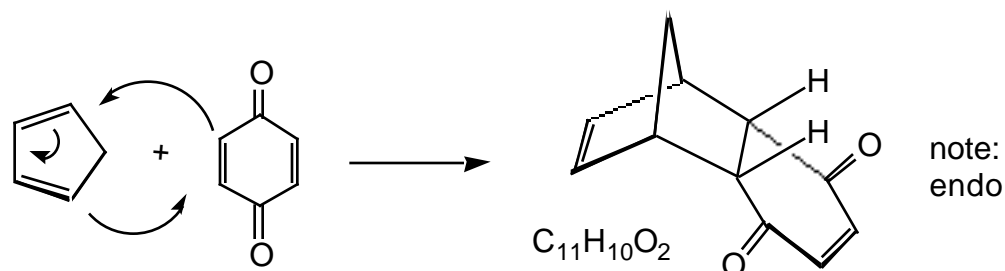
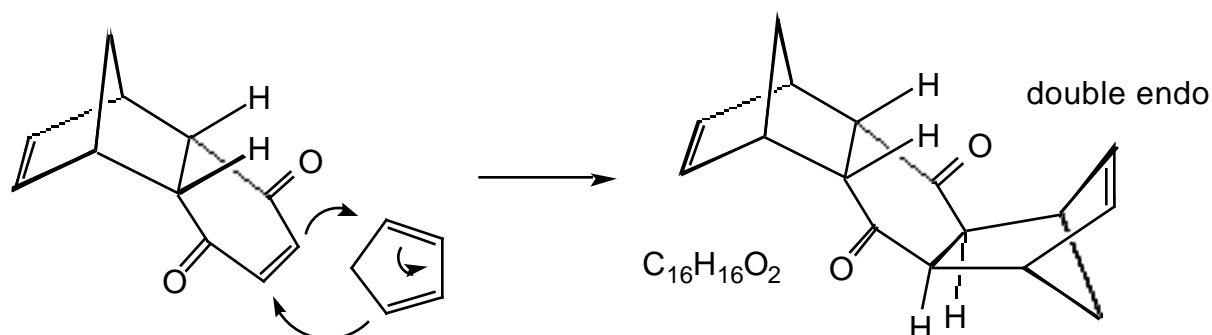


Some Answers to Hour Examination #1, Chemistry 302/302A, 2004

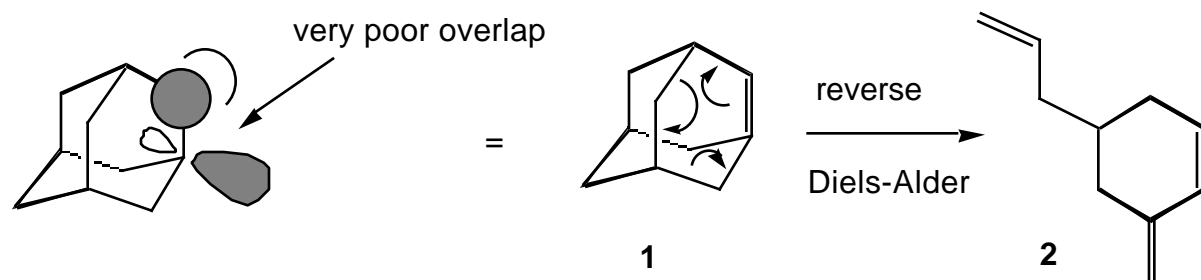
1. In this variation of the Diels-Alder reaction, both the diene and the dienophile are cyclic compounds. The first complication is to decide whether the reaction will pass over an endo or exo transition state. In fact, the cycloadduct has the endo stereochemistry, and this reaction is normal in that respect



You may have noticed that the product of this Diels-Alder reaction still has a double bond with two attached carbonyl groups. This carbon-carbon double bond is also a quite reactive dienophile. When this reaction is run in the presence of two equivalents of 1,3-cyclopentadiene, a 2:1 adduct is readily formed:

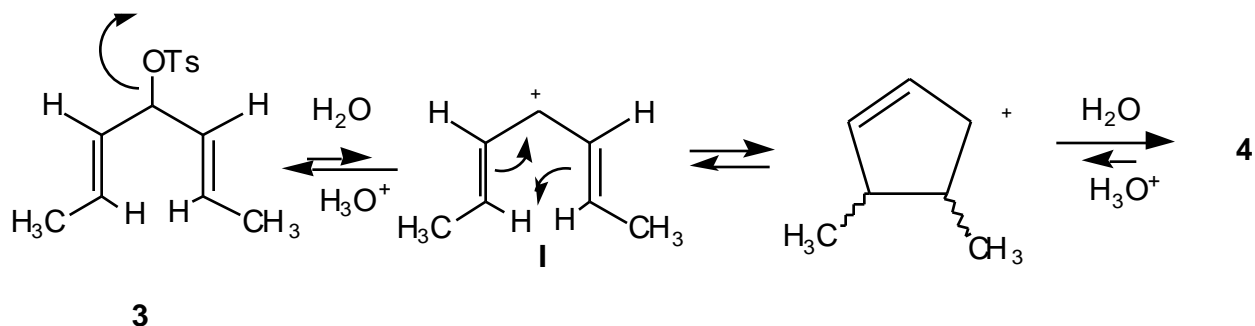


2. Adamantene is unstable because the bond is a very poor one. The orbitals do not overlap at all well.



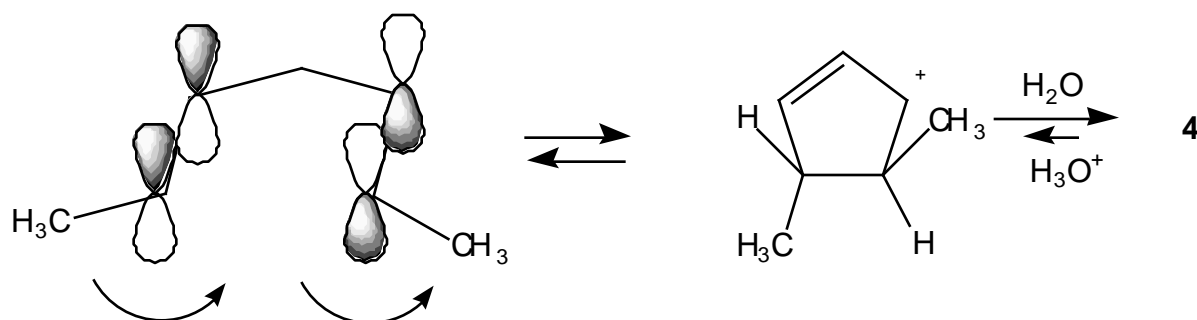
The reaction succeeds, but the unstable adamantene undergoes a reverse Diels-Alder reaction. Remember: all cyclohexenes are related to a diene and a dienophile through the Diels-Alder reaction.

3. Solvolysis gives pentadienyl cation **1** that closes to a cyclic ion. Addition of water, followed by deprotonation gives **4**.

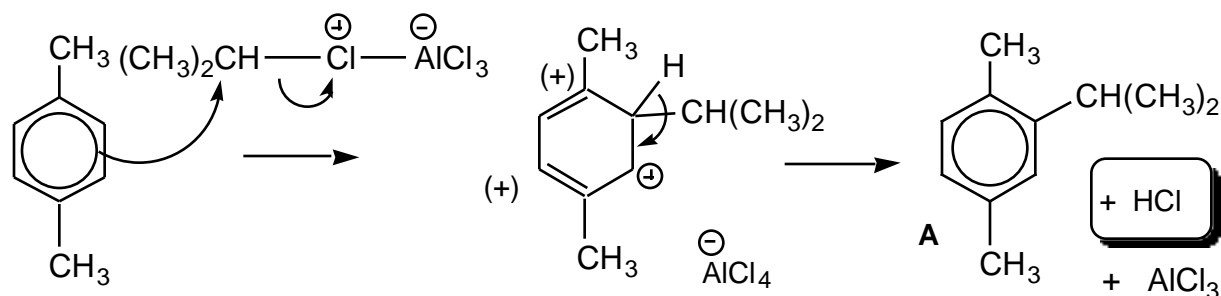


Intermediate **1** is a pentadienyl cation, a four-electron system. Analysis of the HOMO shows that closure must take place in conrotatory fashion to give the compound with trans methyl groups. If you can't figure out the MOs, you do know that all thermal $4n$ electrocyclic reactions are conrotatory.

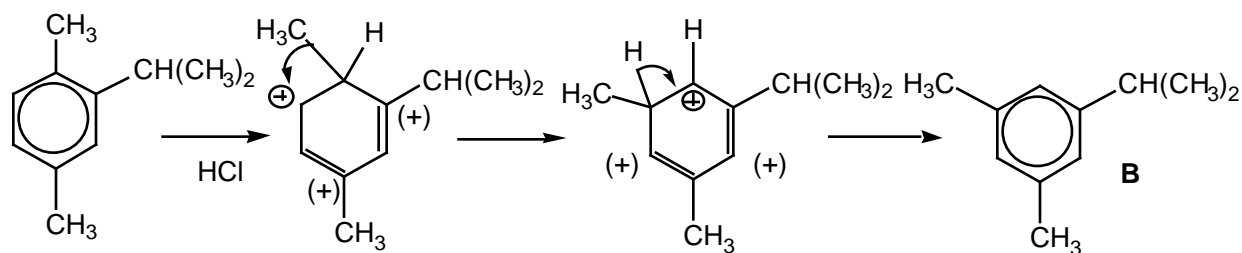
HOMO = ψ_2 , top view + + 0 - -



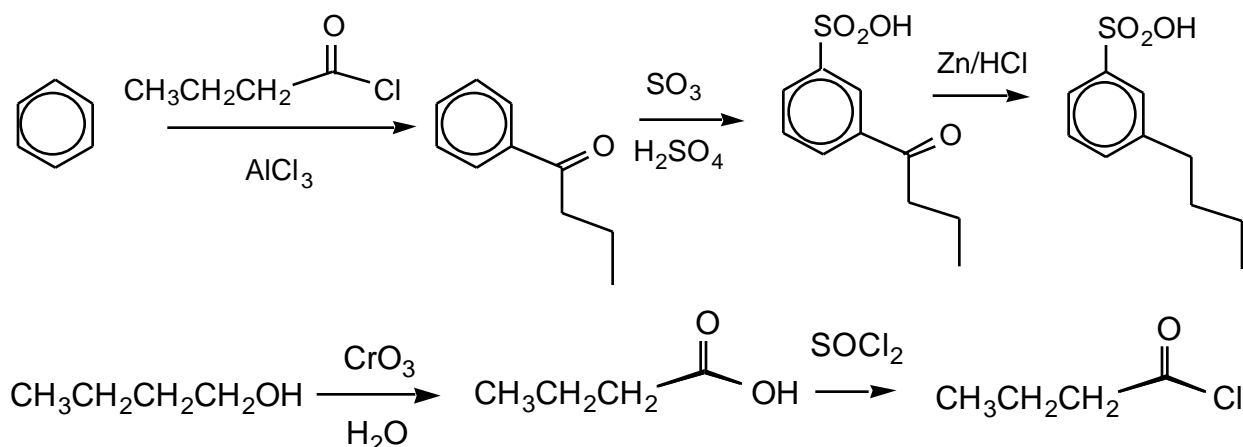
4. Compound **A** is formed through a straightforward Friedel-Crafts alkylation reaction.



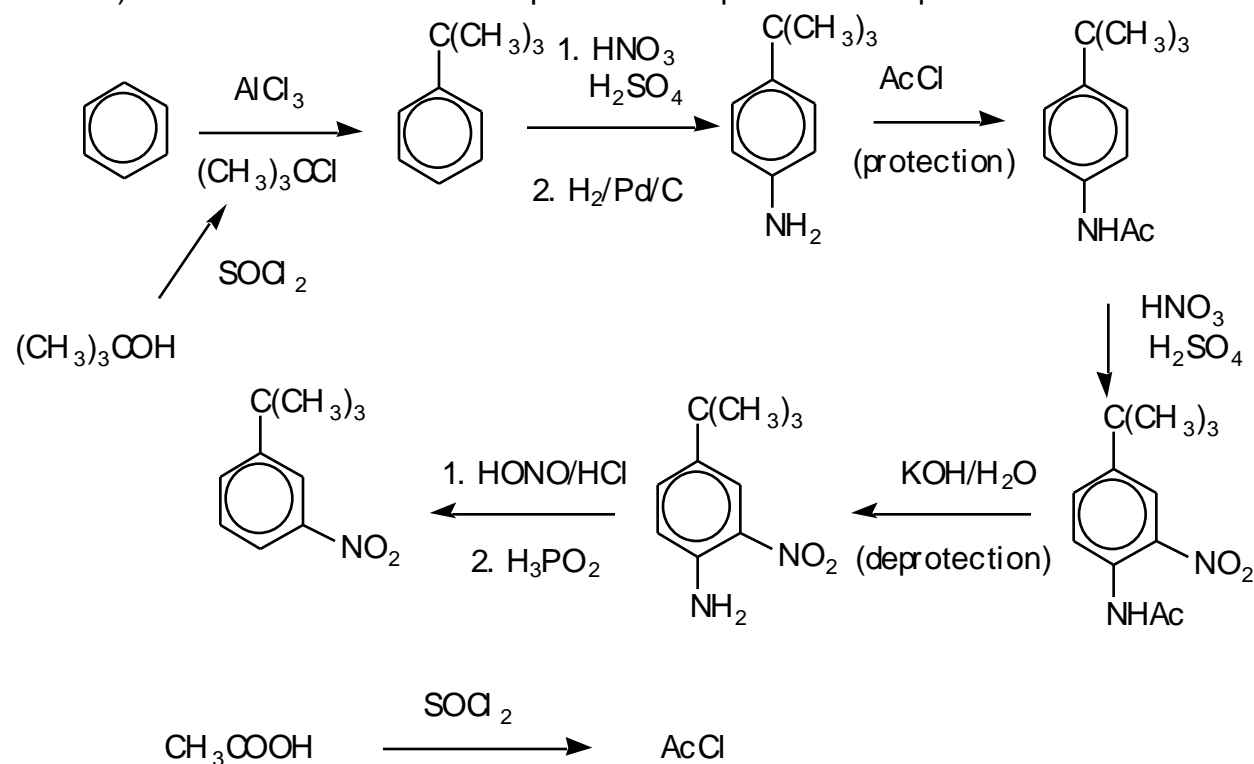
What can HCl do? The hint tells you to focus on this product. If the product **A** is protonated, we can generate an intermediate in which an alkyl shift moves the relatively large alkyl groups apart. That's the key to why this rearrangement happens - the relief of steric strain when the thermodynamically more stable 1,3,5-trisubstituted benzene is formed from a less stable 1,2,4-trialkylbenzene.



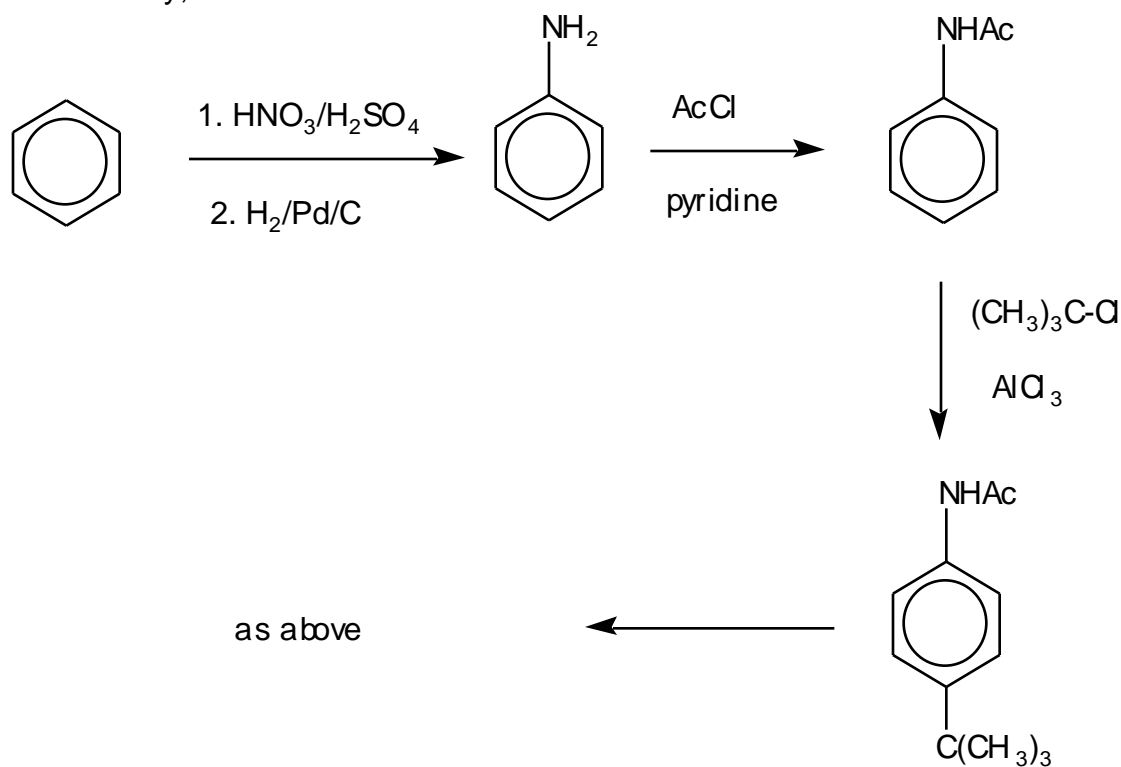
5a. Straightforward. Friedel-Crafts acylation, sulfonation, reduction.



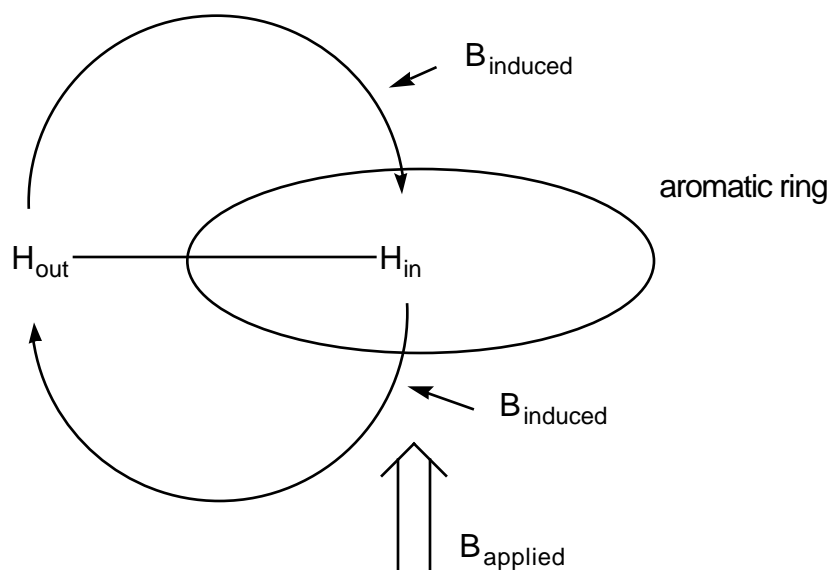
5b. Harder: Indirection must be used because Friedel-Crafts alkylation will not be effective on the strongly deactivated nitrobenzene. Of course, the *tert*-butyl group is an ortho/para director and will not nitrate in the meta position. So, we use the strongly activating amino group to force nitration into the position adjacent to it, and then remove the amine. In the answer, we acylate the amine to avoid substitution in the meta position directed by the protonated amine, but we will let you get away (partially at least) with an answer without the protection-deprotection sequence.



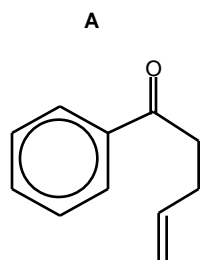
Alternatively,



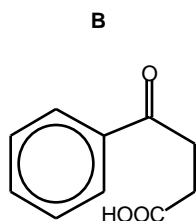
6. Compound **3** is aromatic ($4n + 2$, $n = 4$), whereas compound **4** is not ($4n$, $n = 4$). Accordingly, the 12 outside hydrogens in **3** appear far downfield of the normal alkene position [$B_{\text{net}} = B_0 + B_i$], and the six inside hydrogens are shifted far upfield [$B_{\text{net}} = B_0 - B_i$]. No such effect is apparent in **4**, of course.



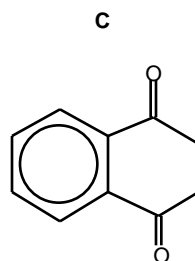
7. Here is a set of structures:



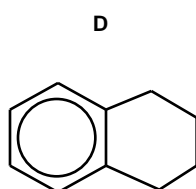
Friedel-Crafts with
the acyl chloride



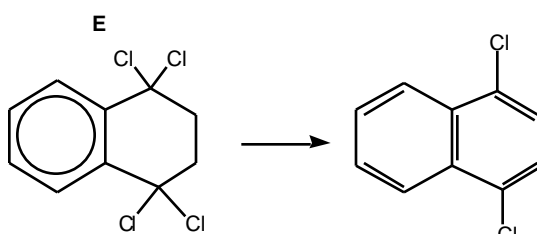
ozonolysis/oxidation
of the double bond



acid chloride formation
and another Friedel-
Crafts



Double Wolff-Kishner
reduces C=O groups



Photochlorinate all
benzyl positions

Double E2

