CHEMISTRY 314-02
FINAL EXAM
May 04, 2005

Name .....

The total number of points in the final is 100. The total exam time is 120 min (2 h). Good luck!

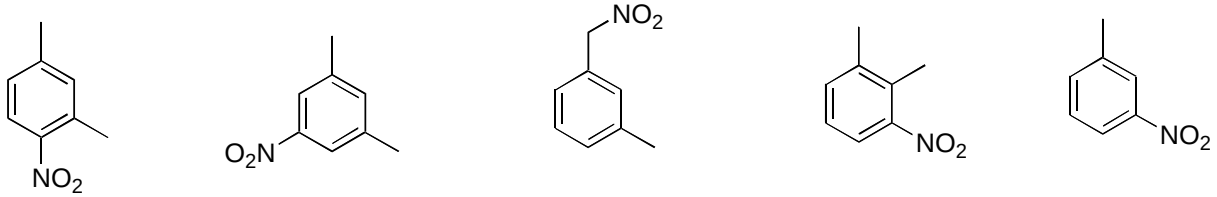
PART I: CONCEPTS

1. (15 pts) Mark as true (**T**) or false (**F**) the following statements. Do not explain!
   - The coupling constant in NMR depends on the operating frequency of the instrument;
   - The chemical shift in NMR depends on the operating frequency of the instrument;
   - In MS, molecules with odd number of nitrogen atoms give odd molecular ions;
   - Ethers are *Lewis* bases;
   - Deactivating groups on aromatic rings are always *meta*-directing;
   - *Friedel-Crafts* reactions do not work with deactivated benzene rings;
   - *Grignard* reagents contain carbon-lithium bonds;
   - Carbenes are electron-deficient;
   - The *Fischer* esterification is conducted only with acid catalyst;
   - The acetal formation is conducted only with base catalyst;
   - Acid chlorides are more reactive than amides;
   - Tertiary amines are less basic than secondary amines;
   - The *Hoffmann* elimination leads to the predominant generation of the less substituted alkene;
   - Epimers are diastereomers;
   - Anomers are C1 epimers;

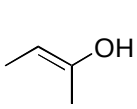
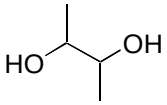
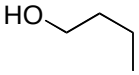
2. Circle all that apply:
   A. (2 pts) The following reactions lead to generation of carboxylic acids:
      a. Oxidation of aldehydes;
      b. *Baeyer-Villiger* oxidation of ketones;
      c. Reaction of *Grignard* reagents with carbon dioxide, followed by acid;
      d. Acid-catalyzed hydrolysis of nitriles;
   B. (2 pts) The following reactions occur through enolate ions:
      a. *Sandmeyer* reaction;
      b. *Claisen* condensation;
      c. *Wittig* reaction;
      d. *Wolf-Kishner* reduction;
   C. (2 pts) The following reactions are used to prepare <u>primary</u> amines:
      a. Reduction of nitriles;
      b. Reduction of azides;
      c. The *Gabriel* synthesis;
      d. The *Hofmann* elimination;
   D. (2 pts) The following reactions <u>are impossible</u>:
      a. Generation of ester from amide and alcohol;
      b. Generation of amide from ester and amine;
      c. Generation of secondary amine *via* reduction of a nitro compound;
      d. Aldol condensation of two molecules of benzaldehyde;

PART II: MULTIPLE CHOICE (15 questions, 2 points for each question).

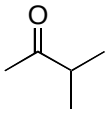
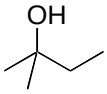
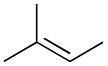
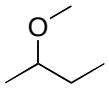
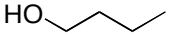
3. Circle the product of nitration of 1,3-dimethylbenzene.



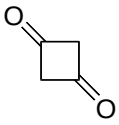
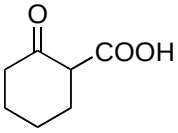
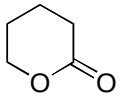
4. Circle the product of reaction of *cis*-2-butene with MCPBA.

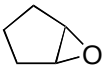




5. Circle the product of reaction of 2-butanone with CH_3MgBr, followed by acid.

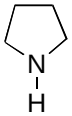
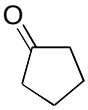
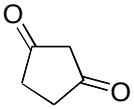
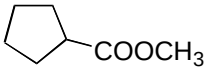






6. Circle the product of *Baeyer – Villiger* oxidation of cyclopentanone.

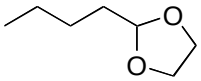
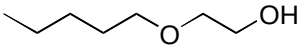
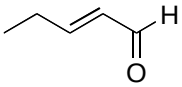
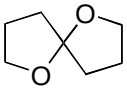
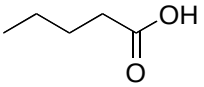






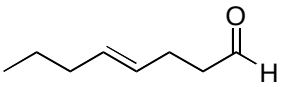
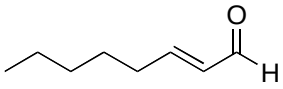
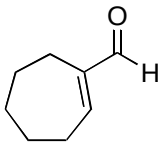
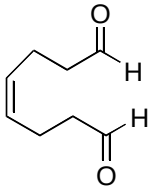
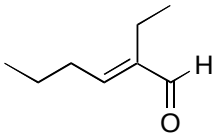
7. Circle the most acidic compound.

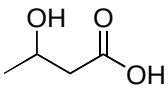
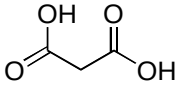
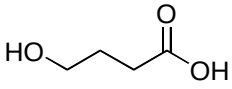
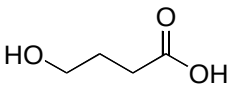
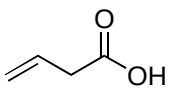

8. Circle the product of reaction of pentanal with 1,2-ethanediol in the presence of TsOH.

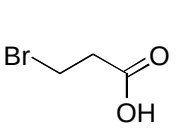
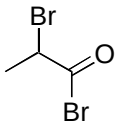
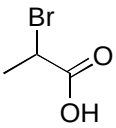
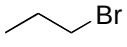
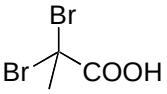
9. Circle the product of aldol self-condensation of butanal.

10. Circle the acid that forms 3-butanolide.

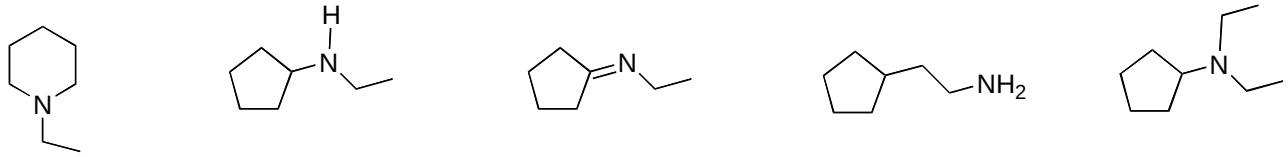






11. Circle the product of reaction of propanoic acid with Br_2/PBr_3, followed by water.

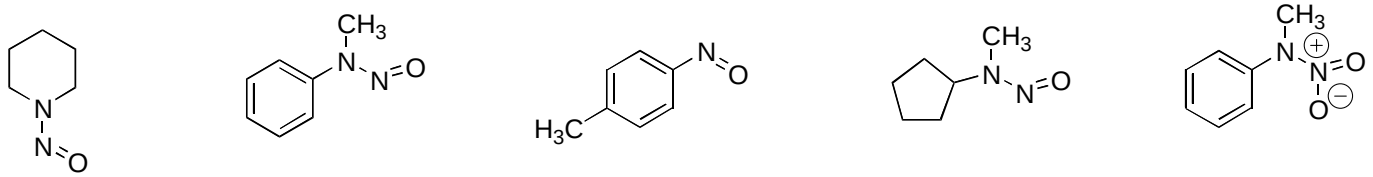






12. Circle the product of reaction of benzyl bromide with NaN_3 in DMSO, followed by reduction with $LiAlH_4$.

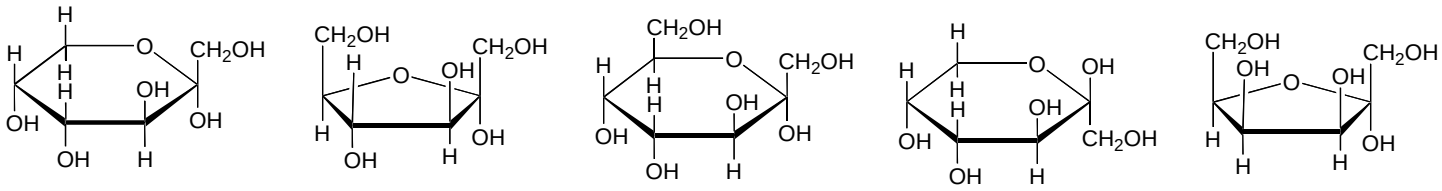
13. Circle the product of reductive amination of ethanal with cyclopentylamine.



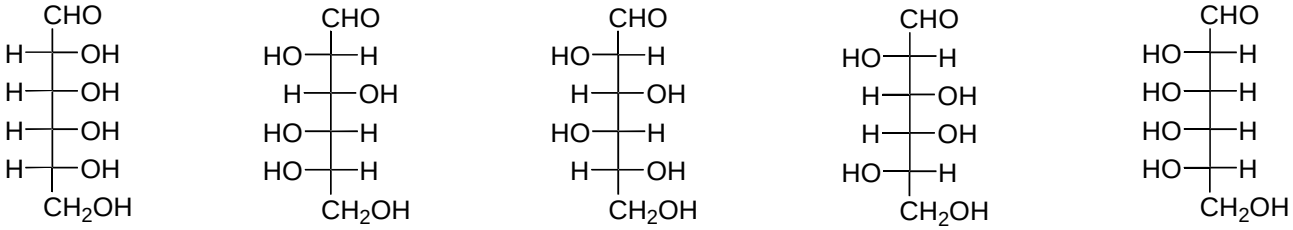
14. Circle the product of nitrosation of N-methylaniline.



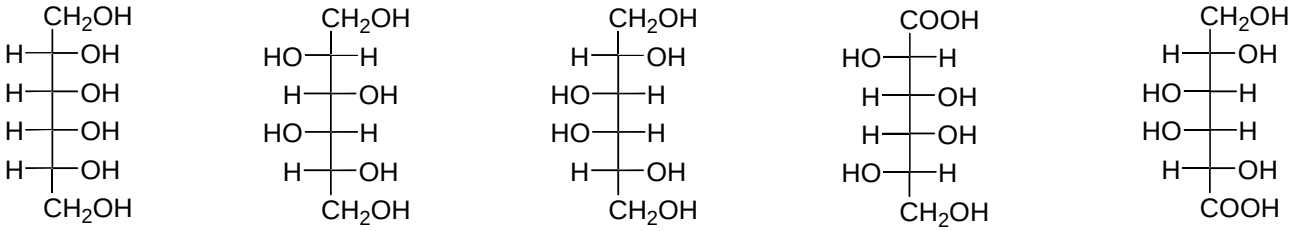
15. Circle the α-anomer of D-fructopyranose.



16. Circle L-glucose.



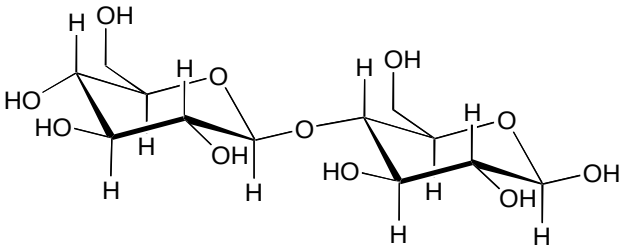
17. Circle the product of reduction of D-galactose (a C4-epimer of glucose) with $NaBH_4$.

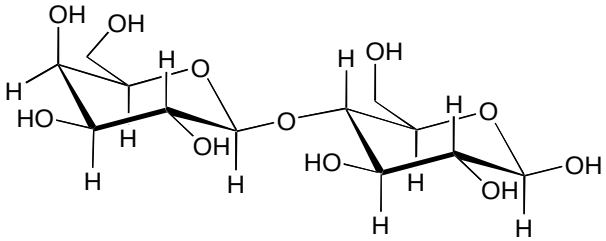


PART III: CARBOHYDRATE STRUCTURE AND NOMENCLATURE.

18. (4 pts) The structures of two monosaccharides are given below in the form of their *Haworth* projections. In each case, provide the *Fischer* projection of the open-chain form.

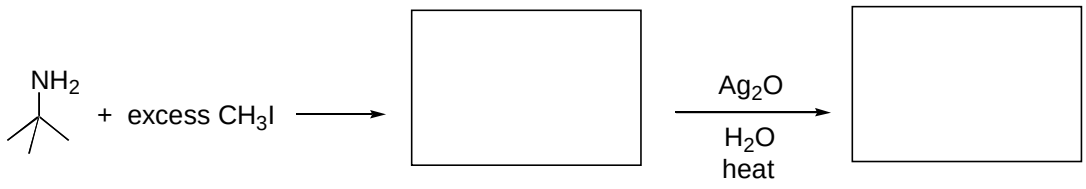
19. (3 pts) Provide acceptable names for the following compounds.

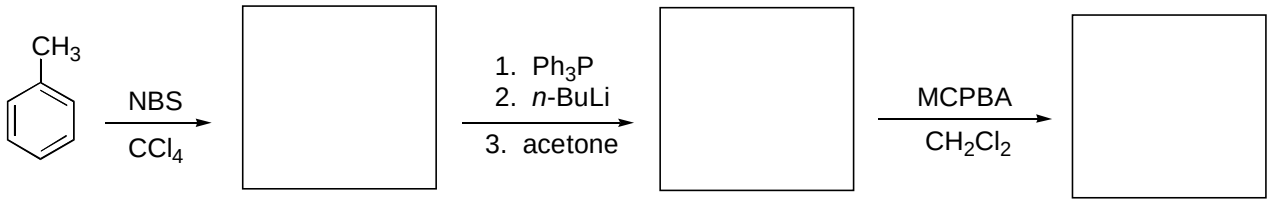


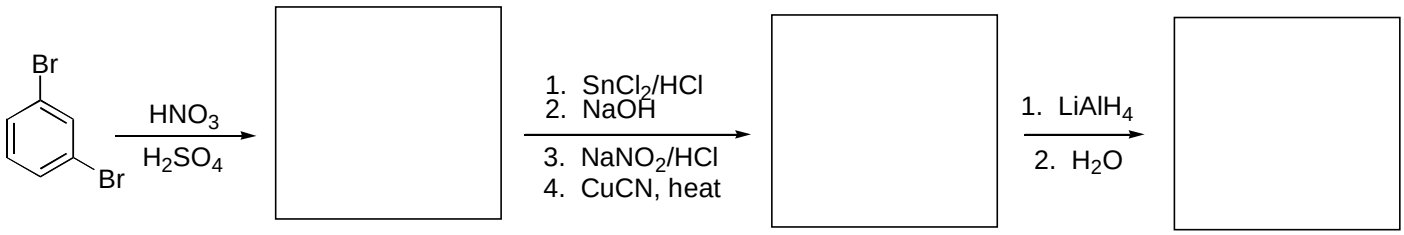


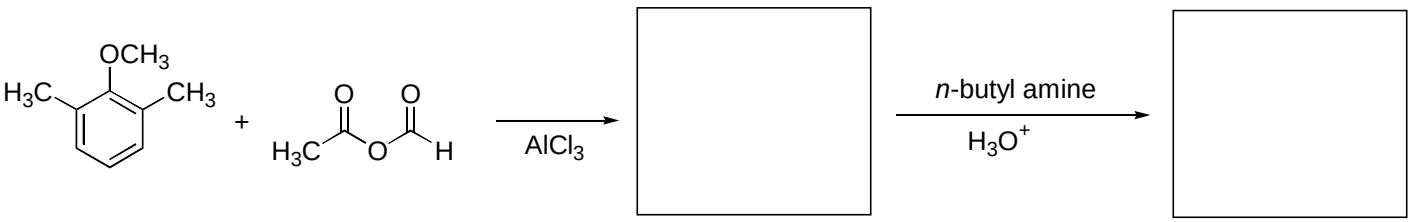
PART IV: REACTIONS

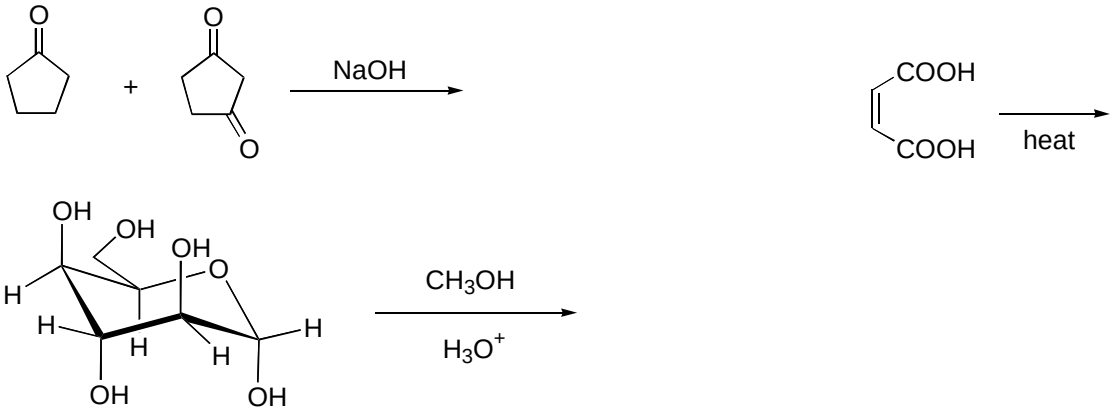
20. (16 pts) Predict the principal organic product in each of the following reactions:





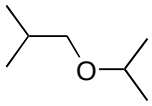


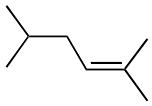


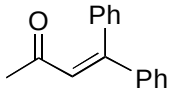


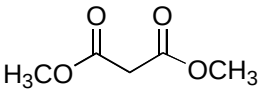
PART V: SYNTHESIS

21. Each of the compounds below is produced by using <u>one of the following synthetic methodologies</u>: **1) The *Williamson* ether synthesis; 2) The *Wittig* reaction; 3) Mixed aldol condensation; 4) Mixed *Claisen* condensation.** Suggest suitable starting materials and then propose a synthetic sequence in each case.

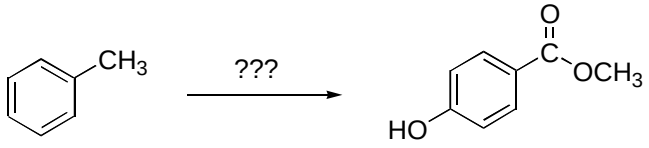
A. (3 pts) 

B. (3 pts) 

C. (3 pts) 

D. (3 pts) 

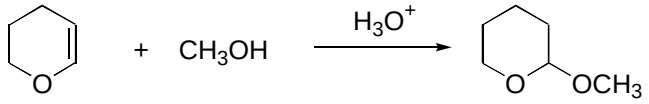
22. (4 pts) Methylparaben is used as a preservative in foods, beverages and cosmetics. Propose a synthesis of methylparaben from toluene and any other necessary organic or inorganic reagent.



methylparaben

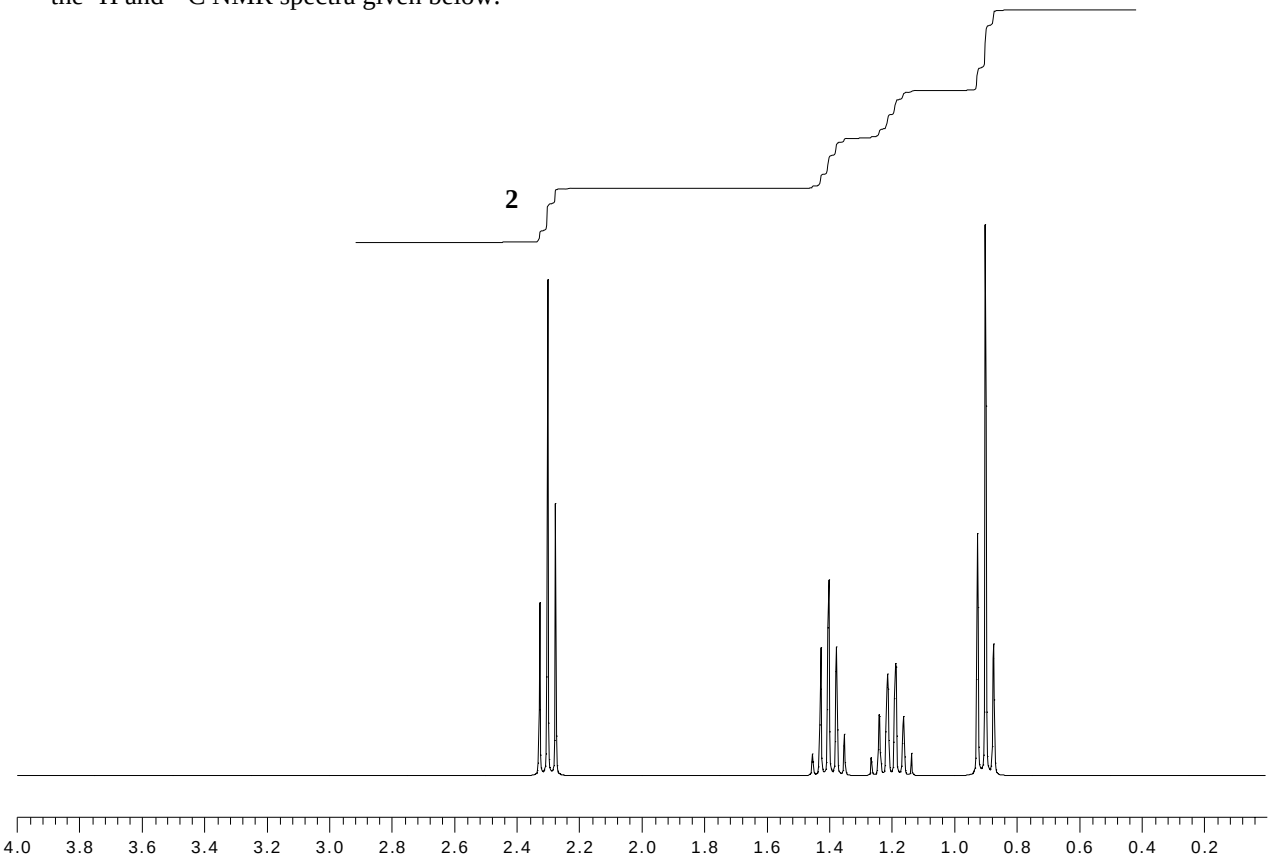
PART VI: MECHANISMS

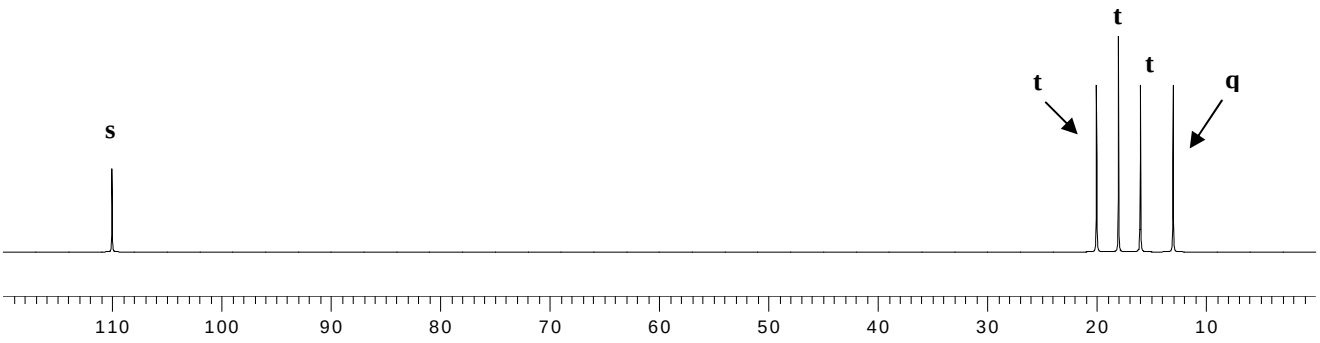
23. (4 pts) Propose a detailed mechanism for the following conversion:



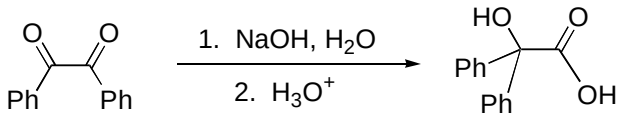
PART VII: SPECTROSCOPY

24. (4 pts) Certain compound has a molecular weight of 83 and contains nitrogen. Elucidate the structure of this compound, based on the ^{1}H and ^{13}C NMR spectra given below.





25. (2 pts) **BONUS PROBLEM (In order to receive credit for this problem, it has to be solved entirely!!)**. The following reaction, called the benzylic acid rearrangement, takes place by typical carbonyl-group reactions. Propose a mechanism.



benzil

benzylic acid