

Last Name

First Name

Email: _____

The exam must be written in ink. You have 2 hours to complete the exam.

CHEM 610B

Exam 3

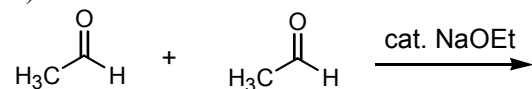
Spring 2000

Instructor: Dr. Pagenkopf

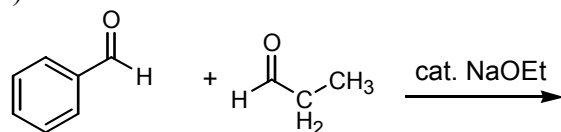
Page	Possible Points	Score
1	35	
2	20	
3	35	
4	20	
5	40	
6	22	
7	30	
8	25	
9	25	
10	15	
Total	267	

Question 1 (35 points). Aldol Reactions. Show the products of the following aldol condensations. For each question where more than one product is possible, show all possible aldol condensation products even if expected to be minor products. In each question show the β -hydroxy aldehyde(s) or β -hydroxy ketone(s). Do **not** eliminate or dehydrate to the α,β -unsaturated product.

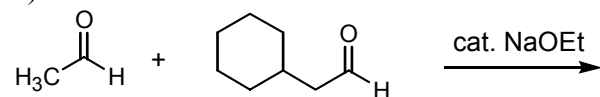
a)



b)

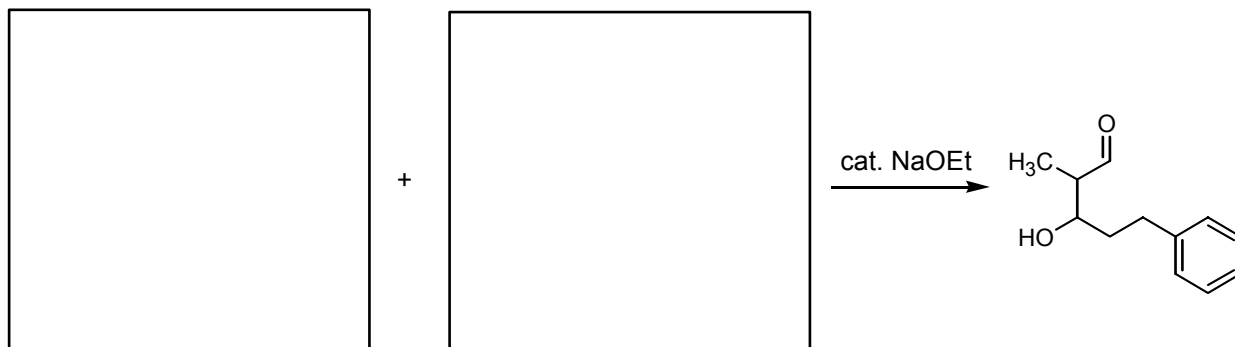


b)

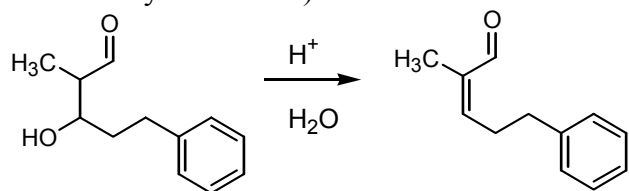


Question 2. (20 points). Aldol Reactions.

a) The following molecule was one of several different structures isolated from an aldol condensation reaction. What were the starting materials?

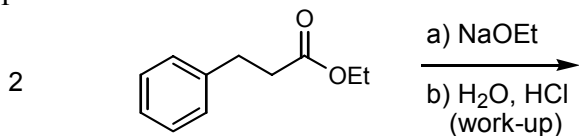


b) The initial products of aldol condensation products readily undergo dehydration. Provide a mechanism for the following dehydration under acidic conditions. (The *E* isomer is also formed but don't worry about that.)

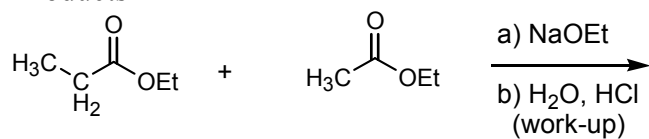


Question 3 (25 points). Claisen Condensations. Draw the major product(s) expected from each of the following reactions. For each question where more than one product is possible, show all possible products. Any product(s) containing a carbon atom should be shown.

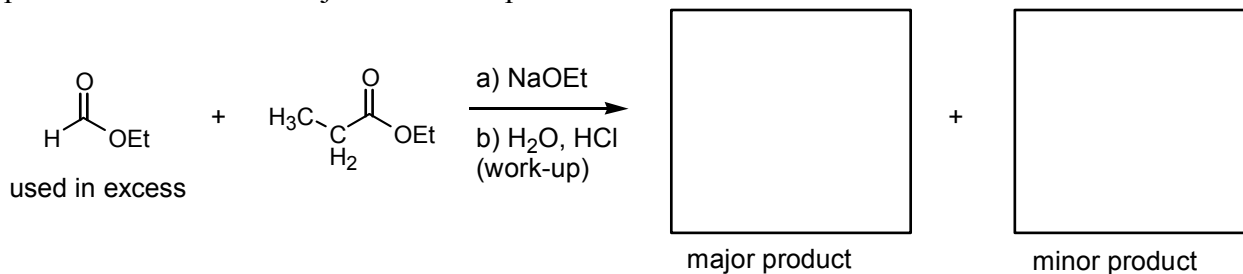
a) One product



b) Four Products

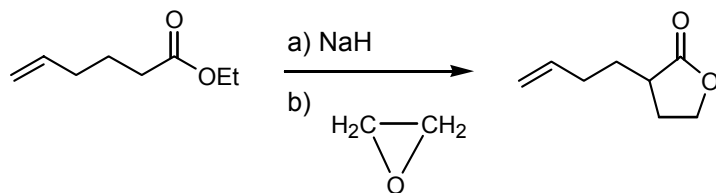


Question 4 (10 points) Claisen and Dieckmann Condensations. In this question only two products are possible. Indicate the major and minor product.



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Question 5 (20 points). Propose a detailed mechanism for the following conversion.



6 — Atomic number
C — Symbol
 12.011 — Atomic mass

PERIODIC TABLE OF THE ELEMENTS

Atomic masses are based on ^{12}C . Atomic masses in parentheses are for the most stable isotope.

Groups

Periods

1A												VIIIA																								
1	2											9	10																							
H	He																																			
1.00794	4.00260																																			
3		4												5		6		7		8		9		10												
Li	Be			11A		12		13		14		15		16		17		18																		
6.941	9.01218																																			
11		12		IIIB		IVB		VB		VIB		VIIB		VIII		IB		IIB		13		14		15		16		17		18						
Na	Mg																			Al		Si		P		S		Cl		Ar						
22.98977	24.305																			26.98154		28.08558		30.97376		32.06		35.453		39.948						
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
39.0963	40.08	44.9559	47.88	50.9415	51.996	54.9380	55.847	58.9332	58.70	63.546	65.38	69.72	72.59	74.9216	78.96	79.904	83.80	85.4678	87.62	88.9059	91.22	92.9064	95.94	(98)	101.07	102.9055	106.4	107.868	112.41	114.82	118.69	121.75	127.60	126.9045	131.30	
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	104	105	106													
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	Fr	Ra	Ac	Unq	Unp	Unh													
132.9054	137.33	138.9055	178.49	180.9479	183.85	186.207	190.2	192.22	195.09	196.9665	200.59	204.37	207.2	208.9804	(209)	(210)	(222)	(223)	226.0254	227.0278	(261)	(262)	(263)													

*Lanthanide series

58	59	60	61	62	63	64	65	66	67	68	69	70	71
Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
140.12	140.9077	144.24	(145)	150.4	151.96	157.25	158.9254	162.50	164.9304	167.26	168.9342	173.04	174.967

†Actinide series

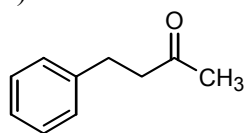
90	91	92	93	94	95	96	97	98	99	100	101	102	103
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
232.038	231.0359	238.029	237.0482	(244)	(243)	(247)	(247)	(251)	(252)	(257)	(258)	(259)	(260)

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Question 6 (40 points). Show how to synthesize the following compounds using either the malonic ester synthesis or the acetoacetic ester synthesis by providing the necessary reagents and conditions.

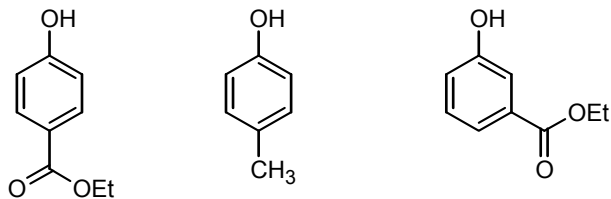
a)



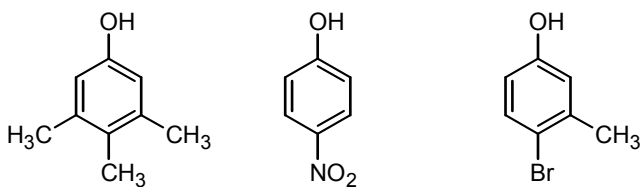
b) $(\text{CH}_3\text{CH}_2)_2\text{CHCO}_2\text{H}$

Question 7 (6 points). For each series, draw a box around the most acidic phenol.

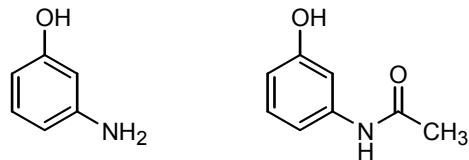
a)



b)

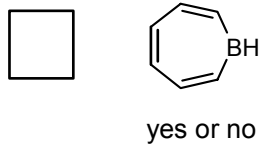


c)

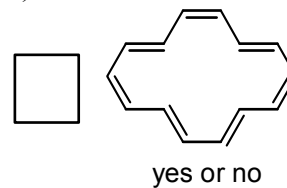


Question 8 (16 points). In the box next to each structure state the number of pi electrons, then answer the question, is the compound aromatic according to Hückel's criteria?

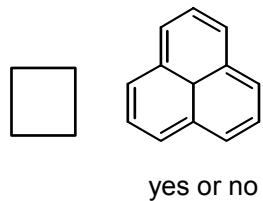
a)



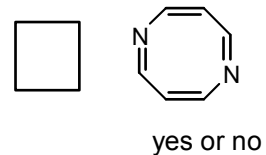
c)



b)

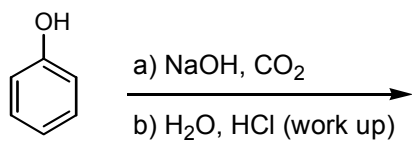


d)

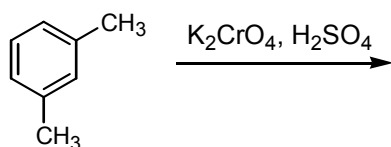


Question 9 (30 points). Reactions. Draw the major product(s) expected from each of the following reactions.

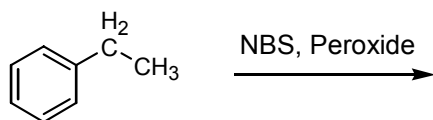
a) hint: Kolbe Reaction



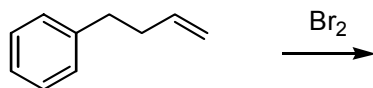
b)



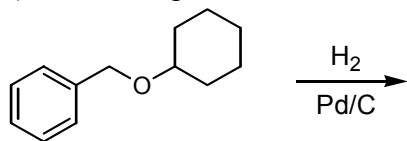
c) Reminder: NBS = *N*-bromosuccinimide.



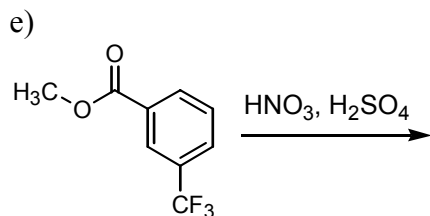
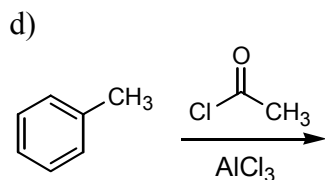
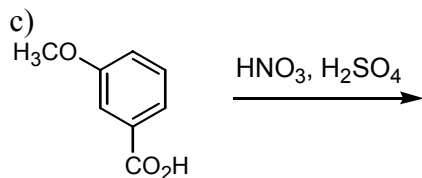
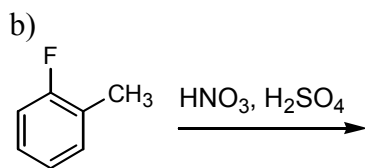
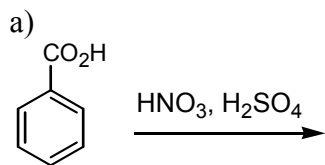
d)



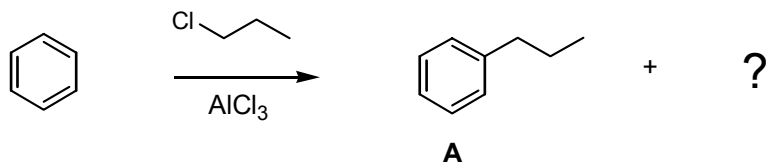
e) Show two products: one with 7 carbons and the other with 6.



Question 10 (25 points). Electrophilic aromatic substitution reactions. Draw the major product expected from each of the following reactions. For each nitration reaction, add only one nitro group to the aromatic ring.



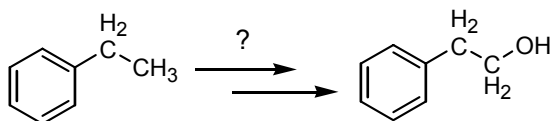
Question 11 (25 points). The following Friedel-Crafts alkylation reaction gives two products, both of formula C_9H_{12} . Show the second product, and provide a mechanism to explain how it is formed. (It is not necessary to show *all* of the resonance structures of the benzene ring delocalizing the positive charge but show at least one.)



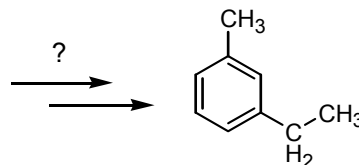
Propose an alternative way of making molecule A from benzene that avoids the other side product you drew above. Show necessary reagents and conditions.

Question 12 (15 points). Synthesis. Starting with molecule **B**, show how it might be converted into molecule **B** using any reagents you want. OR Starting with molecule **D**, show how it might be converted into molecule **E** using any reagents you want. Only do one synthesis.

Circle the reaction the TA is to Grade **B** \rightarrow **C** or **D** \rightarrow **E**.

**B****C**

or try

**D****E**