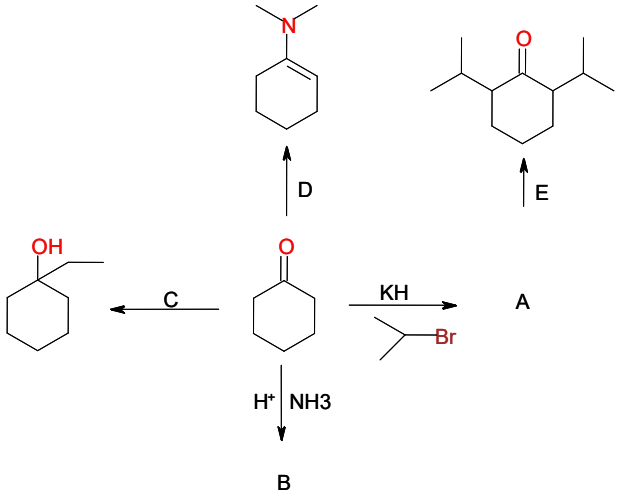
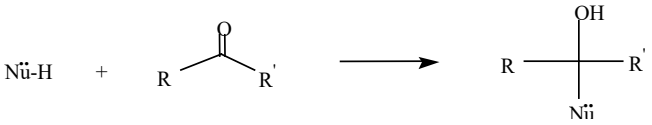
Chem 3325 Name : _____ Exam # 3 April , 2023

Answer **any seven** of questions 1-8 (15 points each) for a total of 105 points.

1. Complete the following reaction scheme by giving products, A and B, and reagents, C,D and E, for the following:

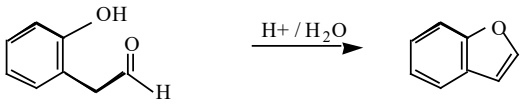


2. (i) For the following general nucleophilic addition reaction give the mechanism for both acid **and** base-catalysis of :

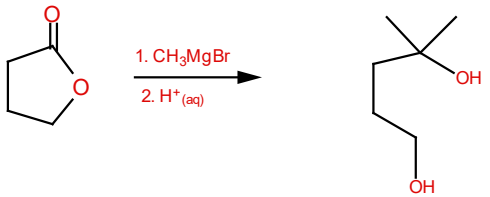


(ii) Give the mechanism for the reverse reactions for **either** acid **or** base-catalysis in (i) above:

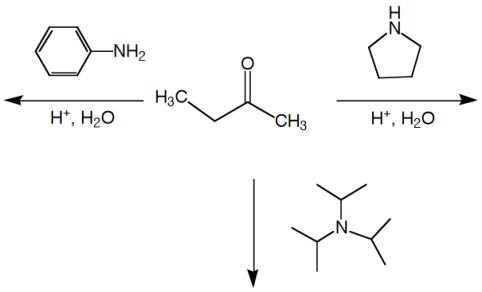
3. (i) Propose a mechanism for the following *acid-catalyzed* reaction that begins with nucleophilic addition:



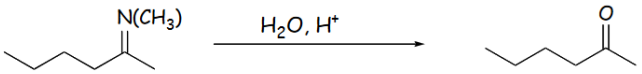
(ii) Propose a mechanism for the following *Grignard* reaction:



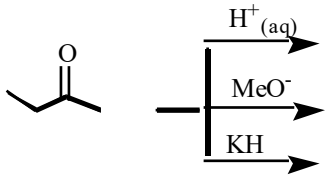
4 (i) For the three reactions below one will give an *amine*, another an *enamine* while a third will not give any product at all:



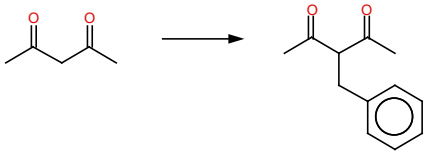
(ii) Give a mechanism for the reaction:



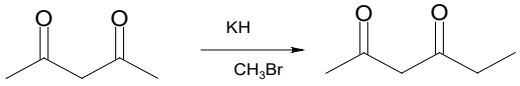
5. (i) Enols or enolates for 2-butanone below can be generated under three different sets of conditions. Give the product for each and identify, **giving your reasoning**, which method is preferred:



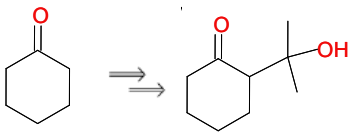
(ii) Provide reagents and a mechanism for the following reaction:



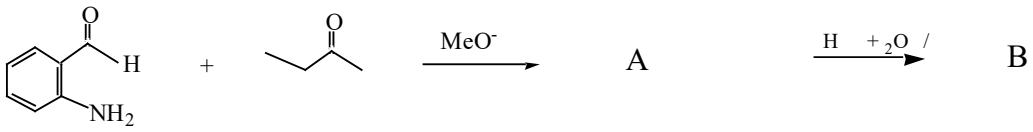
6. (i) Provide a mechanism for:



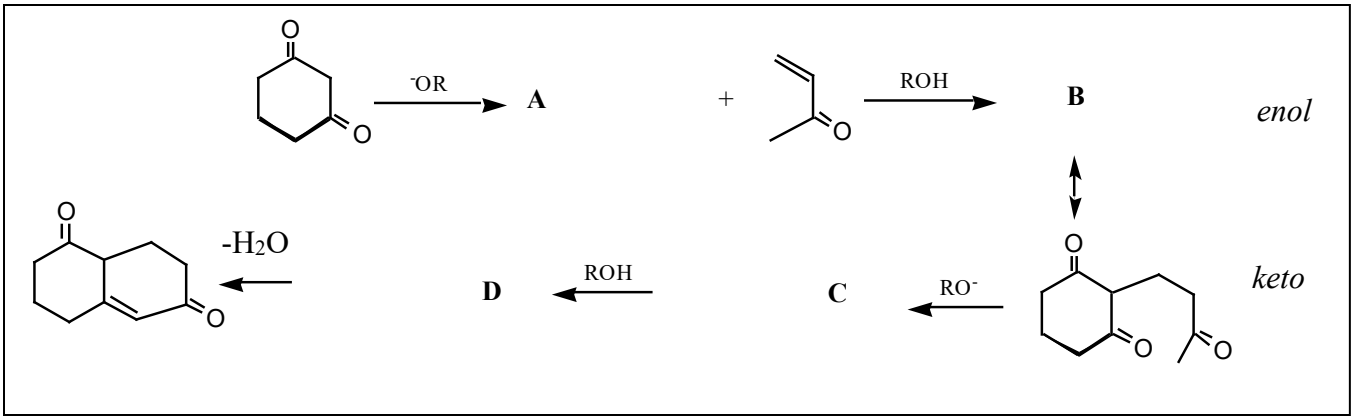
(ii) Propose a <u>multi-step</u> synthesis for the following conversion for :



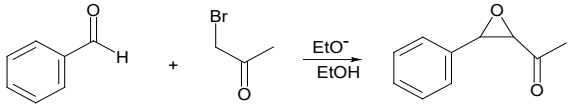
7. (i) Give the mechanism for the synthesis shown below which involves an *aldol* condensation to give **A** followed by *nucleophilic addition* to give the product **B** (IR spectra attached):



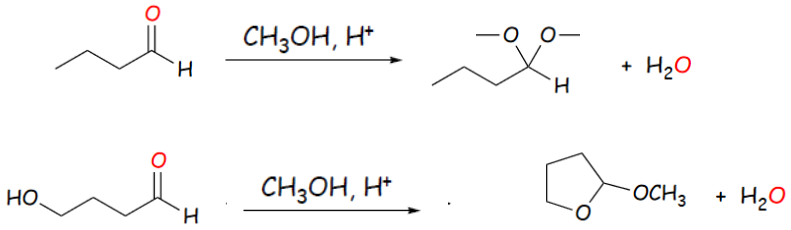
(ii) Draw the missing structures for molecules A-D for the following annulation reaction



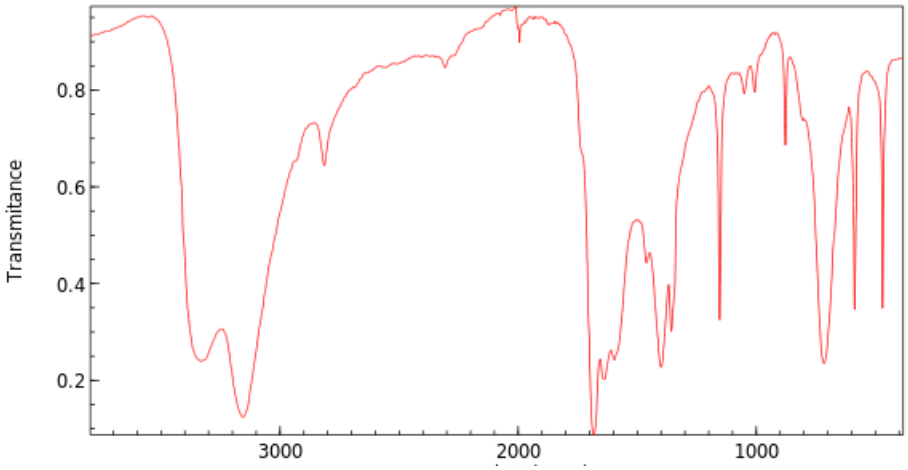
8. (i) Provide a mechanism for the following reaction which involves a reaction at the *alpha* carbon followed by *nucleophilic substitution*:



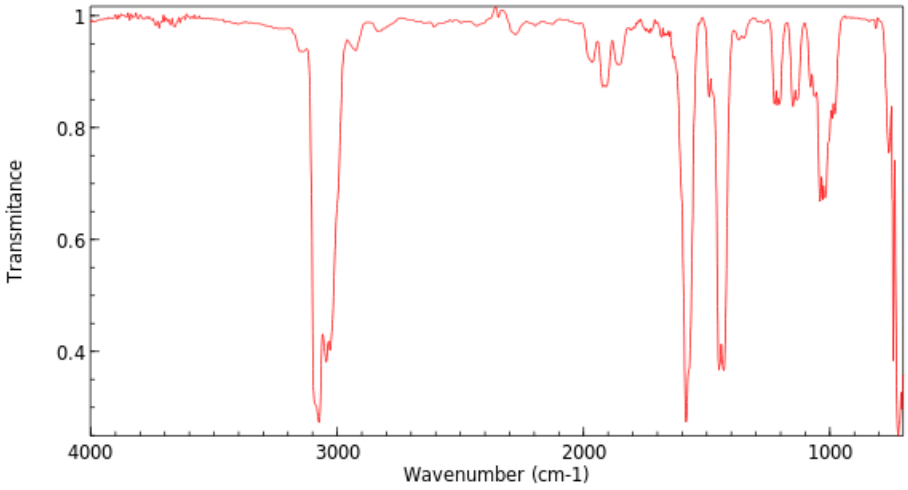
(ii) Explain in terms of mechanism how the two reactions below can give such different products



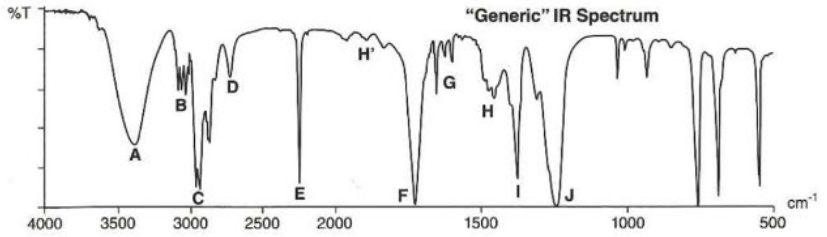
IR spectrum for molecule A in question 7



IR spectrum for molecule B in question 7



IR Interpretation Guide



O-H N-H stretch	A	R–O–H	3600–3200	Phenols 3500
		–N–H	3500–3290 1° 3400–3340 2°	1°→2 peaks 2°→1 peak med. to weak
		–C(=O)–O–H	3550–2500	Broad & often "monstrous"
C-H stretch	B	R–C≡C–H	3300	
		aromatic C–H	3300–3000	No peaks in this area means no aromatic!
		C–H	3300–3100	
		R₂C=C(R)–H	3300–3000	No peaks in this area means no alkene!
	C	–C–C–H	2960–2850	In "all" IR spectra
	D	R–C(=O)–H	2820 & 2720	2720 is key peak

C≡N C≡C	E	R–C≡C–R'	2260–2190	Weak to none if symmetrical
		R–C≡N	2250 aliph. 2230 arom.	
		R–C≡C–H	2140–2100	
C=O	F	cyclic C=O (ring)	1785 4-ring 1750 5-ring 1715 6-ring	Depends on size of ring
		R–C(=O)–O–R	1735 aliph. 1720 arom.	
		R–C(=O)–H	1730–1705	1730 aliphatic 1703 conjugated
		R–C(=O)–R	~1715 cm⁻¹	1685 conjugated
		R–C(=O)–O–H	~1710	1680 conjugated
		R–C(=O)–N(R)–R	1690 1° 1680 2° 1650 3°	Aromatic amides 1675 1°
		C=C–C(=O)–R	1685	Aromatic 1690

C=C	G	R₂C=CH₂	1675	
		R₂C=CHR	1658	Tri- & tetra-substituted ~1670
		R₂C=CR₂	~1653	
		RHC=CHR	~1645	
	H H'	aromatic ring	1600, 1580, 1500, 1450	Move and vary in intensity; H' = overtones 2000–1650
nitro	H I	–N(=O)=O	1550–1490 1355–1315	Aromatic nitro Both strong
C–C & C–H bend	I	gem-dimethyl	1490–1440	Scissor bend
		CH₂	1470–1430 & 1380–1370	Umbrella bend
		t-butyl	1390–1375 & 1370–1360	t-butyl ~1365
C–O	J	C–O ethers esters	1150–1060	1270–1200 aryl & vinyl ethers 1285 acids
		C–O alcohols	1150 3° 1100 2° 1050 1°	Tertiary Secondary Primary