

**Student Name (first, last):**

**Student Number:**

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**CHEMISTRY 3371 (ORG CHEM FOR MAJORS)**  
**FINAL EXAMINATION**

Josef Michl  
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1. (40 points) Check the correct statements only (make no other marks):

- Lithium diethylcuprate reacts with acetyl chloride to yield diethyl ketone.
- Methyl acetate reacts with ammonia to yield acetamide.
- Basic hydrolysis of benzonitrile followed by acidification yields benzoic acid.
- The rhodium atom in  $(\text{Me}_3\text{P})_3(\text{CO})\text{RhH}$  is coordinatively saturated.
- Hofmann rule for the direction of elimination in a quaternary ammonium salt states that the least substituted alkene will be formed.
- Heating pyridine with phenyllithium yields 2-phenylpyridine after workup.
- Benzoic acid reacts with lithium aluminum hydride (LAH) to yield benzyl alcohol after workup.
- Cellulose is a polysaccharide.
- Hunsdieker reaction converts silver butanoate into *n*-propyl bromide.
- The Kiliani-Fischer synthesis converts an aldopentose into a mixture of two aldohexoses.
- Low-molecular weight alkyl azides tend to be explosive and dangerous.
- Imidazole is 1,4-diazine.
- Heating of 2-naphthol with aqueous ammonium sulfite yields 2-naphthylamine.
- Claisen rearrangement of allyl phenyl ether produces *p*-allylphenol.
- Radical polymerization of ethylene yields branched polyethylene.
- The reaction of propanoic acid with bromine and a catalytic amount of red phosphorus yields 2-bromopropanoic acid.
- Thiols react with iodine to yield sulfones.
- Under anhydrous conditions, Curtius rearrangement of acyl azides leads to isocyanates.
- Thermal decomposition of diazotized anthranilic acid (*o*-aminobenzoic acid) produces benzyne.
- Monobromination of ketones by reaction with  $\text{Br}_2$  is best done under basic conditions.
- Benzoic acid reacts with diazomethane to produce methyl benzoate.
- Trichloroacetic acid has a lower  $\text{pK}_a$  than acetic acid.
- An orbital is a region of space where an electron is likely to be found.
- The least bonding of the six pi molecular orbitals of benzene has a node across two CC bonds.
- Conrotatory ring opening of cyclobutene has an antiaromatic transition state and is forbidden.
- Pyrrole is less basic than pyridine.
- The allene,  $\text{C}_2\text{H}_5\text{CH}_2\text{C}=\text{C}=\text{CCH}_2\text{C}_2\text{H}_5$ , is chiral.
- Cyclobutadiene is aromatic and extremely unreactive.
- Friedel-Crafts acylation of benzene with acetyl chloride and a catalytic amount of  $\text{AlCl}_3$  will

proceed to completion.

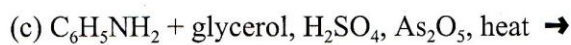
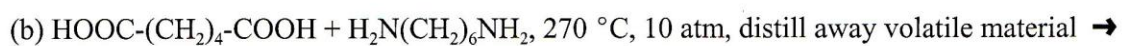
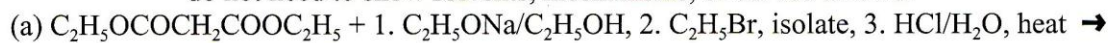
- ( ) Silicones are polymers containing a repeated -SiR'R''-O- unit in the backbone.
- ( ) 2,4,6-Trimethylpyrylium cation reacts with nitromethane and base to yield 2,4,6-trimethylnitrobenzene.
- ( ) Quinhydrone is a 1:1 charge transfer complex of hydroquinone and *p*-benzoquinone.
- ( ) Upon treatment with phenylhydrazine, glucose and ribose yield the same osazone.
- ( ) The primary structure of a protein is its linear amino acid sequence.
- ( ) Sucrose is a disaccharide containing glucose and fructose.
- ( ) Phenolphthalein can be prepared by a condensation of phenol with phthalic anhydride.
- ( ) 9-Anthranol predominates in equilibrium over its tautomer, anthrone.
- ( ) *p*-Cyanoaniline is a weaker base than *p*-methoxyaniline.
- ( ) Nitration of pyridine-N-oxide occurs in position 4.
- ( ) The common form of naturally occurring alanine is a D amino acid..

2. (20 pts) Write a plausible mechanism for the Fischer indole synthesis, using cyclopentanone phenylhydrazone as the starting material, acetic acid as the solvent, and  $\text{BF}_3$  as the catalyst. Include all steps and intermediates and use curved arrows to indicate electron movement in each step.

3. (20 pts) A mixture of two D-aldohexoses, A and B, results from a Kiliani-Fischer synthesis that starts with a D-aldopentose C. Nitric acid oxidizes C to an optically active aldaric acid D. Interchange of the CHO and CH<sub>2</sub>OH groups in B by a complicated reaction sequence ultimately converts B into itself. Write the structure of A and circle it.

4. (20 pts) Write plausible mechanisms for the base-catalyzed and the acid-catalyzed enolization of acetone (include all steps and intermediates and use curved arrows to indicate electron movement in each step).

5. (40 pts) Write the structures of all principal organic products of the following reactions. You do not need to show solvents, mechanisms, or curved arrows.



(e) cyclopentadiene and maleic anhydride →

(f) 1-dimethylaminonaphthalene + 1.  $\text{NaNO}_2$ ,  $\text{HCl}$ , isolate, 2.  $\text{H}_2$ /cat →

(g)  $m\text{-H}_2\text{N-C}_6\text{H}_4\text{-CF}_3$  + 1.  $\text{Br}_2$  (excess), isolate, 2.  $\text{NaNO}_2$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ ,  $0\text{ }^\circ\text{C}$ , 3.  $\text{H}_3\text{PO}_2$  →

(h)  $(\text{HO})(\text{CH}_3)_2\text{C-C}(\text{CH}_3)_2(\text{OH})$  (pinacol) +  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  →

6. (20 pts) Propose an efficient preparation of 2,6-diethyl-4-*tert*-butylpyridine from acyclic materials using the Hantzsch synthesis. Show all steps and all reagents (no mechanisms, no curved arrows, no solvents).

7. (20 pts) Show the mechanism of Robinson annulation: 2-methylcyclohexanone + methyl vinyl ketone + KOH in ethanol. Include all steps and intermediates and use curved arrows to indicate electron movement in each step.

8. (20 pts) Write a plausible mechanism for the monobromination of nitrobenzene with  $\text{Br}_2$  and a suitable catalyst. Show the catalyst explicitly. Show all steps and intermediates and use curved arrows to indicate electron movement in each step. Draw a reaction profile and mark intermediates and transition states (relate them to the structures occurring in the mechanism).