Chemistry 52
Final Exam

Name: _____ 10 March 2003

This exam has six questions, two cover pages, ten exam pages, and three scratch pages.

Please check before beginning to make sure no questions or pages are missing.

120 minutes have been allotted for completion of the exam.

All scratch work should be done on the backs of pages or on the attached blank pages.

Please put your name on **BOTH** cover pages (it makes the grade-recording process easier).

Make sure that your final answers are clearly indicated and that you clearly cross out any mistakes!!

Name: _____

1. _____ (30)

2. _____ (45)

3. _____ (15)

4. _____ (20)

5. _____ (30)

6. _____ (20)

TOTAL:

_____ (160)

TIPS:

- Please look over the entire exam first!
- ***Count and recount the number of carbons*** and double check your structures!
- If you get stuck on a problem, draw out the structures and start moving electrons and/or drawing resonance structures.
- No comments pertaining to the stir-fry will remain off the record.
- If you really get stuck on a problem, move on and come back to it later.

S.E. Van Bramer 9/11/97

Periodic Table of the Elements

1 H																1 H	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		118

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

1. Multiple choice questions. Circle the *best* answer for each question. (3 pts. each, 30 pts. total)

A. In which selection are the amines arranged from most basic to least basic?

a) ammonia, ethylamine, *p*-methoxyaniline, aniline, pyrrole

b) ammonia, aniline, ethylamine, *p*-methoxyaniline, pyrrole

c) pyrrole, aniline, *p*-methoxyaniline, ammonia, ethylamine

d) ethylamine, ammonia, *p*-methoxyaniline, aniline, pyrrole

e) ethylamine, ammonia, aniline, *p*-methoxyaniline, pyrrole

B. In which selection are the organic compounds arranged from most acidic to least acidic (consider only the most acidic proton on each compound)?

a) 2,4-pentanedione, ethyl acetate, acetic acid, toluene, diethylamine

b) 2,4-pentanedione, acetic acid, ethyl acetate, diethylamine, toluene

c) acetic acid, ethyl acetate, 2,4-pentanedione, diethylamine, toluene

d) acetic acid, 2,4-pentanedione, ethyl acetate, toluene, diethylamine

e) acetic acid, 2,4-pentanedione, ethyl acetate, diethylamine, toluene

C. Which of the following functional groups will not react with a Grignard reagent?

a) aryl halide

b) ketone

c) acid chloride

d) alcohol

e) amine (primary or secondary)

D. Which of the following synthetic methods would provide the *best* synthetic route to *N*-*tert*-butyl-*N*-isopropylamine?

a) Reaction of ammonia with isopropyl bromide and *tert*-butyl bromide

b) Nucleophilic attack of isopropylamine on *tert*-butyl bromide

c) Nucleophilic attack of *tert*-butylamine on isopropyl bromide

d) Reductive amination of acetone with *tert*-butylamine

e) Lithium aluminum hydride reduction of *N*-*tert*-butyl propanamide

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E. Which two components would effectively form a single Claisen condensation product?

a) ethyl acetate and ethyl propionate
b) ethyl formate and ethyl benzoate
c) ethyl acetate and ethyl benzoate
d) acetaldehyde and propionaldehyde
e) phenyl benzoate and phenyl formate

F. Which of the following selections does NOT describe an issue with electrophilic aromatic substitution on aminobenzenes?

a) Polyalkylation is impossible to avoid in Friedel-Crafts alkylation of aminobenzenes
b) Complexation of Lewis acid catalysts with the amine group can occur
c) Polyhalogenation is difficult to avoid in electrophilic halogenation
d) Attempts at nitration lead to protonation of the amine group and ring deactivation
e) Acylation of the amine group is required to mitigate the reactivity of the aromatic ring to allow introduction of a single bromine atom.

G. Which of the following sequences of reactions would convert toluene to 2-bromo-4-cyanotoluene? ('*reduction*' refers to Pt/H_2 reduction; '*reaction w/ cyanide anion*' refers to treatment with KCN/CuCN, '*diazotization*' refers to treatment with nitrous acid and sulfuric acid)

a) bromination, nitration, diazotization, reduction, reaction w/ cyanide anion
b) bromination, nitration, reduction, diazotization, reaction w/ cyanide anion
c) nitration, reduction, bromination, diazotization, reaction w/ cyanide anion
d) nitration, bromination, reduction, diazotization, reaction w/ cyanide anion
e) bromination, reaction w/ cyanide anion, nitration, reduction, diazotization

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H. Which of the following compounds will NOT react with a Gilman cuprate?

a) conjugated enone
b) ketone
c) alkyl halide
d) α,β-unsaturated ketone
e) acid chloride

I. Which of the following compounds will NOT be reduced by lithium aluminum hydride?

a) cyanobenzene (benzonitrile)
b) butanamide
c) butanoic acid
d) benzoyl chloride
e) 1-butene

J. Which of the following compounds CAN be reduced by sodium borohydride?

a) nitrobenzene
b) *N,N*-dimethylbutanamide
c) butanoic acid
d) acetophenone (methyl phenyl ketone)
e) ethyl benzoate

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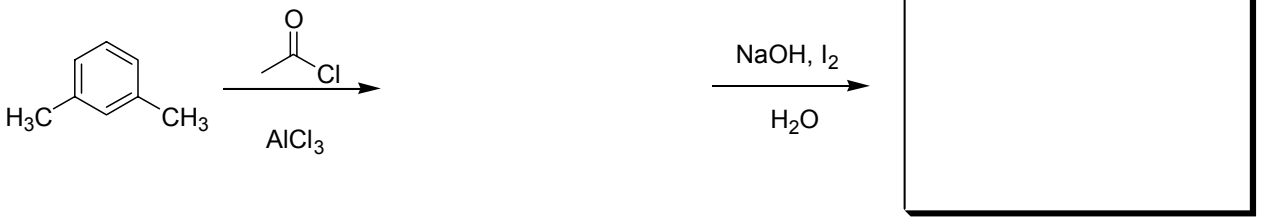
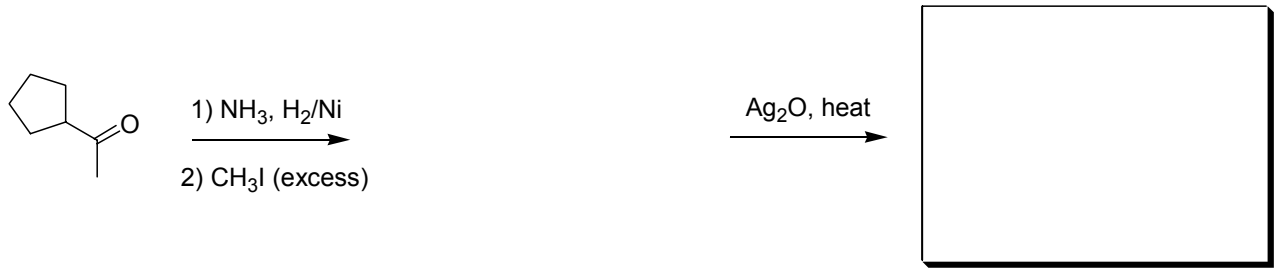
2. Predict the major organic product for each set of reactions (nine total) given below. For each reaction, show the intermediate product in the space provided and draw your final product in the box. Reaction by-products have not been shown. (5 pts. ea., 45 pts. total)

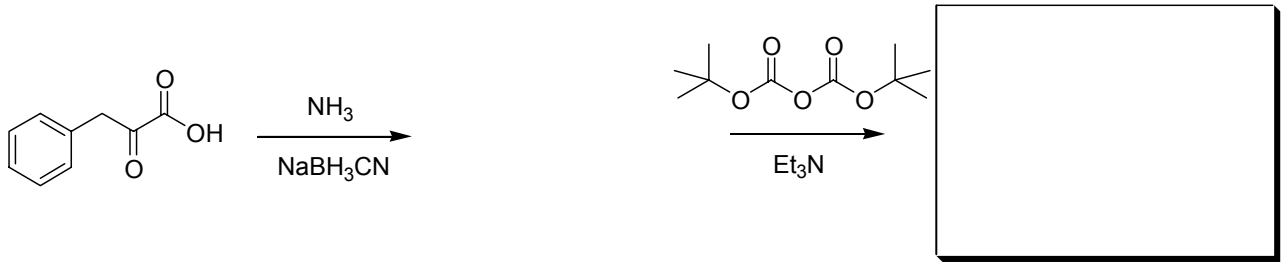
a)



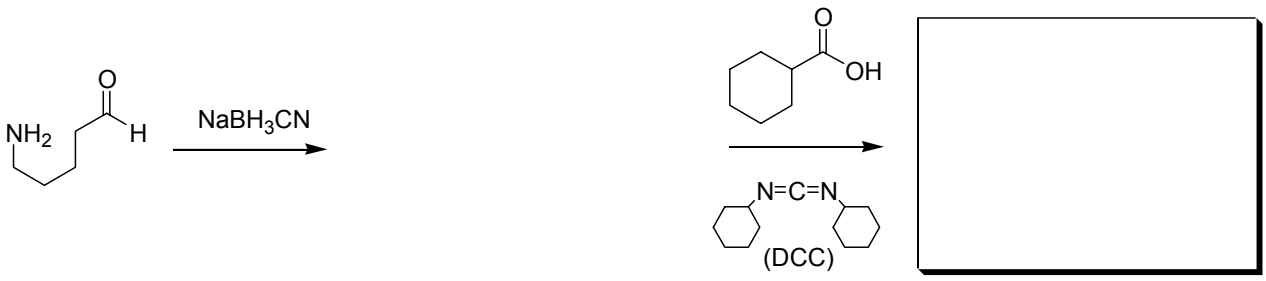
b)



c)



d)



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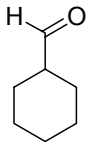
2. (continued)

e)



1) CrO_3, H_3O^+

2) $SOCl_2$

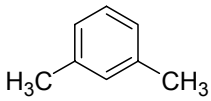
3) NH_3 (excess)

$NaOH$, Br_2

H_2O

Hint -- IR: *absorption from3300 – 3500 cm^{-1} (nothing from 1650 - 1850 cm^{-1})*

f)



HNO_3

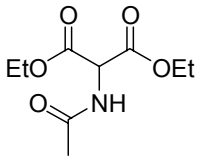
H_2SO_4

1) HNO_2, H_2SO_4

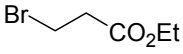
2) Cu_2O, $Cu(NO_3)_2$

H_2O

g)



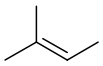
$NaOEt/EtOH$



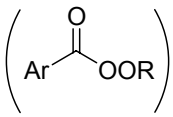
H_3O^+

heat

h)



MCPBA

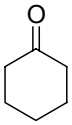


1) $PhMgBr$, ether

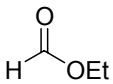
2) H_3O^+

3) $POCl_3$, pyridine

i)



1)



$NaOEt/EtOH$

2) H_3O^+

1) $LiAlH_4$

2) H_3O^+

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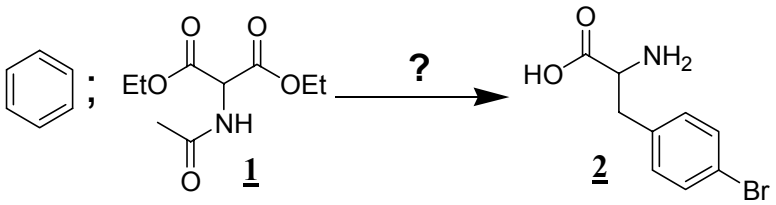
3. Propose an efficient route for the synthesis of *p*-bromophenylalanine (**2**) from benzene and diethyl acetamidomalonate (**1**). Use any other reagents you need.
(15 pts.)



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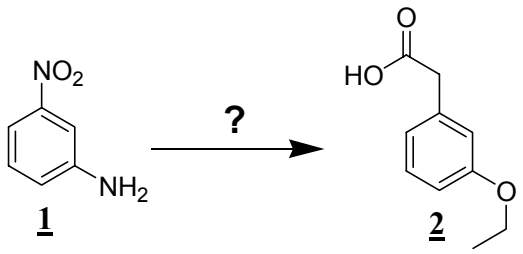
4. Propose an efficient route for the synthesis of (3-ethoxyphenyl)acetic acid (**2**) from 3-nitroaniline (**1**). Use any other reagents you need. The easiest route involves diazonium salts and doesn't require any electrophilic aromatic substitution steps.
(20 pts.)



1 **2**

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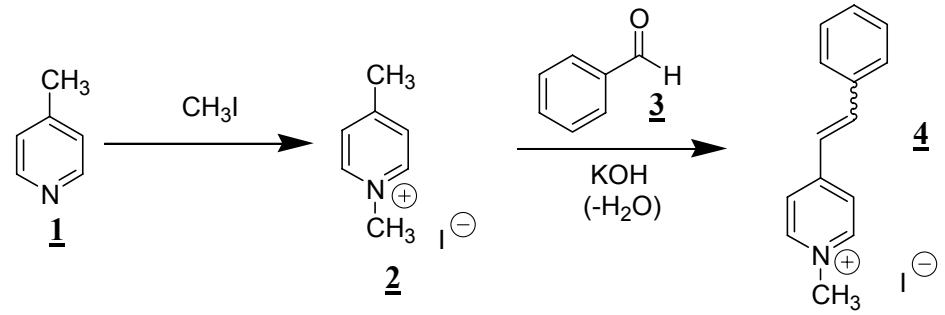
5. Consider the reaction scheme drawn below. The wavy bond in 1-methyl-4-(2-phenylethenyl)pyridinium iodide (**4**) indicates a mixture of *cis*- and *trans*-stereochemistry (30 pts.)



(A) The first step of this scheme involves the alkylation of 4-methylpyridine with methyl iodide to give the *N*-methylpyridinium salt (*N*-methylpicolinium iodide, **2**).

Draw a mechanism for this reaction.

(B) The following questions concern the second step of the reaction sequence.

(i) Potassium hydroxide is sufficiently basic to deprotonate the methyl group bound directly to the aromatic ring of the pyridinium salt **2**. Benzylic protons typically have a pK_A of approximately 42.

Explain with resonance structures why these protons are acidic enough to be removed by hydroxide anion.

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5.B. (continued)

(ii) The deprotonated pyridinium salt then reacts with benzaldehyde (**3**) to give an alcohol in a reaction reminiscent of an aldol addition .

Draw a detailed mechanism for the formation of the initial addition product.

(iii) Base-catalyzed dehydration of the addition product formed in part (ii) gives the final product **4**.

Show a detailed mechanism for this dehydration step.

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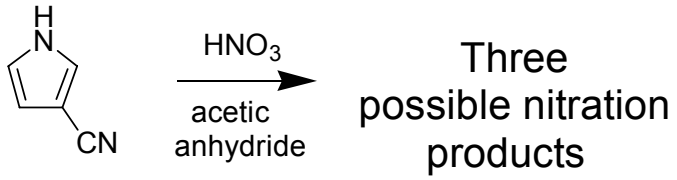
6. Consider the electrophilic nitration of 3-cyanopyrrole:



(Think of what you have learned about electrophilic aromatic substitution reactions of substituted benzene rings.)
(20 pts.)

A) Draw resonance structures for the cationic intermediate formed upon nitration at carbon 2 of the pyrrole ring. Indicate any particularly favorable or unfavorable resonance structures.

B) Draw resonance structures for the cationic intermediate formed upon nitration at carbon 4 of the pyrrole ring. Indicate any particularly favorable or unfavorable resonance structures.

C) Draw resonance structures for the cationic intermediate formed upon nitration at carbon 5 of the pyrrole ring. Indicate any particularly favorable or unfavorable resonance structures.

(D) Based upon electronic arguments, draw the nitrated cyanopyrrole you would expect as the major product.

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