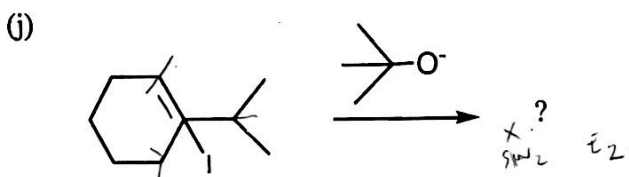
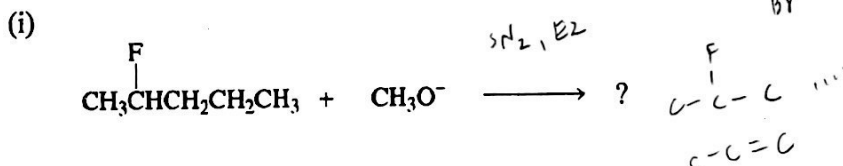
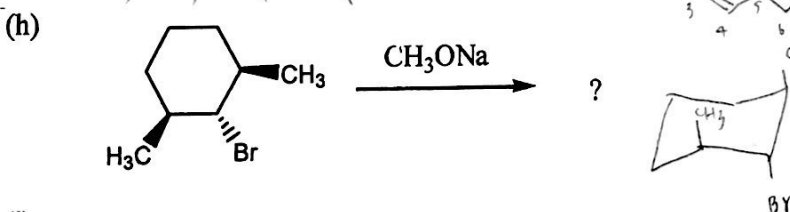
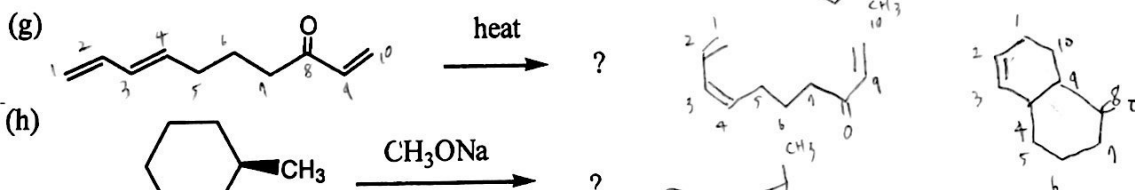
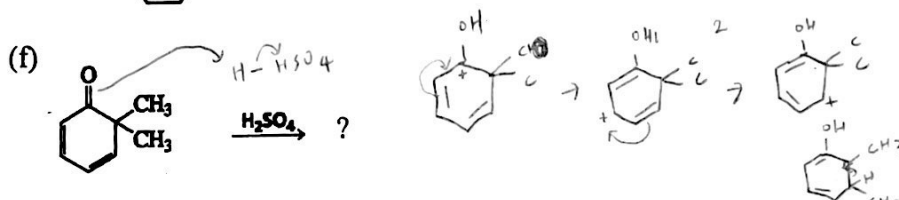
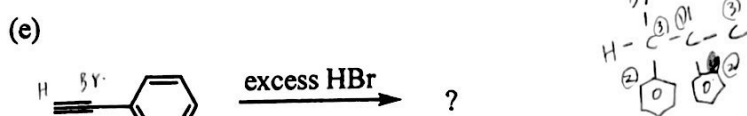
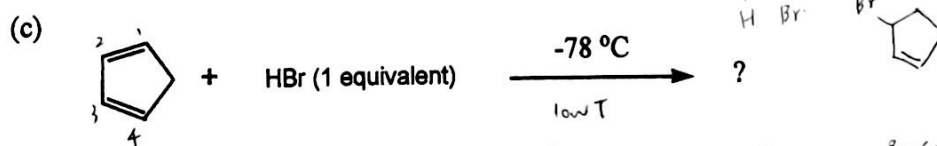
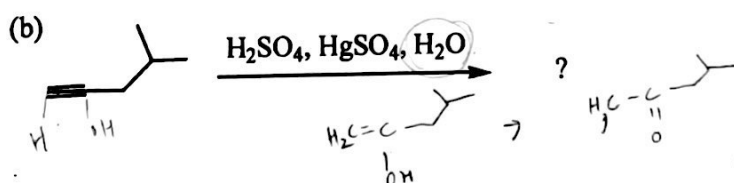
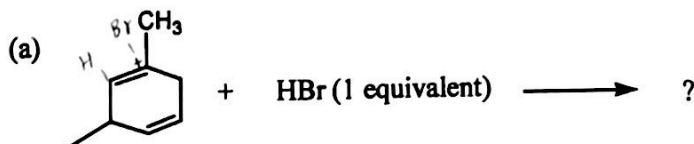


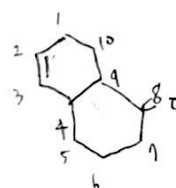
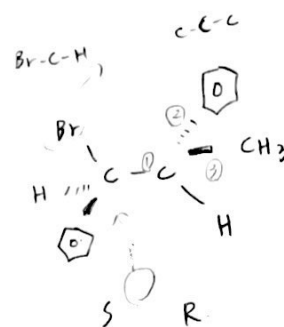
December 18, 2020

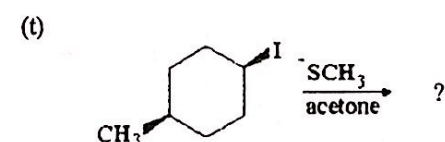
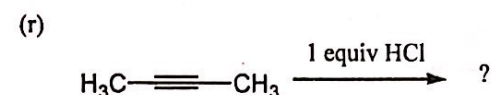
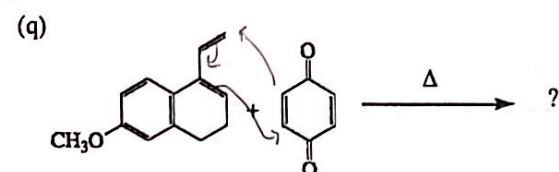
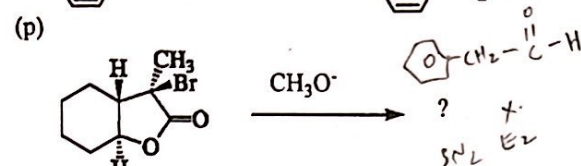
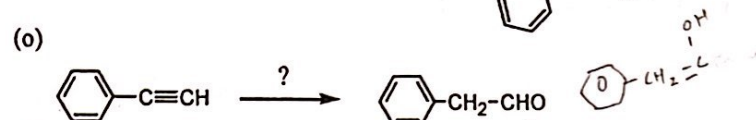
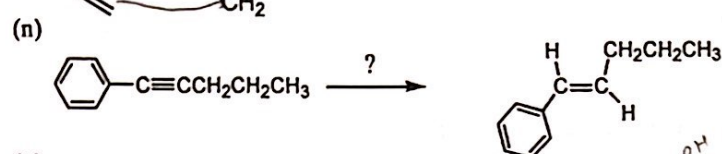
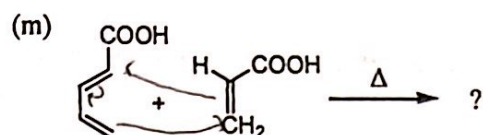
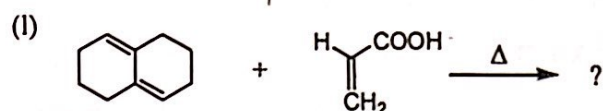
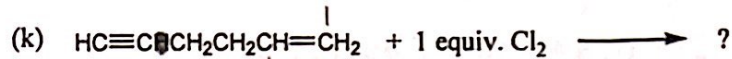
1. Predict the structure of major product, if any, or provide necessary reagent(s) for each of the following reactions. (40%)



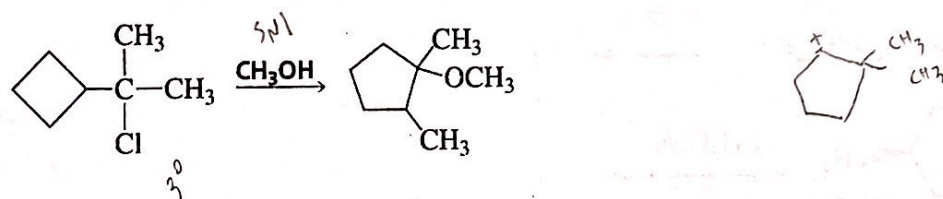
any reagent(s) for each of

	$\text{H}_2\text{C}=\text{CH}-$	$\text{H}_2\text{C}=\text{CH}-$	$\text{H}_2\text{C}=\text{CH}-$	$\text{H}_2\text{C}=\text{CH}-$
	$\text{S}_\text{N}1$	$\text{S}_\text{N}2$	E_1	E_2
1°	X	✓	X	✓
2°	X	✓	X	✓
3°		✓	X	✓
		↑		↑
		1° 2°		3° 2°

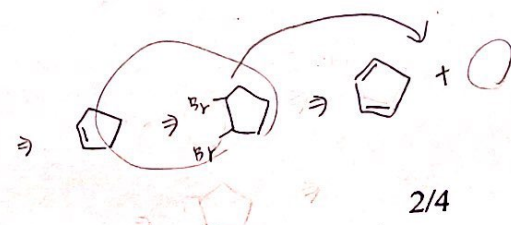
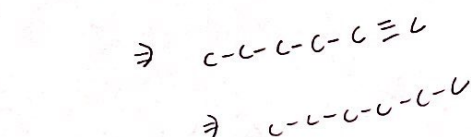
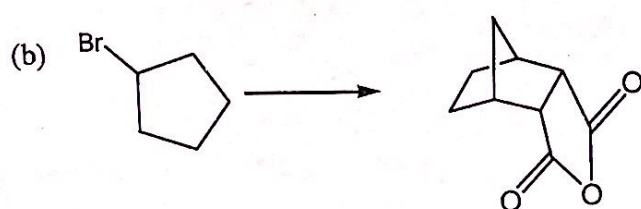
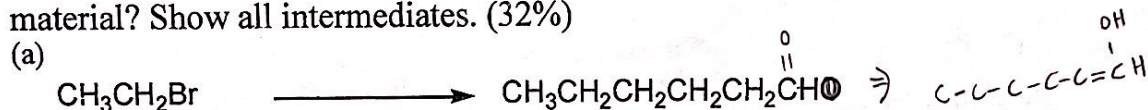


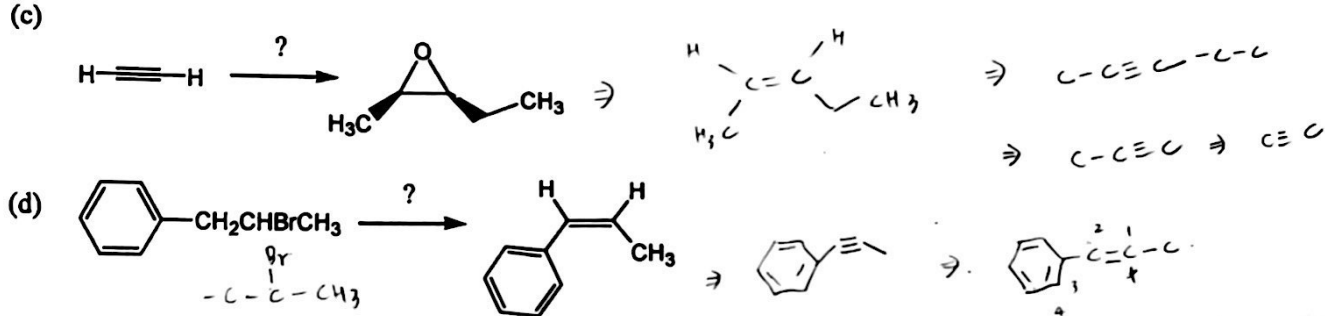


2. Draw the reaction mechanism for the following reaction: (5%)

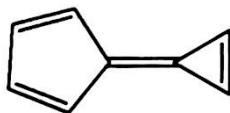


3. How could each of the following compounds be synthesized from the given starting material? Show all intermediates. (32%)

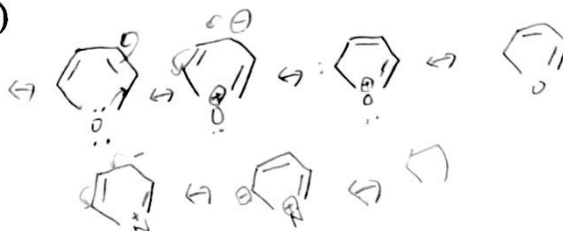
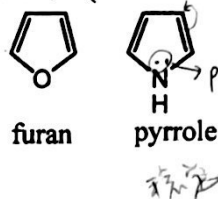




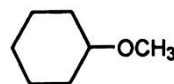
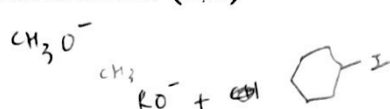
4. In what direction is the dipole moment in calicene? Explain. (5%)



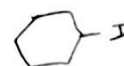
5. Why is the resonance energy of pyrrole (21 kcal/mol) greater than the resonance energy of furan (16 kcal/mol)? (5%)



6. What is the best way to synthesize the following ether using an alkyl halide and an alkoxide ion? (4%)

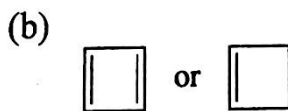
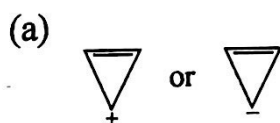


$\text{S}_\text{N}2$

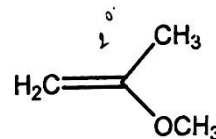
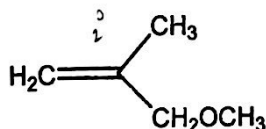
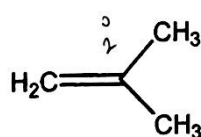


7. Would you expect acetate ion (CH_3CO_2^-) to be a better nucleophile in an $\text{S}_\text{N}2$ reaction with an alkyl halide carried out in methanol or in dimethyl sulfoxide (CH_3SOCH_3)? Why? (5%)

8. Which ion in each of the following pairs is more stable? Why? (6%)



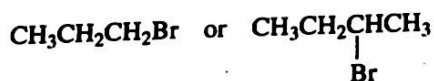
9. What is the relative reactivity of the following compounds toward the addition of HBr ? Give a brief explanation of your answer. (5%)



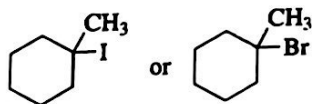
10. The pK_a of cyclopentane is >60 , which is about what is expected for a hydrogen that is bonded to an sp^3 carbon. Explain why cyclopentadiene is a much more stronger acid (pK_a of 15) even though it too involves the loss of a proton from an sp^3 carbon. (3%)



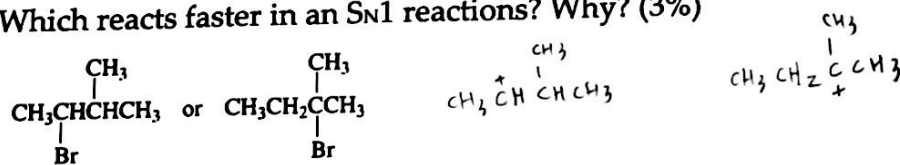
11. a) Which reacts faster in an $\text{S}_\text{N}2$ reactions? Why? (3%)



b) Which reacts faster in an E1 reactions? Why? (3%)



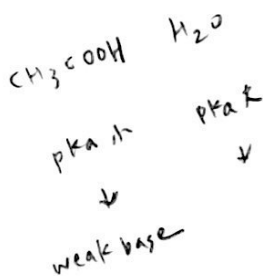
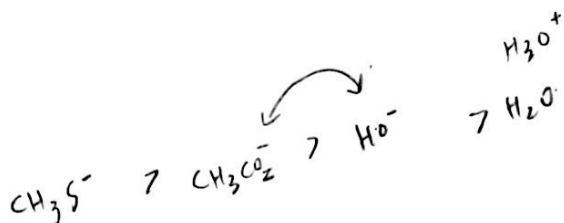
c) Which reacts faster in an S_N1 reactions? Why? (3%)



12. Rank the species below in order of increasing nucleophilicity in protic solvents. Explain your result. (5%)



S_N2



國立清華大學試卷

記		分	
1	28	2	3.5
3	23	4	5
5	5	6	0
7	5	8	4
9	5	10	0
11	9	12	4
13		14	
15		16	
17		18	
19		20	
總分		91.5	

系 化學 23

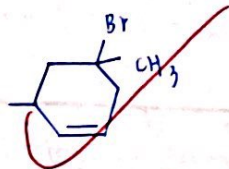
科目 有機

學號 108023025

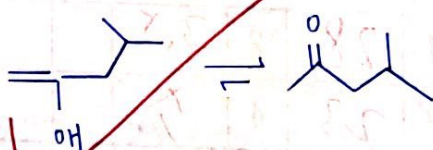
姓名 張小萱

日期 12/18

1. (a)



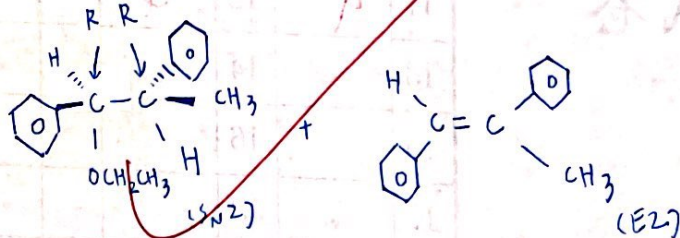
(b)



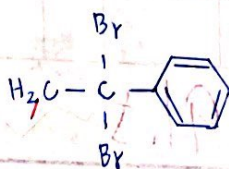
(c)



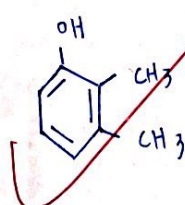
(d)



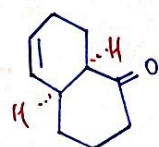
(e)



(f)



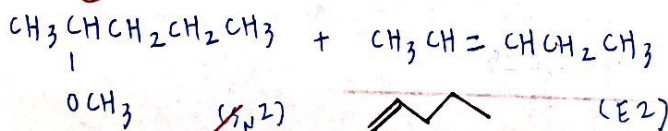
(g)



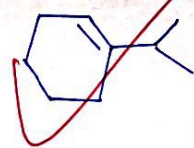
(h)

no reaction

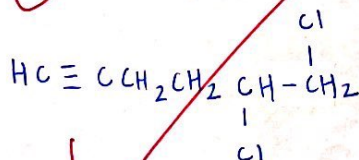
(i)



(j)

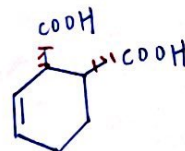


(k)

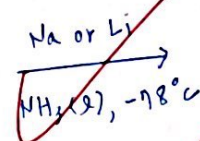


(l) no reaction

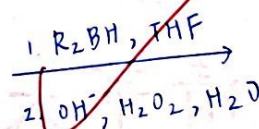
(m)



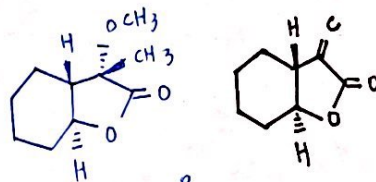
(n)



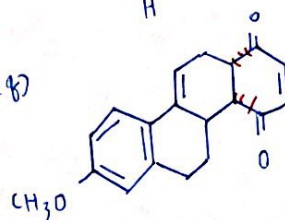
(o)



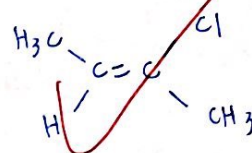
(p)



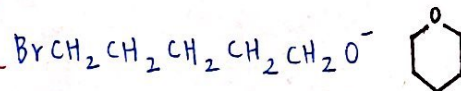
(q)



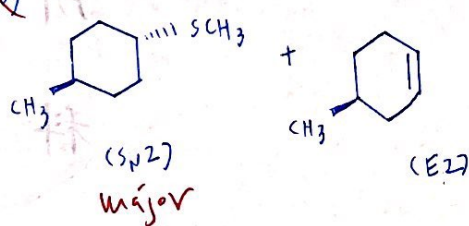
(r)



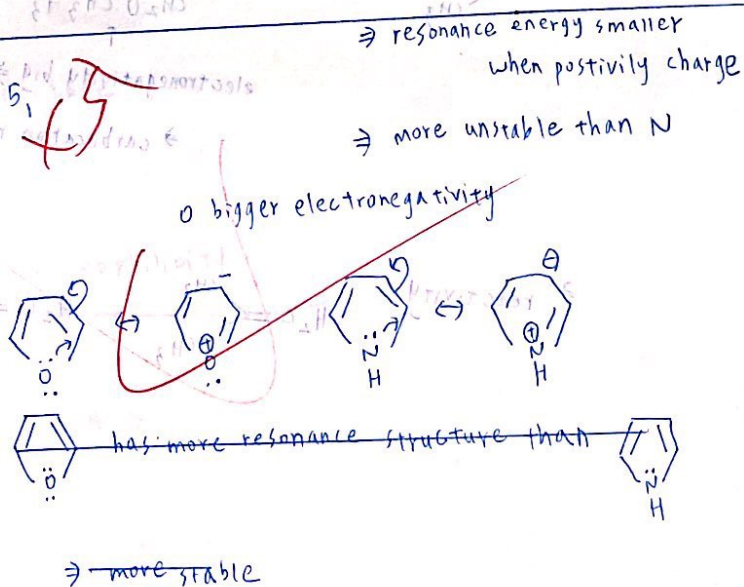
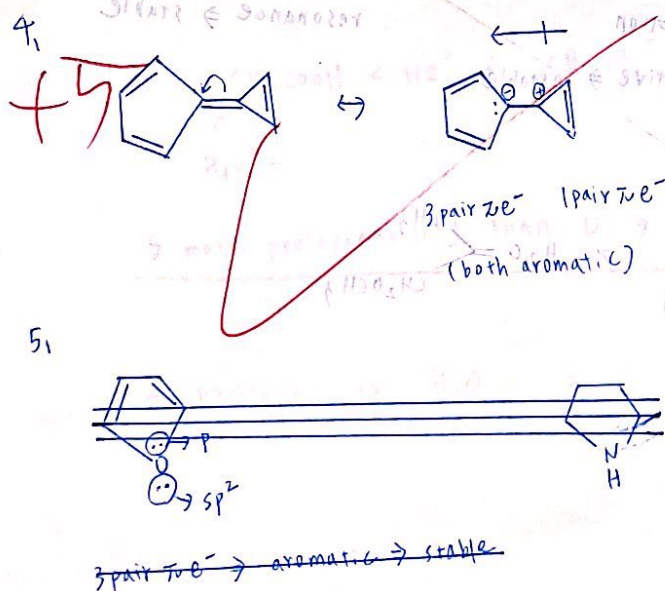
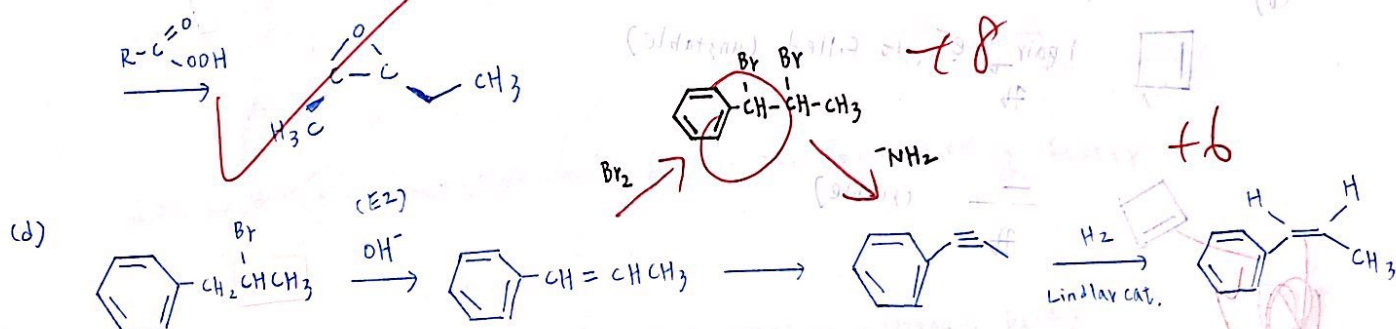
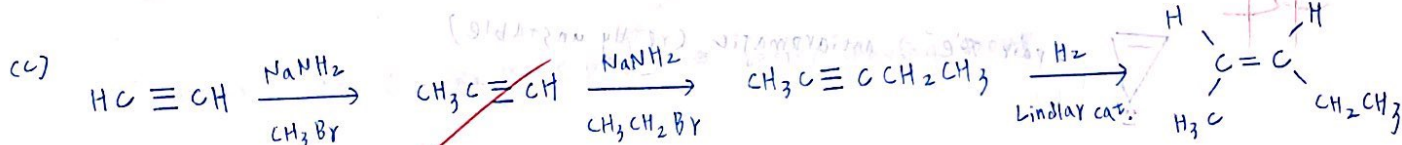
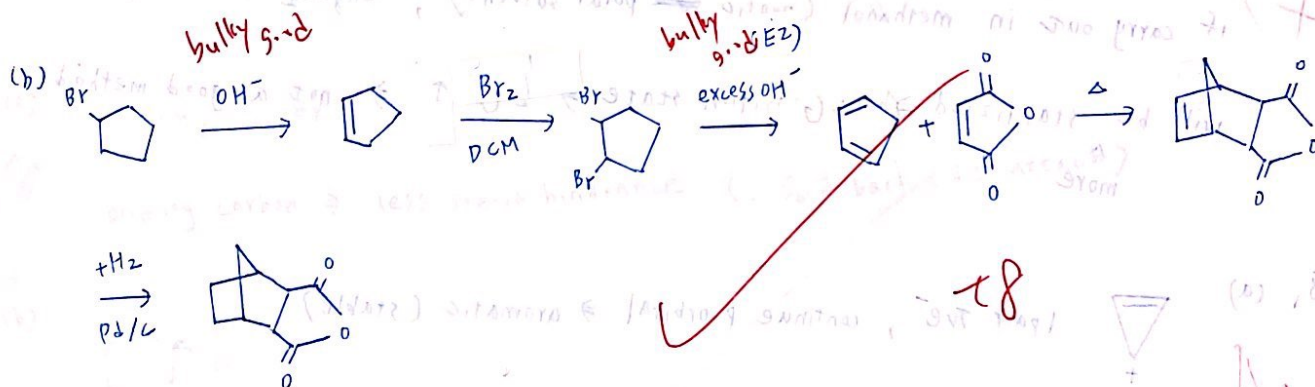
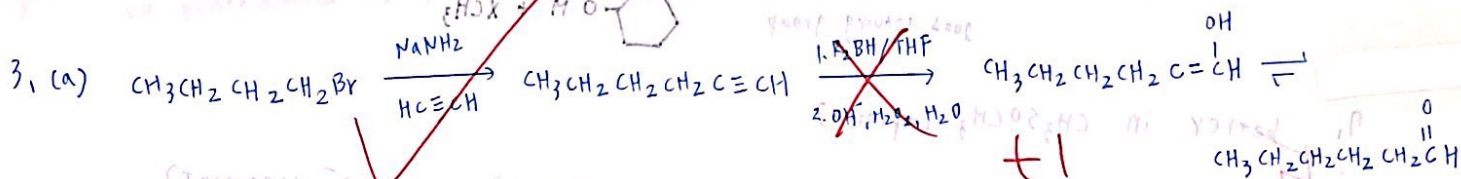
(s)

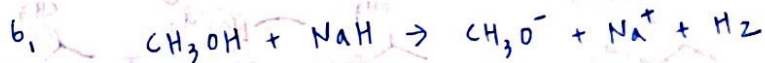


(t)

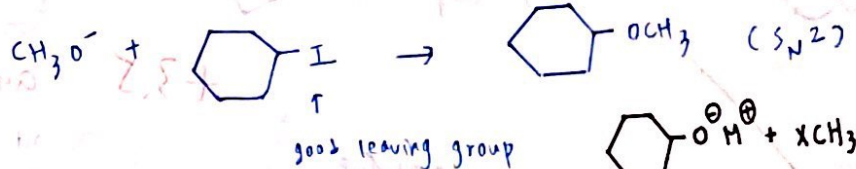


+24+4





+10



7, better in CH_3SOCH_3 (aprotic)

+5

if carry out in methanol (protic ~~and~~ polar solvent), CH_3CO_2^- (reactant)

will be stabilized than transition state $\Rightarrow \Delta G^\ddagger \uparrow \Rightarrow$ not a good method
 ^
 more

8, (a)



1 pair Ive^- , continue p orbital \Rightarrow aromatic (stable)

+4



2 pair $\text{Ive}^- \Rightarrow$ antiaromatic (really unstable)

(b)

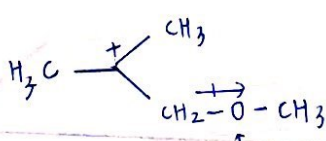
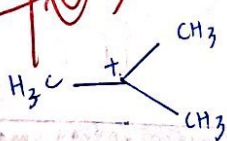


not filled (unstable)



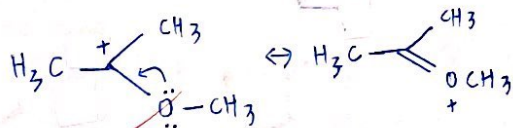
(stable)

9,



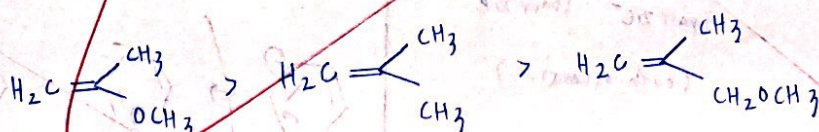
electronegativity big \Rightarrow pull electron

\Rightarrow carbocation more positive \Rightarrow unstable



resonance \Rightarrow stable

\Rightarrow reactivity



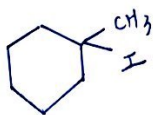
10, conjugate base has resonance structure \Rightarrow more stable (weak base)

+0 pentadiene's
so pentadiene is strong acid (pKa smaller)

11, (a) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

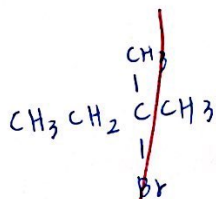
+9 primary carbon \Rightarrow less steric hindrance (\because $\text{S}_{\text{N}}2$ back side attack)

(b)



I^- weaker base (\because $\text{pK}_{\text{a}} \text{HI} < \text{HBr}$) \Rightarrow better leaving group

(c)



don't need 1,2-methyl shift to form tertiary carbocation \Rightarrow faster

12, increasing nucleophilicity \Rightarrow in protic solvent $\text{S}_{\text{N}}2$ more reactive (stronger base)

+4 H_2O no charge \Rightarrow weak base

$\text{pK}_{\text{a}}: \text{CH}_3\text{COOH} < \text{H}_2\text{O}^+ \Rightarrow \text{CH}_3\text{CO}_2^-$ weaker base

$\text{H}_2\text{O}^+ <$

S more polarizability than $\text{O} \Rightarrow$ bigger nucleophilicity

\Rightarrow nucleophilicity $\text{H}_2\text{O} < \text{CH}_3\text{CO}_2^- < \text{HO}^- < \text{CH}_3\text{S}^-$