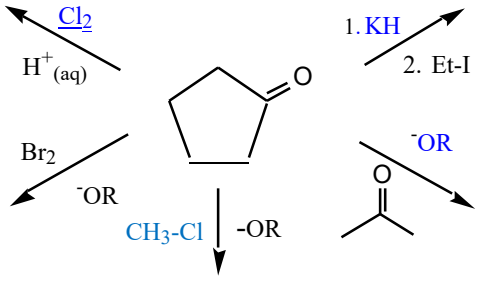
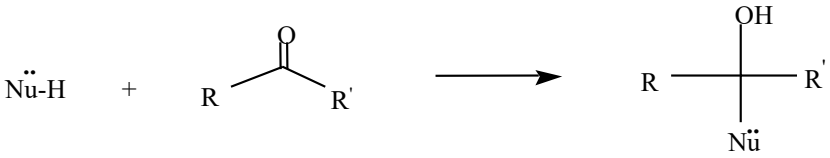
Chem 3325 Name :_____ Exam # 3 2021

Answer **all seven** questions 1-7 (15 points each) for a total of 105 points.

1. Provide products for the following reactions:

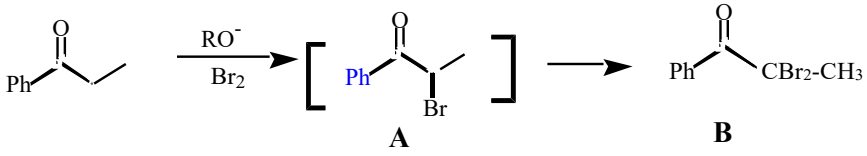


2. (i) For the following general nucleophilic addition reaction give the mechanism for both acid **and** base-catalysis of :

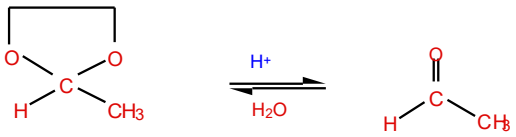


(ii) Give the mechanism for the reverse reactions (both acid **and** base-catalysis) in (i) above of :

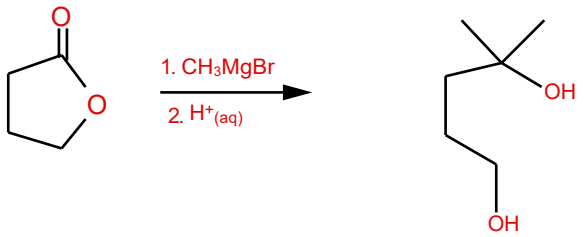
(iii) Explain the observation that for the following α-bromination of a ketone the intermediate **A** is not isolated and only the dibrominated product, **B**, is found :



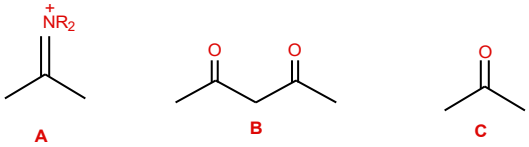
3. (i) Propose a mechanism for the *deprotection* reaction below :



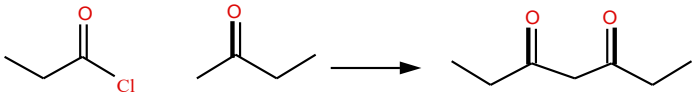
(ii) Propose a mechanism for the following reaction:



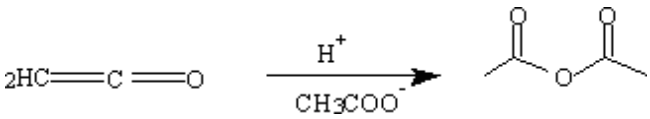
4 (i) Arrange, giving your reasoning, the following molecules in order of <u>increasing</u> acidity :



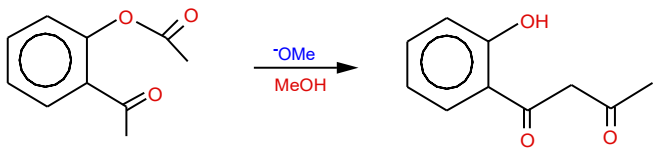
(ii) Provide a reagent and a mechanism for the following reaction :



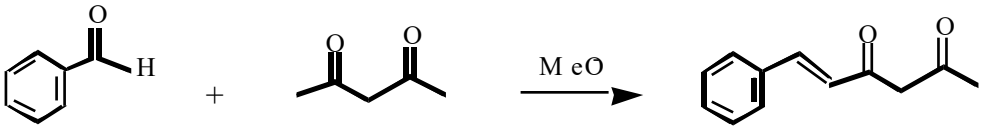
(iii) Propose a mechanism for the following reaction:



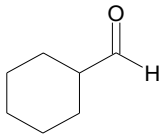
5. (i) Provide a mechanism for the following reaction which starts with formation of the appropriate enolate :



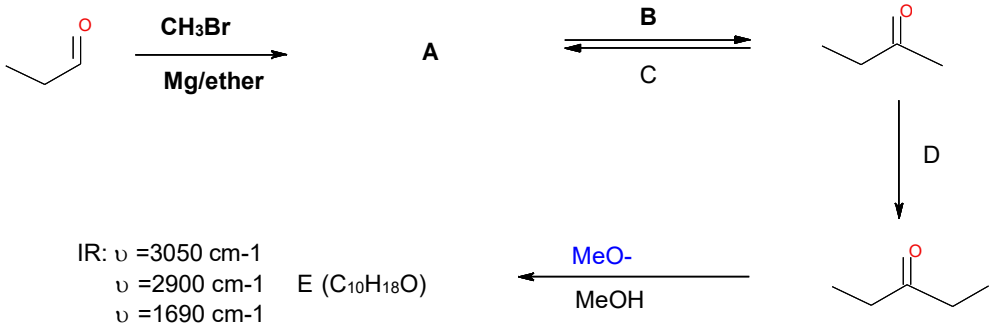
(ii) Identify any potential problems for the following *condensation* reaction : HINT



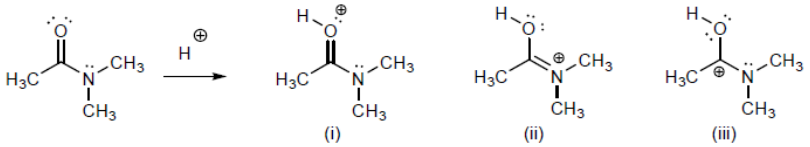
(iii) Changing the aldehyde in (ii) above to the molecule shown below complicates the reaction. Explain in terms of mechanism HINT



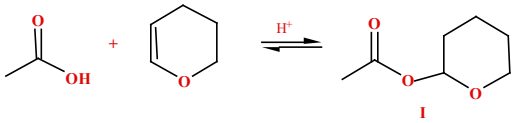
6. Provide the products **A** and **E** and the missing reagents **B,C** and **D** for the following scheme, **Note**: IR spectral data for **E**:



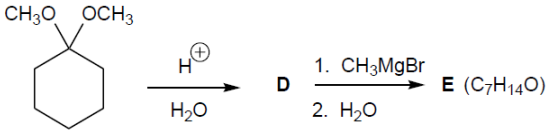
7. (i) For the three possibilities shown below for the protonation of N,N-DMF choose, giving your reasoning, the correct structure:



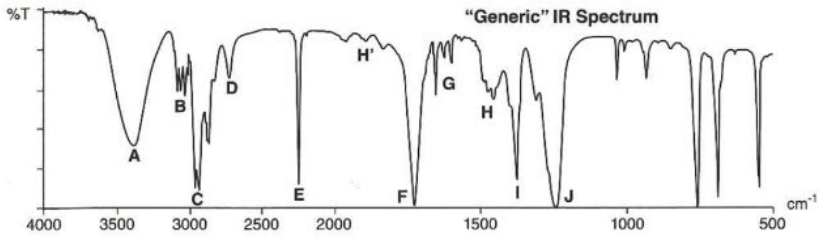
(ii) propose a mechanism for the **reverse** of the reaction shown below, using <u>acid and water</u> :



(iii) propose structures for D and E in the reaction below:



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	
		=C–H	3300–3000	No peaks in this area means no aromatic!
		–C=C–H	3300–3100	
		R₂C=C–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	R–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	R,H C=C H,R	1675	
		R,H C=C R,H	1658	Tri- & tetra-substituted ~1670
		R,R C=C H,H	~1653	
		R,H C=C H,H	~1645	
	H H'	benzene	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	R,R C H,H	1490–1440	Scissor bend
		H,R C H,H	1470–1430 & 1380–1370	Umbrella bend
		CH3,CH3 C	1390–1375 & 1370–1360	t-butyl ~1365
C–O	J	C–O ethers esters	1150–1060 alkyl ethers and esters	1270–1200 aryl & vinyl ethers 1285 acids
		C–O alcohols	1150 3° 1100 2° 1050 1°	Tertiary Secondary Primary