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CHM 2123 ORGANIC CHEMISTRY LABORATORY

YELLOW - MIDTERM EXAM – NOVEMBER 2013

Check to see that your exam contains 9 pages

Professor: Katherine McGilvray

Date: Saturday, November 2nd, 2013 9:30 am - 11:00 am

Time: 90 minutes

Name:_____**MARKING SCHEME**_____ Student #:_____

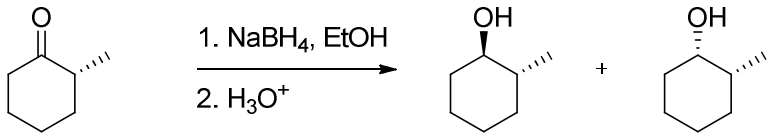
Section:_____ Your TA:_____

QUESTION	POINTS	RESULT
1	7	
2	**8**	
3	**10**	
4	6	
5	**7**	
6	6	
7	8	
TOTAL	**52**	**/52**

Note: Q5 and Q7 contain bonus questions!

Good luck!!

1. . (**7 points**) A student dissolved 1.14 mL of 2-methylcyclohexanone (MW = 112.17 g/mol, ρ = 0.924 g/mL) into a 50 mL round bottom flask containing 20 mL ethanol. 0.25 g $NaBH_4$ (MW = 37.83 g/mol) was then added in small portions. The reaction was left to stir for 15 minutes at room temperature, followed by the addition of 10 g crushed ice and then 10 mL of water. 1 mL of 3 M HCl was added drop-wise to the reaction mixture and considerable foaming occurred for about five minutes, and an additional 5 mL water was finally added. Following work-up, 0.60 g of the anti product (on the left), and 0.36 g of the syn product were each isolated, where scratching the flask with a glass rod was necessary to induce recrystallization of the syn product.



a) Calculate the conversion of the reaction. (**3 points**)

Option 1:

(1)
$$n_{SM} = \frac{\text{mass}}{\text{molar mass}} = \frac{\text{density x volume}}{\text{molar mass}} = \frac{(1.14\ \text{mL})(0.924\ \text{g/mL})}{112.17\ \text{g/mol}} = 0.0094\ \text{mol}$$

(1)
$$\text{Theoretical yield} = n_{SM} \times MM_p = (0.0094\ \text{mol})(114.19\ \text{g/mol}) = 1.07\ \text{g}$$

(1)
$$\%\ \text{yield} = \frac{\text{actual yield}}{\text{Theoretical yield}} = \frac{0.60\ \text{g} + 0.36\ \text{g}}{1.07\ \text{g}} = 89.7\ \%$$

Option 2:

(1)
$$n_{SM} = \frac{\text{mass}}{\text{molar mass}} = \frac{\text{density x volume}}{\text{molar mass}} = \frac{(1.14\ \text{mL})(0.924\ \text{g/mL})}{112.17\ \text{g/mol}} = 0.0094\ \text{mol}$$

(1)
$$n_p = \frac{m_{syn} + m_{anti}}{\text{molar mass}} = \frac{0.60\ \text{g} + 0.36\ \text{g}}{114.19\ \text{g/mol}} = 0.0084\ \text{mol}$$

(1)
$$\%\ \text{yield} = \frac{n_p}{n_{SM}} = \frac{0.0084\ \text{mol}}{0.0094\ \text{mol}} = 89\ \%$$

b) Determine the diastereoselectivity of the reaction. (**1 point**)

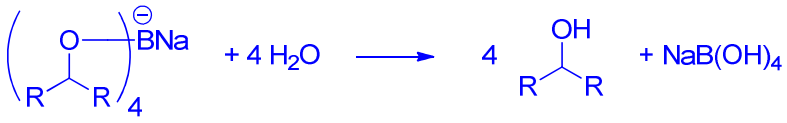
$$\frac{\text{syn}}{\text{anti}} = \frac{0.60\ \text{g}}{0.36\ \text{g}} = 5{:}3$$ (1)

or 1.6 : 1 syn : anti

c) Following the reaction, work-up by addition of water, ice, and HCl was necessary. Why? Explain with words and a balanced equation. (**2 points**)

THERE ARE TWO POSSIBLE ANSWERS TO THIS QUESTION

(1) Water, ice, HCl are added to hydrolyze the borate ester and product alcohol

(1) 

OR

0.5 each
- HCl and water are added to quench the excess $NaBH_4$
- Ice is used to contain the heat from the exothermic reaction above

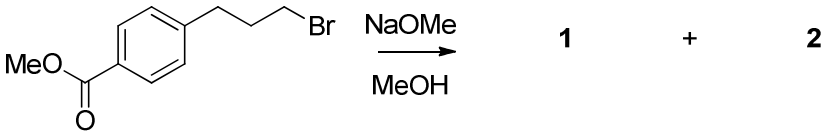
(1) $4\ H_2O + NaBH_4 \longrightarrow 4\ H_2 + NaB(OH)_4$

d) Explain how scratching helps to induce crystal formation. (**1 point**)

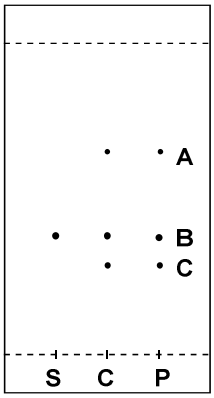
(1) Scratching produces small defects which act as a fresh surface for crystals to grow.

(Something along this line is worth 1 pt, where a defect provides a catalytic site for crystal formation.)

2. (8 points) Elimination and Substitution: While performing the reaction shown below, a student decides to monitor the progress of the reaction using thin layer chromatography. The TLCs for the reaction is represented below.



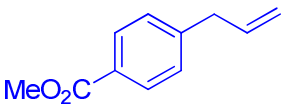
a) Calculate the R_f values of **A** and **B**. Show your calculations. (**1 point**)

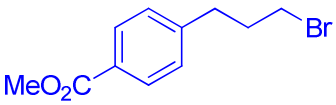


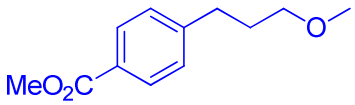
A: $Rf = \frac{27}{41} = 0.66$ B: $Rf = \frac{16}{41} = 0.39$

0.5 pts each

b) Draw the structure of the reactant and products **1** and **2** corresponding to spots A, B and C. (**2 points**) 2 points for all 3; 1 point for 2/3

A: 

B: 

C: 

c) Using key words, briefly justify your reasoning for this assignment (in part b) based on the principles of thin layer chromatography. (**3 points**)

(1) Polar compounds hydrogen bond to polar silica plate via hydrogen bonds

(1) B is starting material as indicated by presence in S lane

0.5 each: A is alkene; no H-bonding so weakest interaction and highest R_f

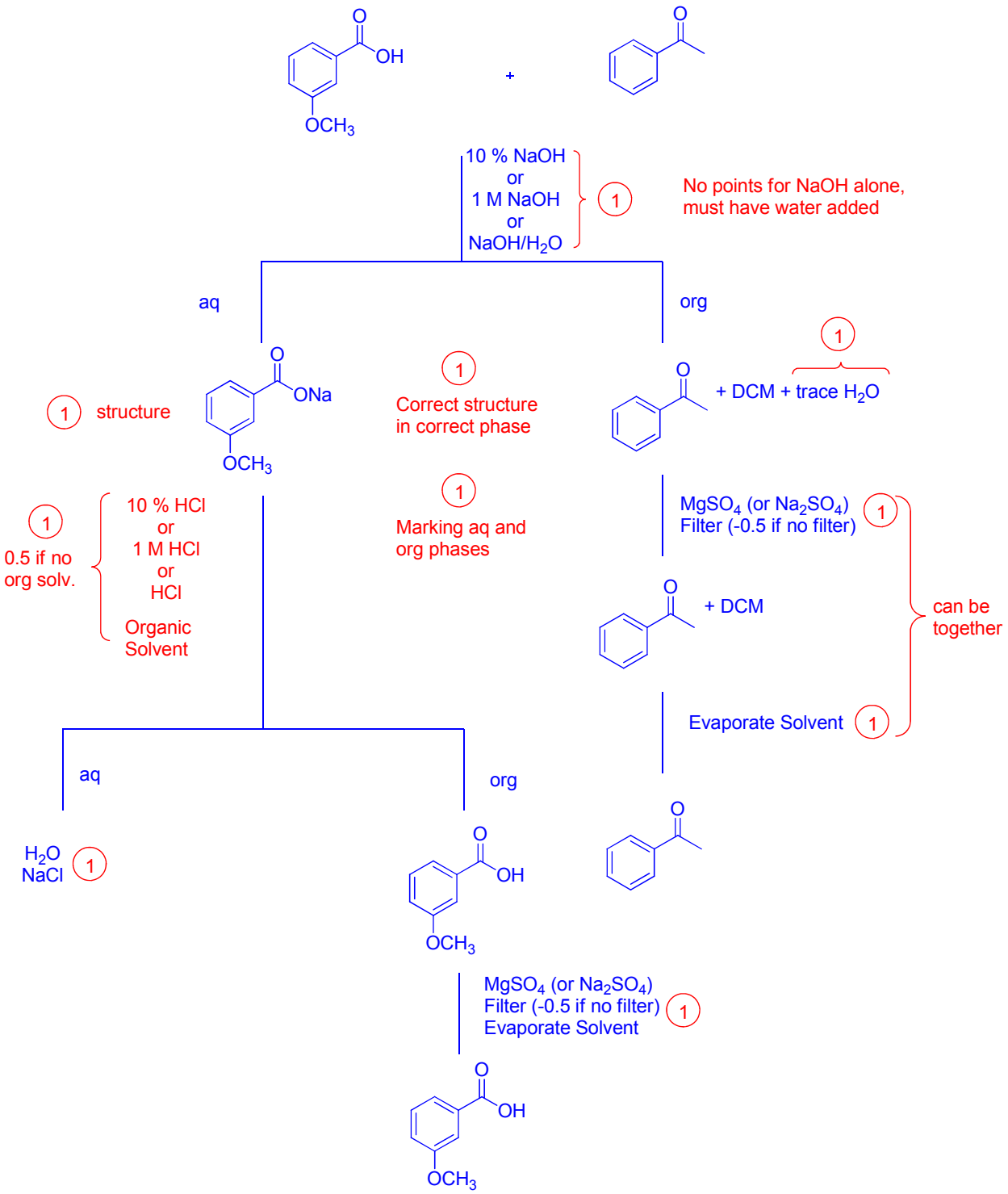
0.5 each: C is ether; H-bonding acceptor is more polar and moves least on plate

d) A student is attempting to favour the elimination product over the substitution product for the reaction above. List two changes to the reaction conditions that will increase the yield of the elimination product. (**2 points**)

(1) Increase reaction temperature

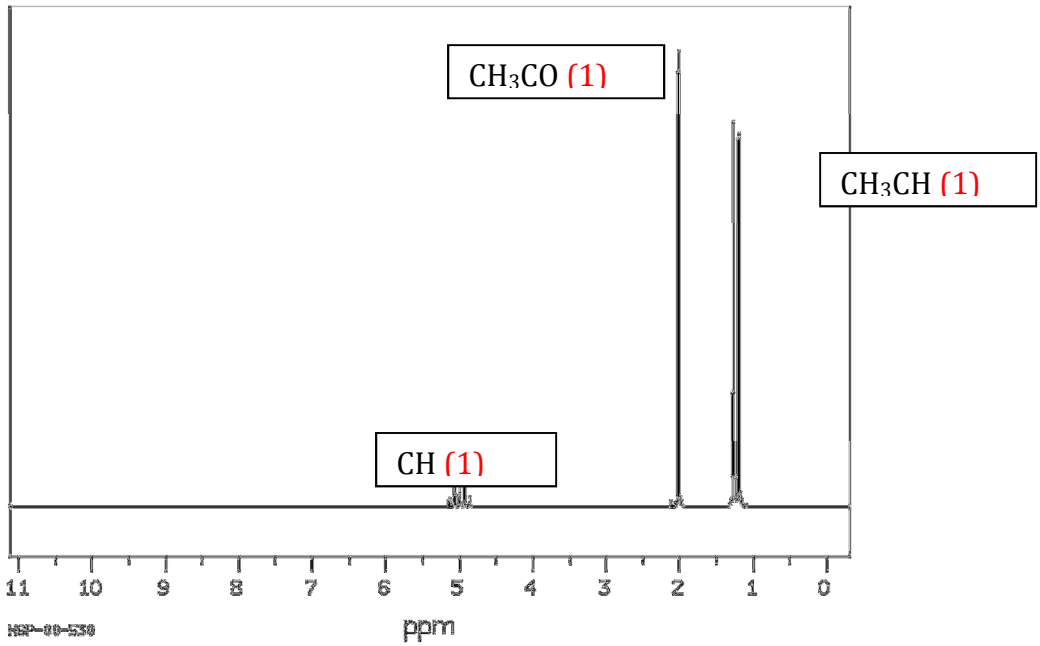
(1) Use stronger base or bulkier nucleophile

3. (**10 points**) **Separations**. Using a **flowchart**, provide a method for the separation of the following mixture of compounds in dichloromethane. Isolate each compound to the **crude product**. (Recrystallization not necessary).

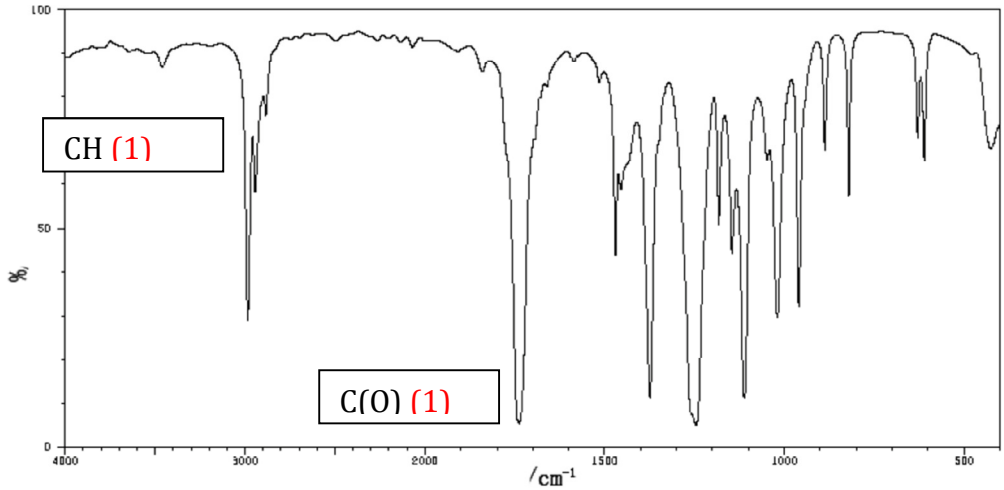


*(Please use **common sense** while correcting this question, as students will propose many approaches. If student prepipitates ROOH from aqueous phase and does not do 2nd extraction (as shown above), this is still acceptable. They just need to wash their crystals with H_2O to ensure removal of NaCl (**1 point**)*

4. (**6 points**) Sodium acetate, CH_3COONa, was dissolved in 2-bromopropane in an Erlenmeyer flask, and the mixture was left to stir for 20 minutes at room temperature, until an aliquot was extracted for a ^1H NMR. Determine the structure of the product(s) and justify your choice based on the ^1H NMR and FTIR spectra, respectively, shown below. *Assign each peak to the representative atoms in the NMR spectrum., and assign distinctive peaks in the IR spectrum.*

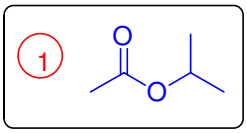


Part marks for logical interpretation of their proposed product. ***-1 point*** *if not 2-bromopropane*

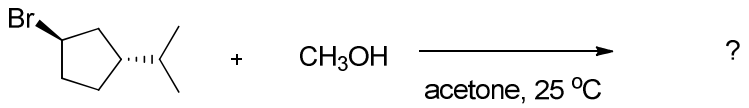


3460	84	1584	84	1146	42	629	68
2984	27	1514	79	1111	10	611	62
2944	55	1470	42	1049	84	426	66
2884	72	1456	67	1020	28		
1841	81	1374	10	960	31		
1736	5	1248	4	886	86		
1590	86	1183	49	821	66		

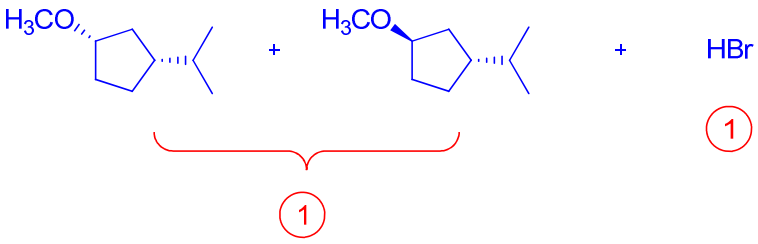
product



5. ***Mechanistic and kinetic analysis of reactions (7 points)***



a) Indicate the possible substitution product(s) and byproducts of the reaction illustrated above. (**2 points**)



Can be shown as racemic mixture

b) Based on what you have learned and performed in this course, briefly describe a series of experiments (120 minutes max.) that could allow you to determine the mechanism of the reaction. (**5 points**)

(1) Monitor formation of HBr over time to determine kinetics

(1) Set up experiment with [alkyl bromide] = [MeOH]

(1) Titrate aliquots with NaOH at regular time points

(1) Plot data: a) ln[HBr] vs t = 1st order
b) 1/[HBr] vs t = 2nd order

(1) Line of best fit will indicate reaction mechanism as S_N1 or S_N2

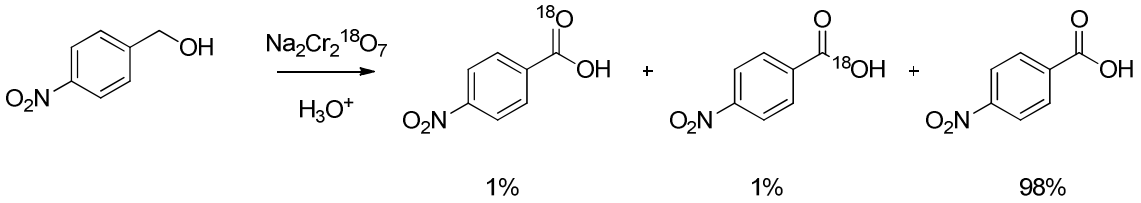
c) Explain how you could use IR/NMR spectroscopy to validate your mechanistic findings?

(1)
- Diastereomers will show 2 different NMR spectra
- S_N1 = two different spectra
- S_N2 = one single spectrum

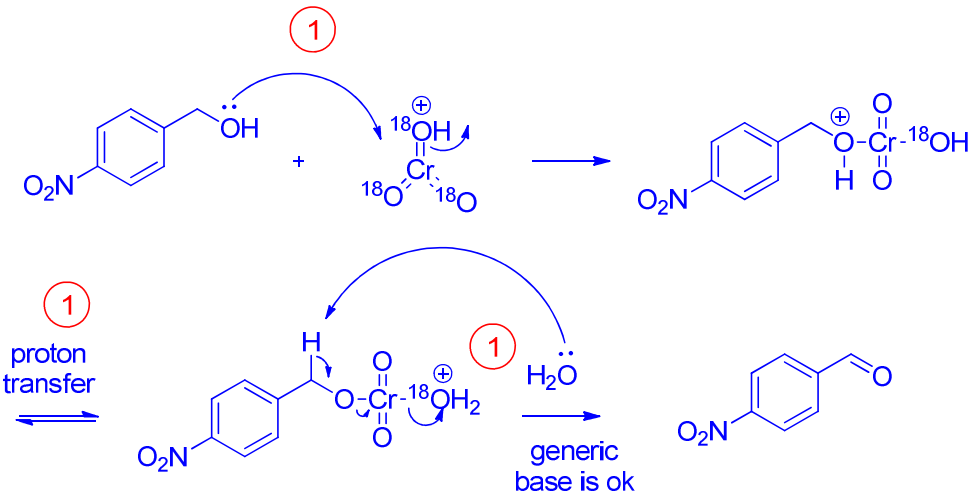
NOW BONUS = 1 point

6. (**6 points**) One method of determining the mechanism of a reaction is to use radio-labeled atoms. For example, ^{18}O can be used to trace oxygen over the course of a reaction.

A student assumes that the source of the oxygen in the carbonyl of the carboxylic acid is from the chromate, and sets up an experiment using radio-labeled sodium dichromate. After performing the experiment as shown in the lab manual, he observes the following results:



a) With the aid of a mechanism, explain why the major product contained no radio-labeled oxygen. (**4 points**)



1 No ^{18}O is incorporated into the product since the alcohol in the starting material is the source of oxygen in the carboxylic acid in the product

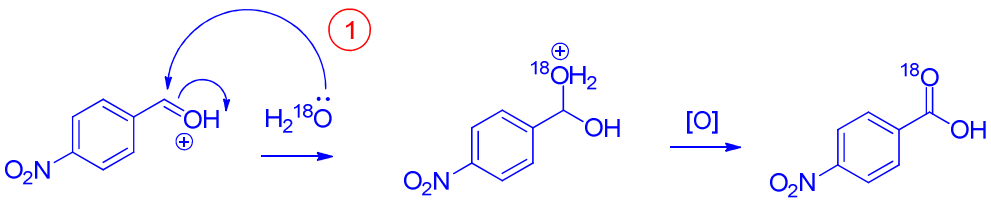
b) Why does a small amount of ^{18}O appear in the final *p*-nitrobenzoic acid product? (**2 point**)

IF THESE POINTS APPEAR IN SECTION (a) MARK AS CORRECT

1 Radiolabeled $H_2{}^{18}O$ is produced in the oxidation mechanism in small amounts

1 $H_2{}^{18}O$ can attack aldehyde to form a diol which can be oxidized to the carboxylic acid

OR students can show H_2O attack with a mechanism



7. ***Odds and ends (8 points)***

a) Substitution and elimination reactions can often compete to yield a range of products, particularly with secondary substrates such as 3-chloropentane. Rank the nucleophiles/bases in descending order (best to worst) to exclusively favour of a substitution reaction, and briefly justify your choice. (**3 points**)

CH_3CH_2ONa CH_3COONa $NaOH$ $(CH_3)_3OK$ NaI

$NaI > CH_3CO_2Na > NaOH > CH_3CH_2ONa > (CH_3)_3COK$

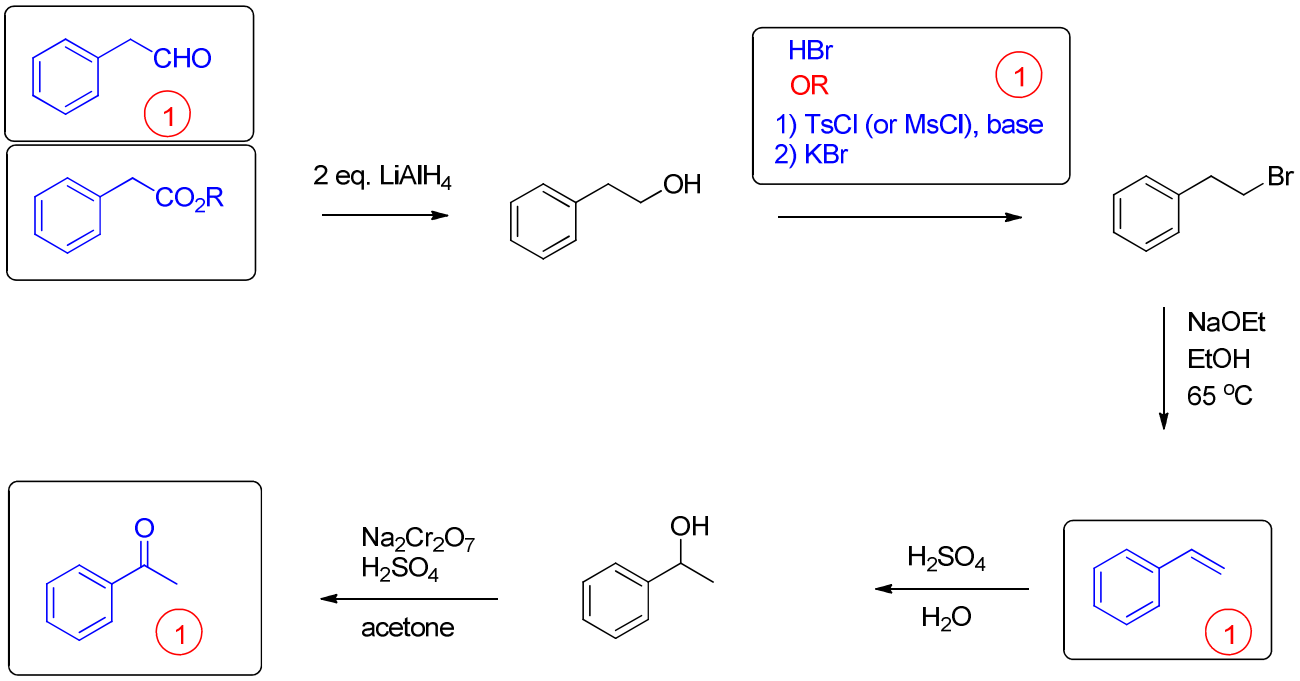
order (2)

Strong bases must be avoided to favour exclusively S_N2 over E2 (1)

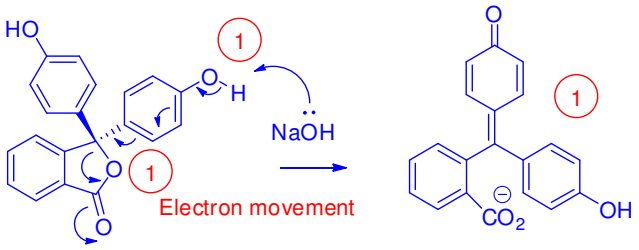
b) Why was the tea boiled for the caffeine experiment? Why was it subsequently chilled in an ice bath? (**1 point**)

0.5 each
- The tea is boiled because caffeine is more soluble in hot water than cold water
- DCM has a bp of 40 °C and the solvent would evaporatore upon transfer

c) Fill in the missing reactants, products, and/or reagents for the following multi-step synthesis. (**4 points**)



Bonus: Phenolphthalein is a common indicator used for titrations. It is colourless in acidic solutions and pink in basic solutions. Provide the structure of the pink form of phenolphthalein and show the mechanism of the reaction from the colourless form of phenolphthalein to the pink form **(3 points)**.



colourless

^{1}H NMR

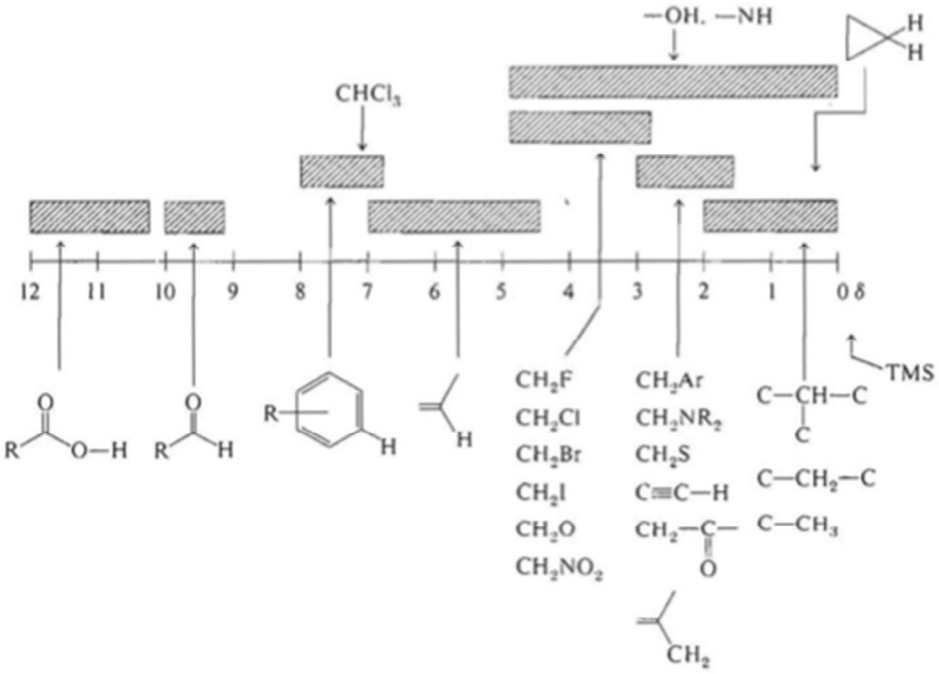


Table 1 Absorption frequencies of some common bonds (shown in bold type)

bond		*type of compound*	*frequency*
–C–H	(stretch)	alkanes	2800–3000
=C–H	(stretch)	alkenes, aromatics	3000–3100
≡C–H	(stretch)	alkynes	3300
–O–H	(stretch)	alcohols, phenols	3600–3650 (free) 3200–3500 (H-bonded) (broad)
–O–H	(stretch)	carboxylic acids	2500–3300
–N–H	(stretch)	amines	3300–3500 (doublet for NH_2)
–C(=O)–H	(stretch)	aldehydes	2720 and 2820
–C=C–	(stretch)	alkenes	1600–1680
C=C	(stretch)	aromatics	1500–1600
–C≡C–H	(stretch)	alkynes	2100–2270
–C(=O)–	(stretch)	aldehydes, ketones, carboxylic acids	1680–1780
–C≡N	(stretch)	nitriles	2220–2260
C–N	(stretch)	amines	1180–1360
–C–H	(bending)	alkanes	1375 (methyl)
–C–H	(bending)	alkanes	1460 (methyl and methylene)
–C–H	(bending)	alkanes	1370 and 1385 (isopropyl split)