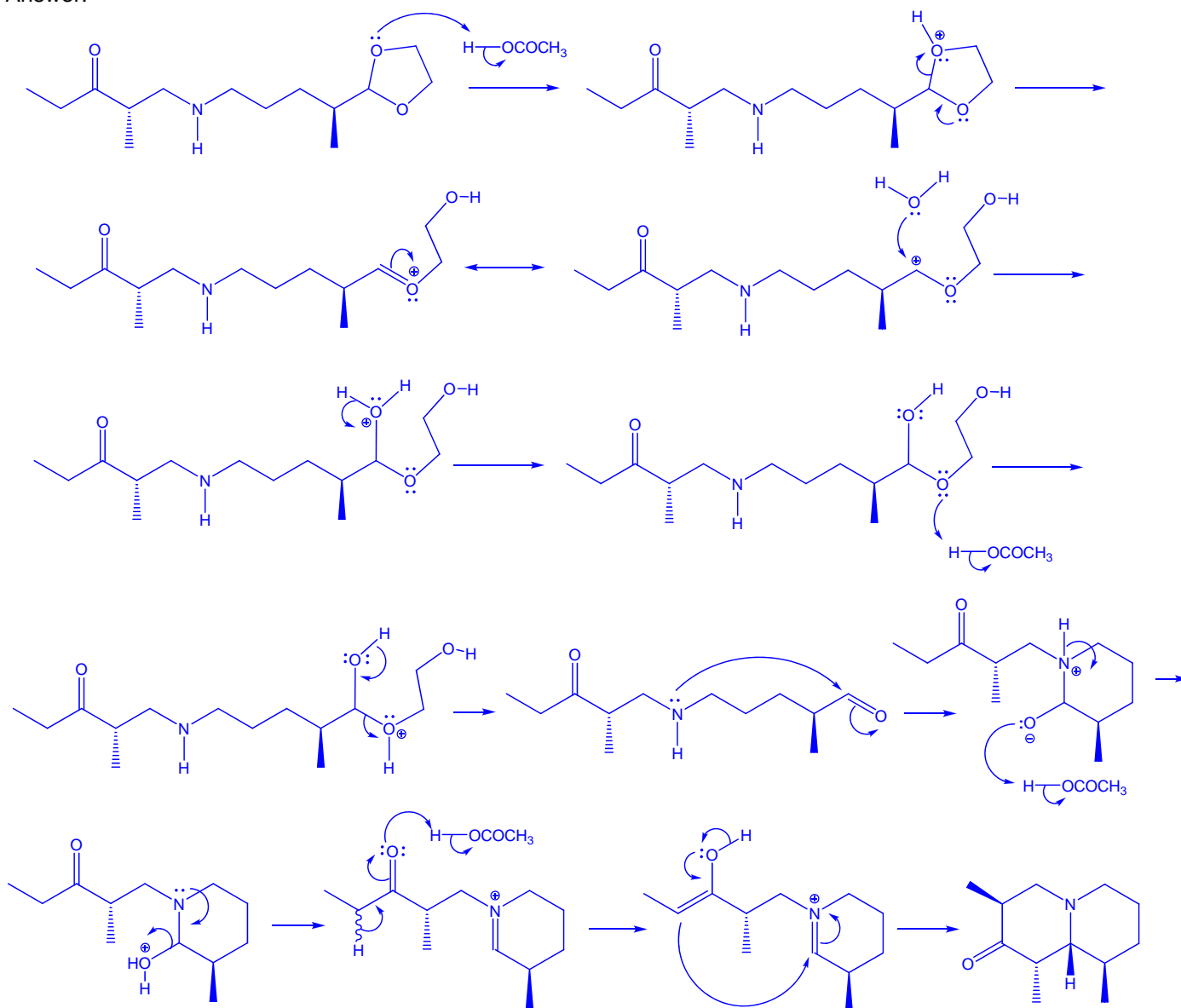


4. Propose mechanism for the following reactions:

_____ /30

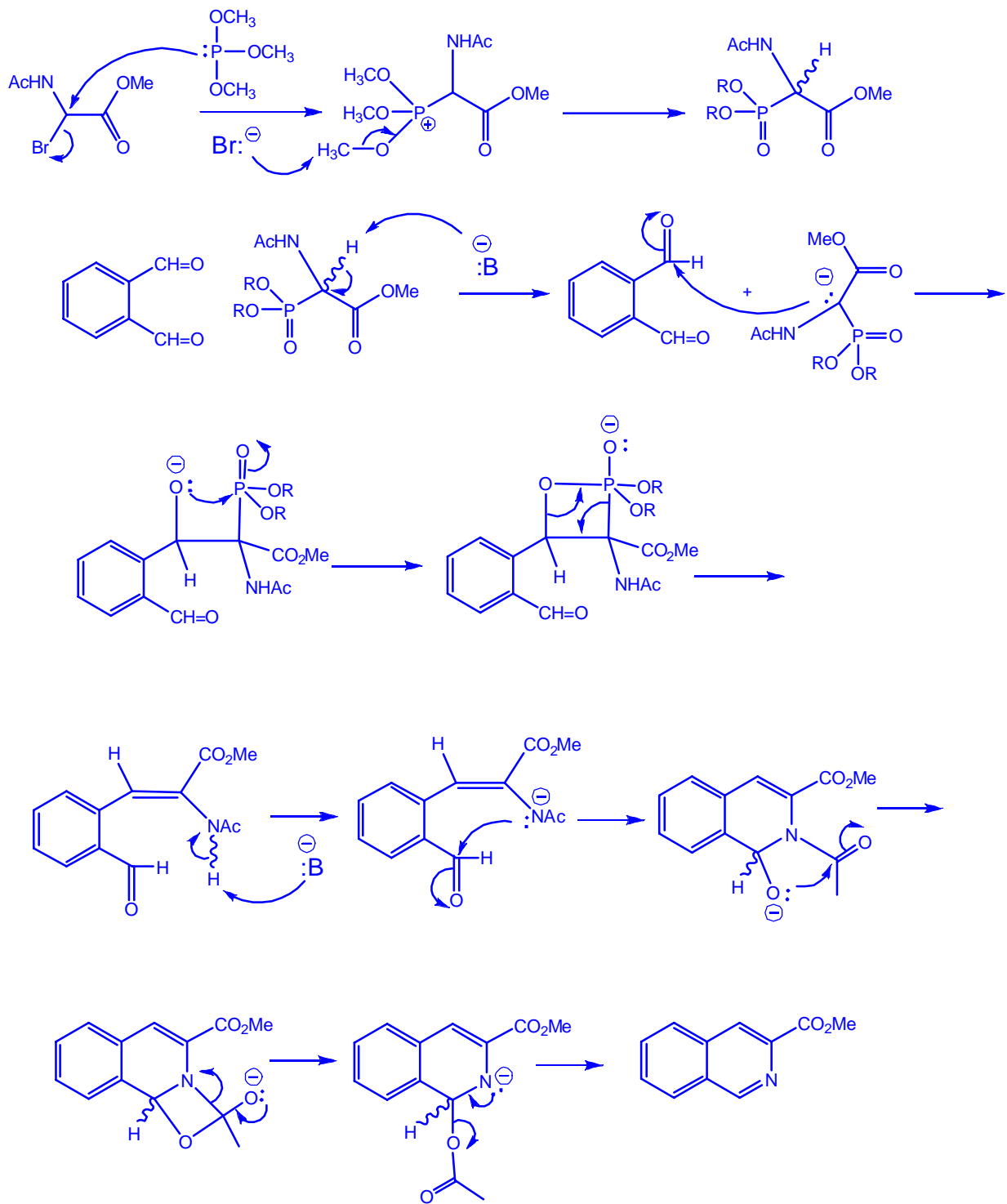
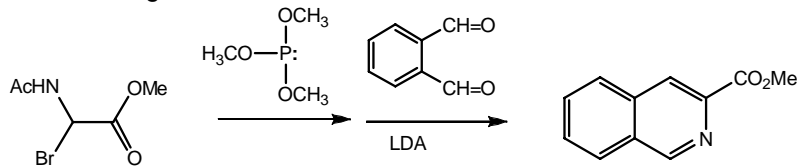


Answer:

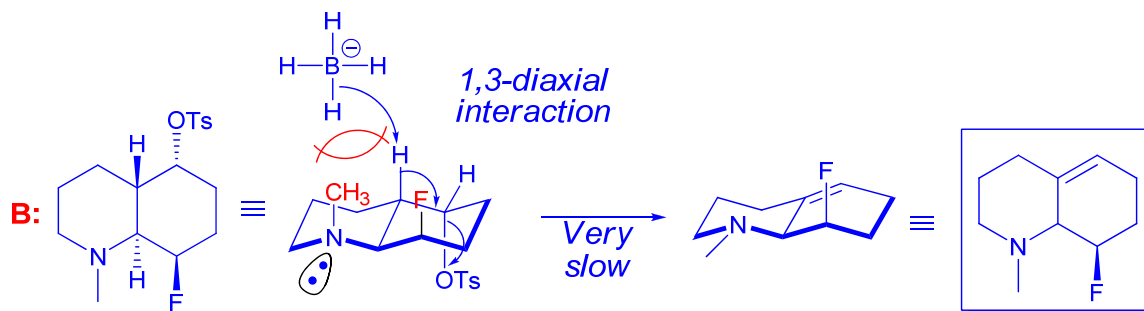
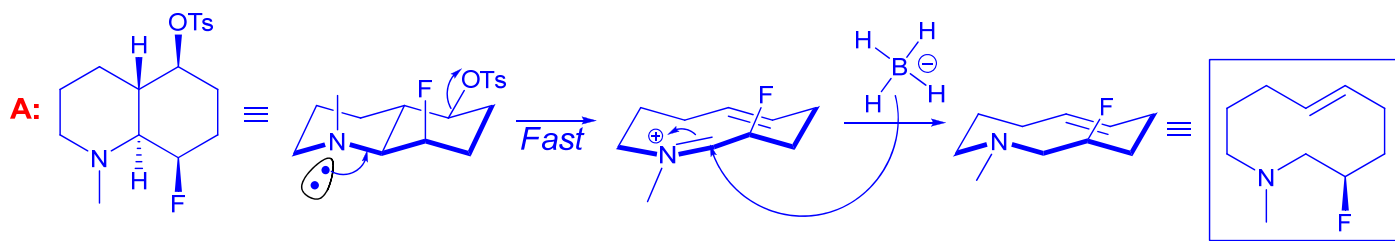
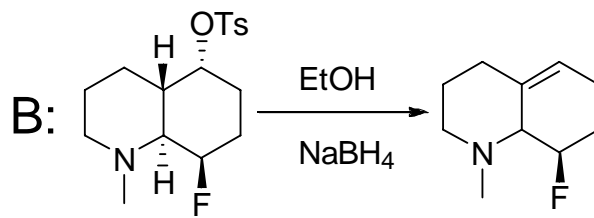
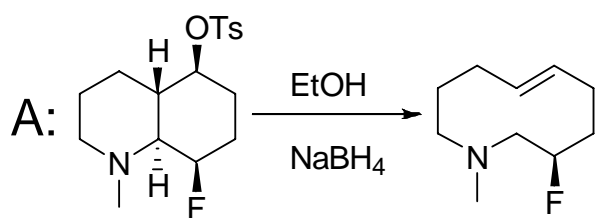


5. Draw a mechanism for the following reaction:

_____ / 30



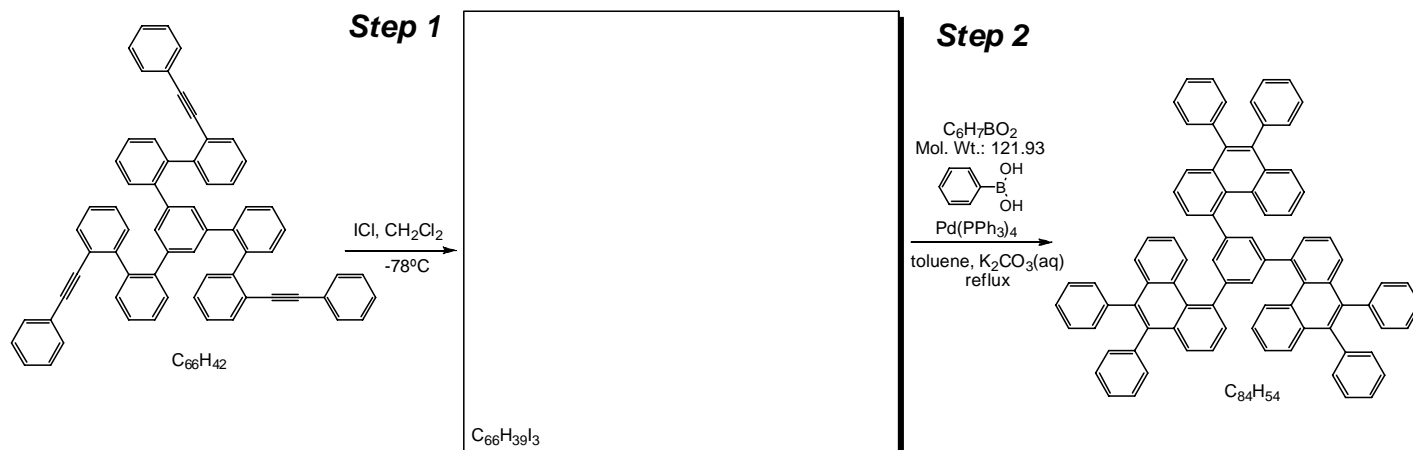
6. Which of the two reactions A and B proceed faster? Remember: A) you have to draw a detailed mechanism for both reactions, and B) clearly (and briefly) explain why A or B is faster than the other one. Note that if one reaction works well, it does not automatically mean that this reaction is faster – what if the other one works even better?



Elim A is much faster (it proceeds reasonably well), but most importantly the elimination B proceeds very slowly due to multiple diaxial interactions that prevent the BH_4^- anion to access the beta-Hydrogen.

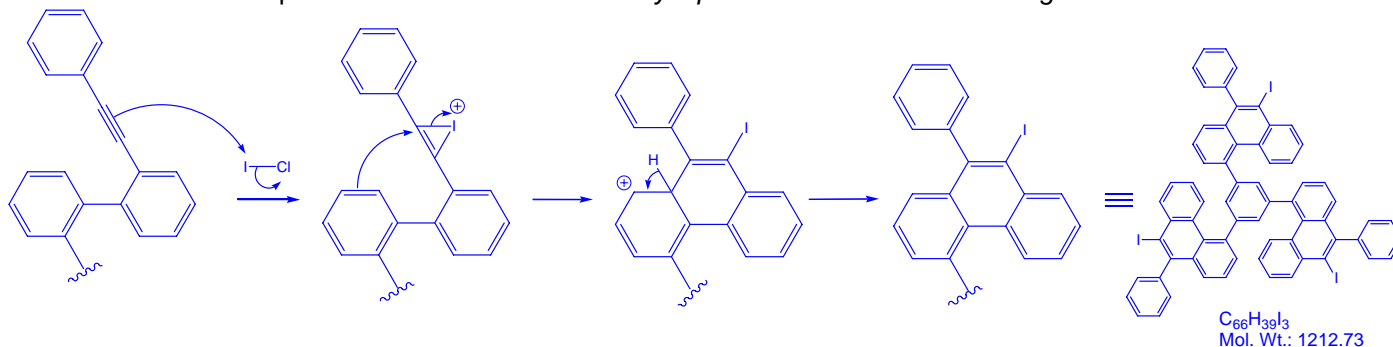
_____/20 pts

8. In a recent paper (Müllen, K.; *et al. Angew. Chem. Int. Ed.* **2007**, 46, 3033), triangle-shaped polycyclic aromatic hydrocarbon precursor synthesis was achieved by ICl-induced low temperature ring cyclization, followed by Suzuki-Miyaura coupling with phenylboronic acid as follows:

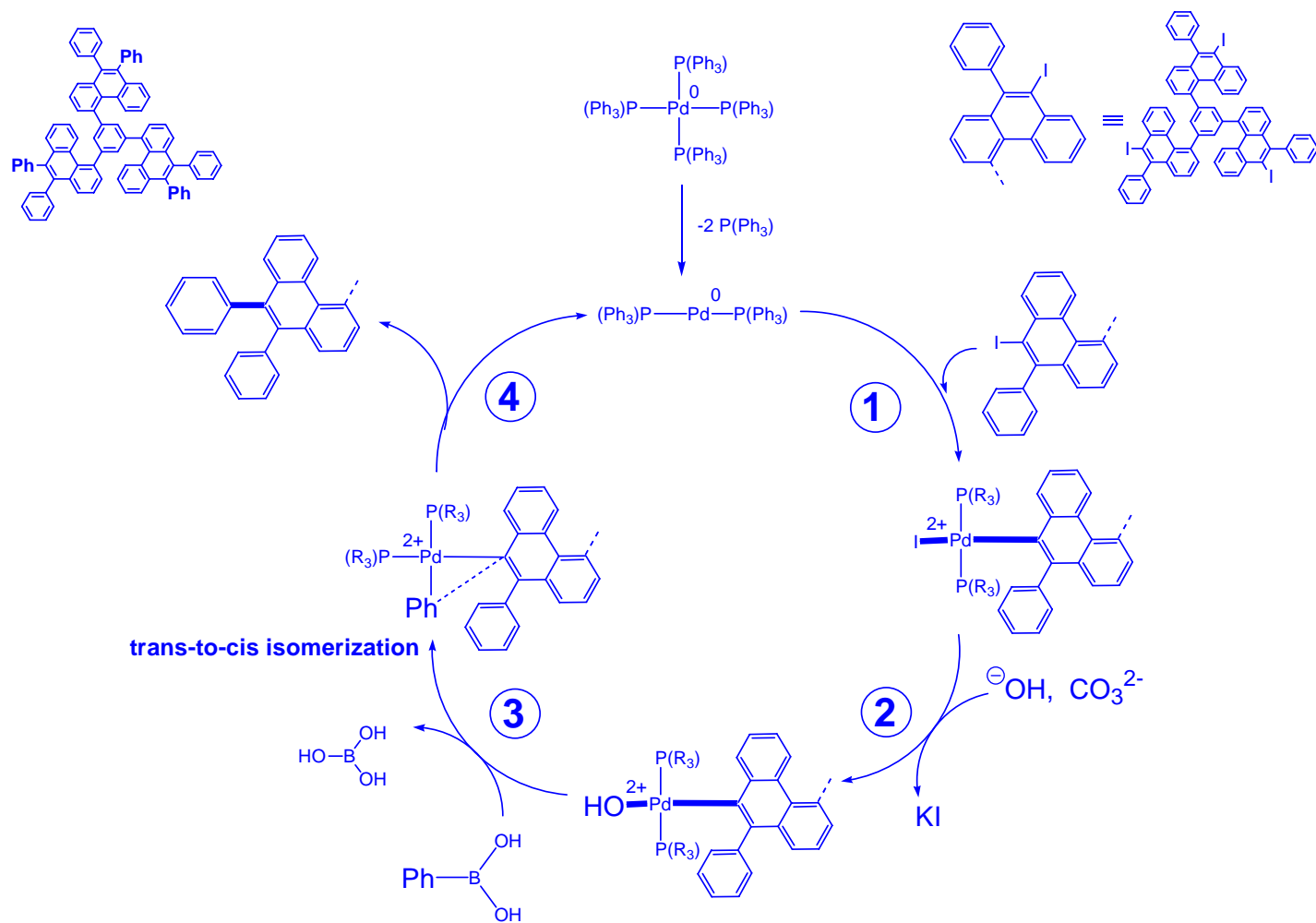


Propose a mechanism for the whole transformation (step1 and step 2) and suggest a structure for the first step product.

Draw mechanism – Step 1 You are advised to draw only a part of the molecule and designate the rest as R=:



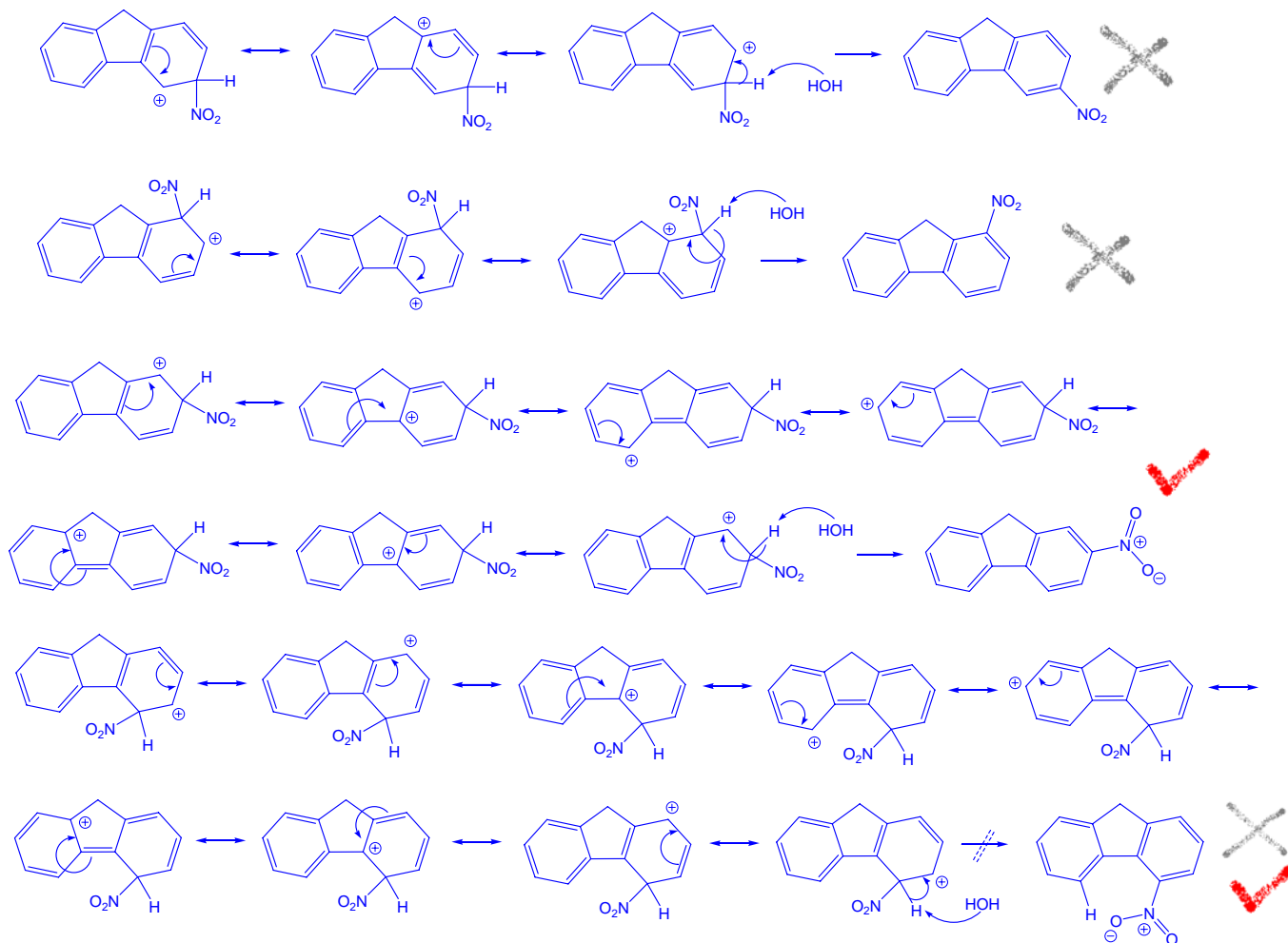
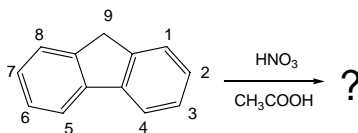
Draw mechanism – Step 2: In this mechanism, identify the main important features of the mechanism by their appropriate “names”.



1) Oxidative addition, 2) Anion methathesis (halide-oxoanion exchange), 3) Transmetalation, 4) Reductive elimination

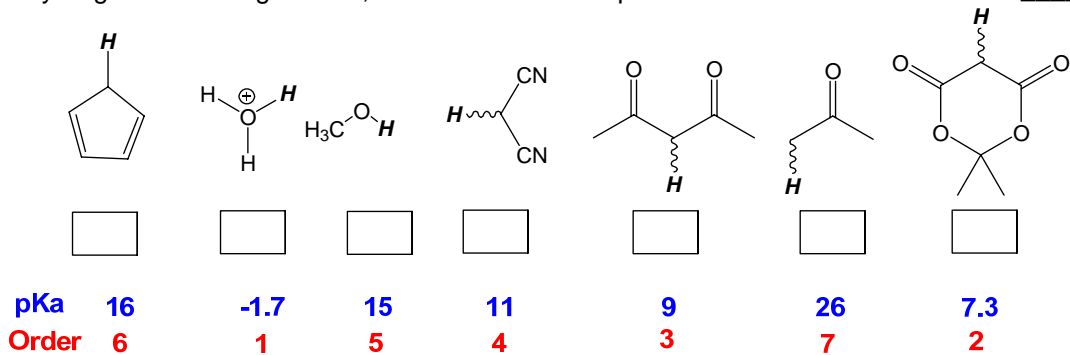
_____/50 total for both steps

9. What is the product of fluorene nitration? Draw complete mechanism, explain regioselectivity. Indicate whether you expect one or more products and explain (briefly) why.

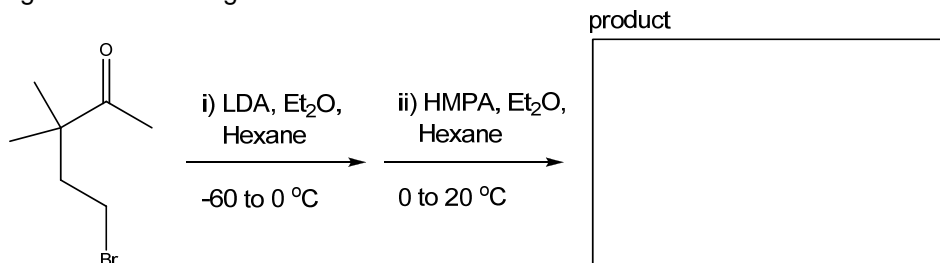


M+ effect of phenyl is stronger than the I+ of the alkyl. Phenyl is therefore the directing substituent. Phenyl is predominantly *para*-directing substituent. Although the Wheland intermediate for the *ortho*-substitution is electronically possible, it has high energy of rearomatization due to steric reasons.

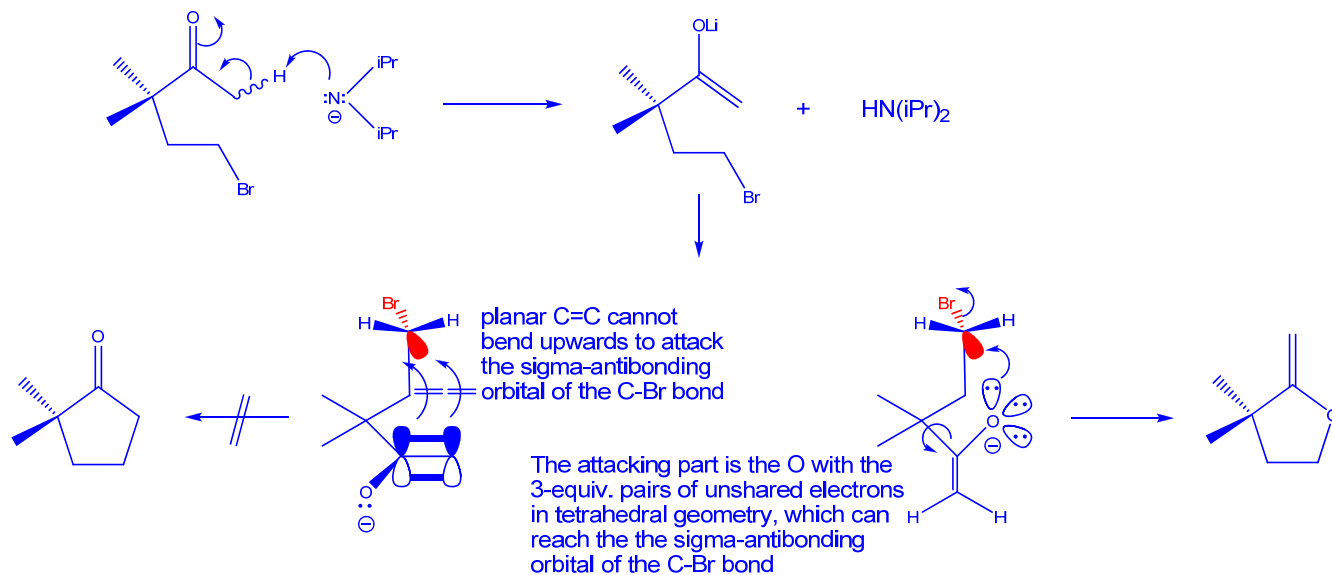
10. Acidity of hydrogens. 1=strongest acid, 7=weakest acid. No pKa. _____ / 10



11. Predict the product of the reaction below. Include a rationalization based on a detailed analysis of competing transition state geometries. _____/10

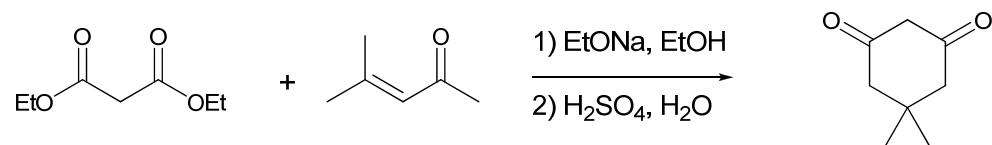


Mechanistic answer:

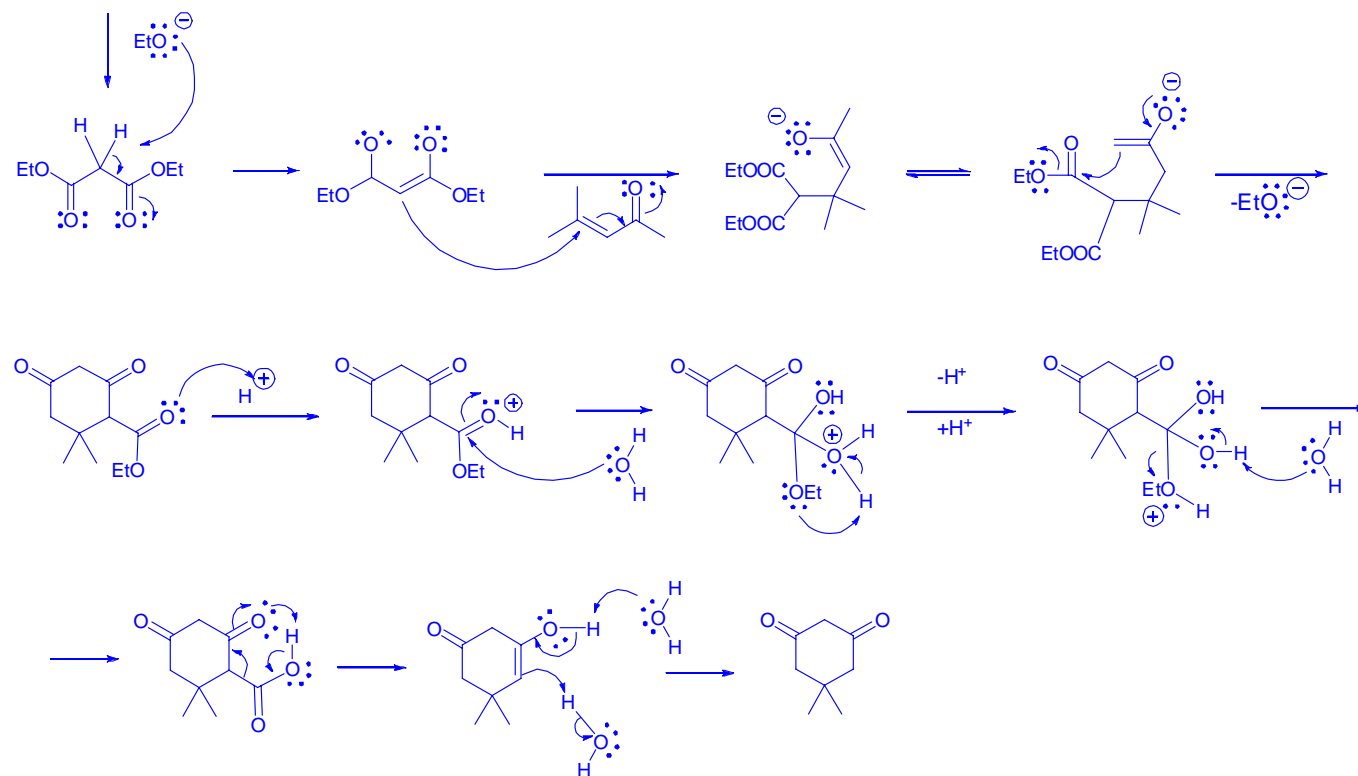


12. Propose mechanism for the following reactions:

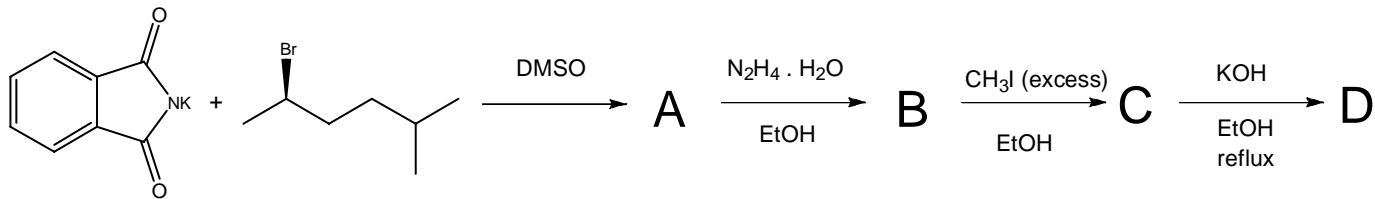
_____ /20



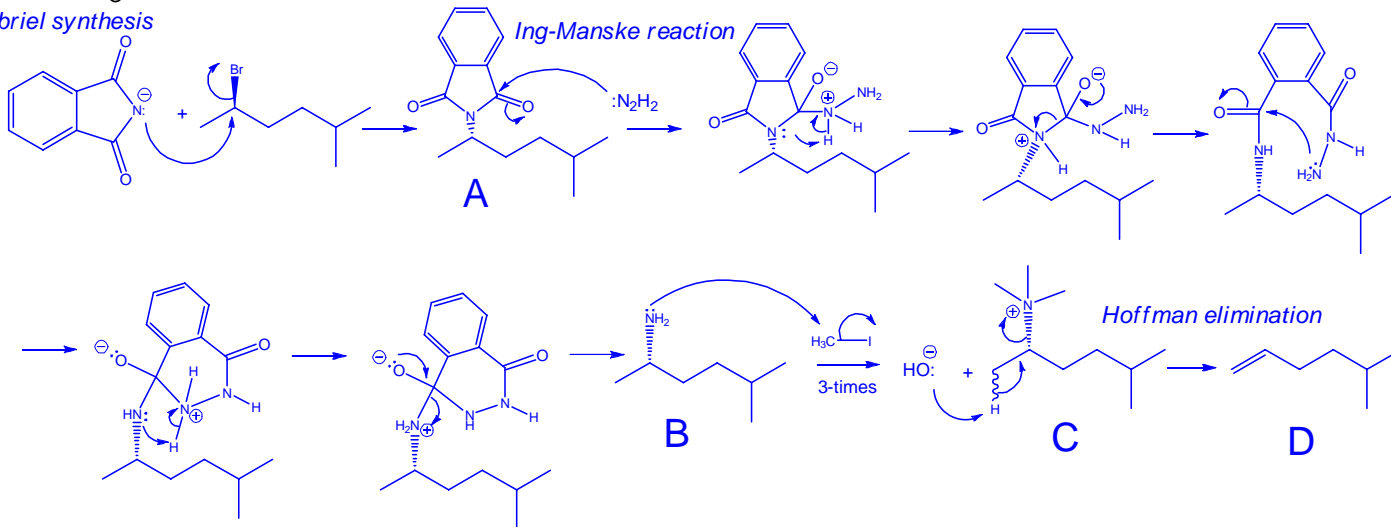
Answer:



13. Consider the reaction sequence outlined below, which departs from potassium phthalimide and 2-bromo-5-methylhexane. Use your mechanistic insight to identify products A-D. Also, provide a detailed mechanism for each of the reactions.



Gabriel synthesis



_____ /30 pts

14. Predict the main product of the reaction below. Include a rationalization based on a detailed Discussion of transition state geometry, product stereochemistry, etc. Note: The final products must be drawn in zig-zag representation. _____/30

