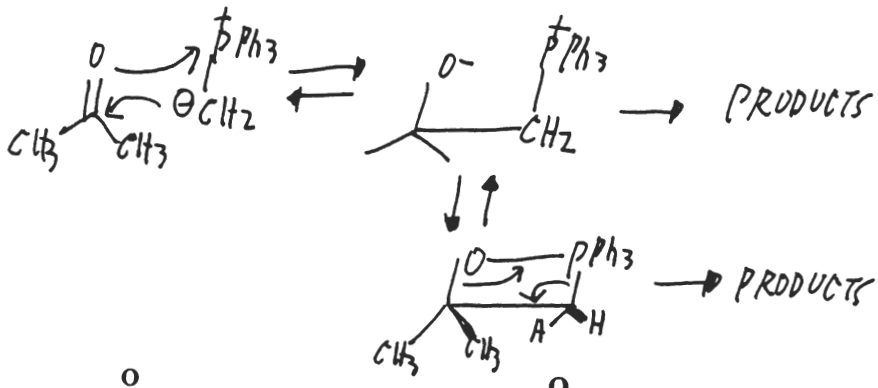
Name: _____ *Grade:* _____

Please use a **non-red** pen. Answer questions in the provided space. If you write any answers on the back of the page, indicate this on the **front** of that page. Points appear in parentheses ( ) and margin. ***Good Luck!***

Question	Max. Pts.	Pts	Question	Max. Pts	Points
1. 5 + 5 + 5	=	15	4. 4 + 6 + 6	=	16
2. 4 + 6 + 4 + 4 + 4	=	22	5. (3 + 3) + 3 + 3 + 3	=	15
3. 3 + (2 + 2 + 2) + (2 + 2)	=	13	6. 4 + 4 + 3 + 4 + 2 + 2	=	19
				Total	= 100

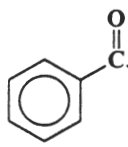
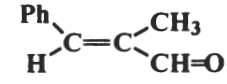
1. (15) Write a detailed mechanism for each of the following reactions. Use arrows to show electron flow.

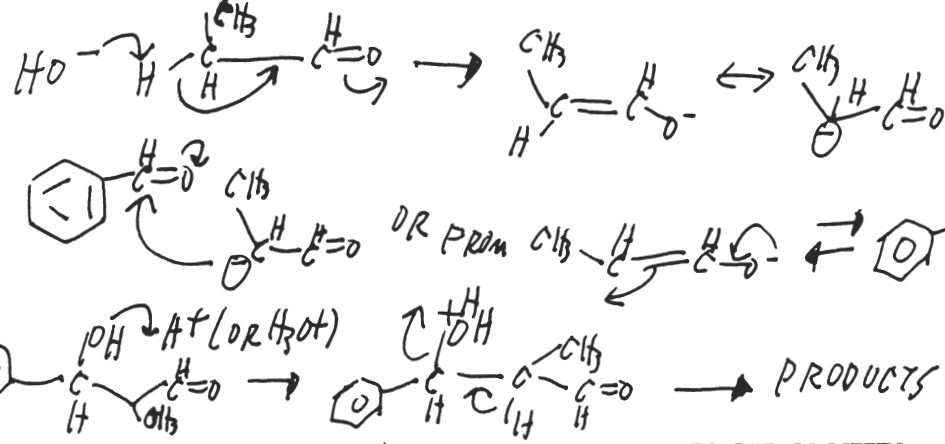
a. $(CH_3)_2C{=}O$ + $^{\ominus}{:}CH_2{-}\overset{\oplus}{P}Ph_3$ **dimethoxy ethane** $(CH_3)_2C{=}CH_2$ + $Ph_3P{=}O$



5

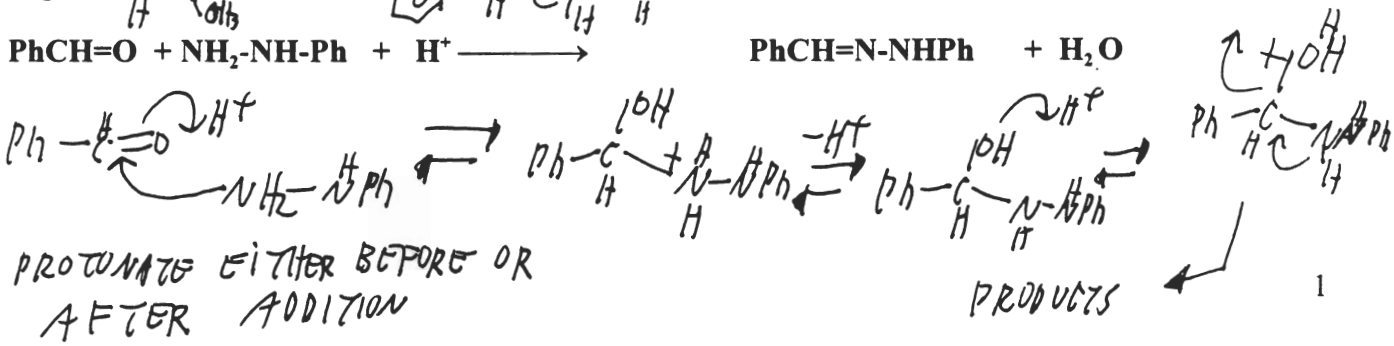
GRADERS ACCEPT LOSS OF O=PPh3 FROM OPEN OR CLOSED FORM

b.  **NaOH, H_2O** $CH_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$ **added slowly** **$H_3O^{\oplus}$, H_2O**  + H_2O



5

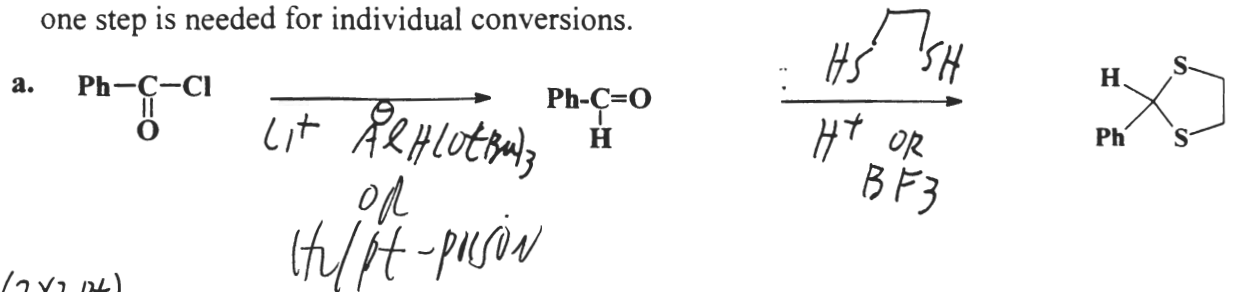
c. $PhCH{=}O + NH_2{-}NH{-}Ph + H^+ \longrightarrow$ $PhCH{=}N{-}NHPh + H_2O$



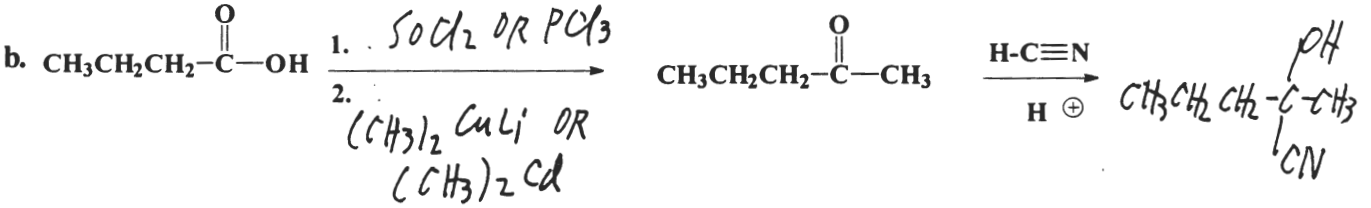
5

PROTONATE EITHER BEFORE OR AFTER ADDITION

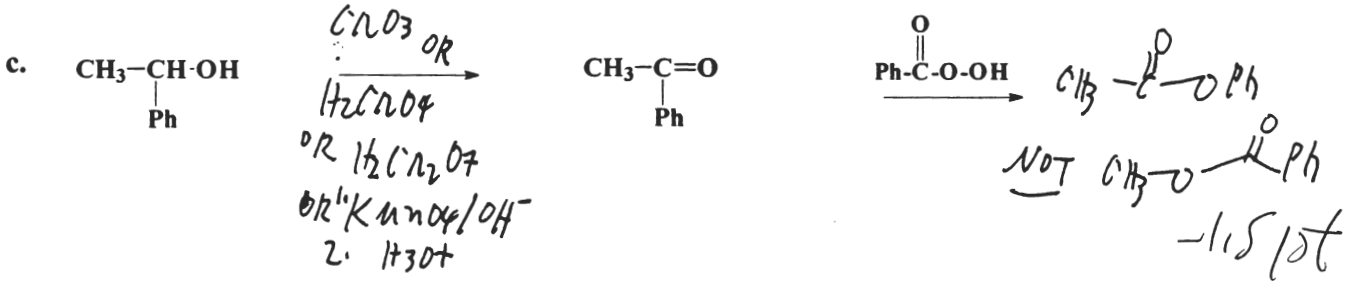
2. (22) Fill in the missing reagents, or products A-I for the following reaction sequences. Sometimes more than one step is needed for individual conversions.

a. 

4 (2X2pt)

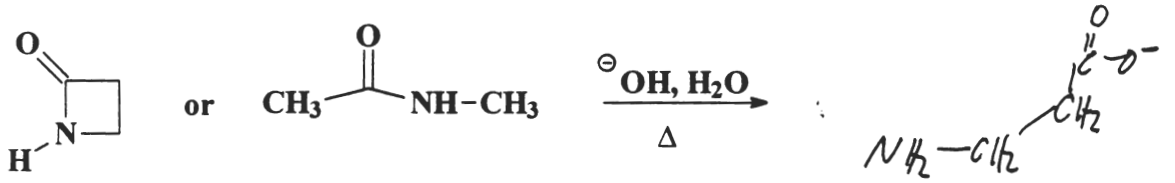
b. 

6

c. 

4

d. Circle which molecule below reacts FASTER and give the product(s) of that reaction



This ring is FASTER

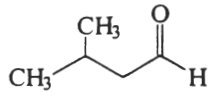
4pt

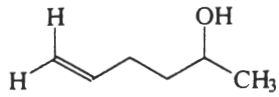
e. Briefly explain the **FASTER** rate in **2d.**

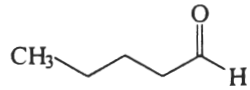
The β-lactam (4-membered cyclic amide) reacts FASTER since it has ring strain which is relieved upon opening

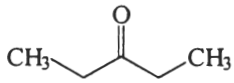
4pt

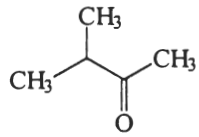
3. (13) a. A compound, $C_5H_{10}O$, reacts with **2,4-dinitrophenylhydrazine** solution to give a yellow precipitate. It gives a negative **Iodoform** test **with $I_2/^-OH$** and **no reaction** with cold $KMnO_4$ /OH^-. The compound could be which of these. **Answer= No. 4 : 3-pentanone**


(1)


(2)

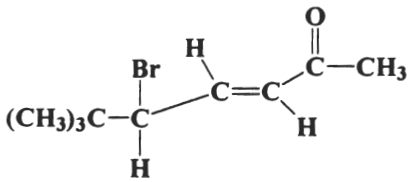

(3)


* (4)

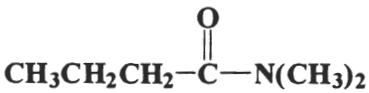

(5)

3

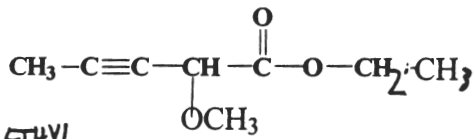
b. Write the ***IUPAC*** name for each of the following compounds:

(1) 

2 TRANS or *E*-5-bromo-6,6-dimethyl-3-hepten-2-one

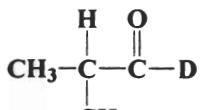
(2) 

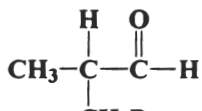
2 N,N-dimethylbutanamide

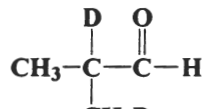
(3) 

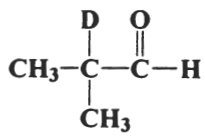
2 ETHYL 2-methoxy-3-pentynoate

c. Circle the correct product formed from **2-methylpropanal** dissolved in cold **D_2O / NaOD (trace).**

(1) 

(2) 

(3) 

(4) 

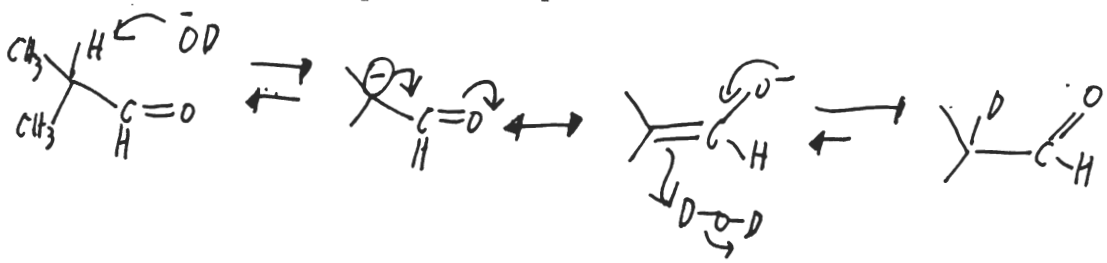
(5) 1,,2, 3

(6) none of these

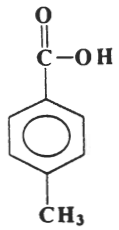
2pt

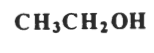
Answer= No. 4

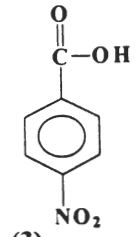
d. Show the mechanism that produces this product.

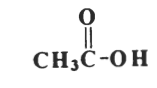
2 

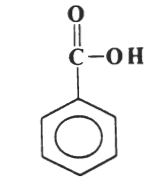
4. **(16)** a. Rank the following compounds in order of decreasing acidity (strongest = 1 to weakest = 5).


(1)


(2)


(3)


(4)

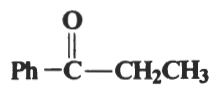

(5)

4

Ranking: 3 5 1 4 2

b. Distinguish between the members of **each** of the following pairs of compounds by the requested number of chemical tests or reactions. Write the equations and the structures of all the major organic and inorganic products. Note the **observations** for the tests.

(1) **Use one test or reaction with equation and visible result and one specific IR or ^{1}H NMR fact to distinguish.**



6pt

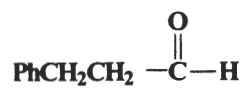
CrO_3: no color change

tollens, $KMnO_4$ also no change

Or $NaBH_4$: reduction to 2° alcohol (then a moderate rxn with $ZnCl_2$/HCl → R-Cl)

IR PhC=O 1690 cm^{-1}

NMR δ 1.2 CH_3 (t,3); 2.5 CH_2 (quart,2)
Ph: 2 mult 7-8 (ortho downfield)
Not a singlet; no sextet



Tollens: $Ag(NH_3)_2^+$ → Ag mirror

$KMnO_4$ purple soln → brown ppt MnO_2

CrO_3 (and other oxid. Agents) ⟶ $PhCH_2CH_2CO_2H + Cr^{+3}$

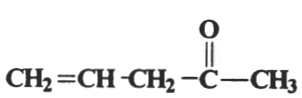
If a test: orange solution ⟶ green

reduction to a 1° alcohol (very slow rxn with $ZnCl_2$/ HCl)

RCH=O 1725 cm^{-1}

no quartet; δ 9.5 O=CH (s,1); Ph 7.1 (s,5); $PhCH_2$ (t,2)
CH_2CH=O (*ca* 2.2-2.4 (sextet, 2)

(2) **Use one test or reaction with equation and visible result and any two specific IR or ^{1}H NMR facts to distinguish.**

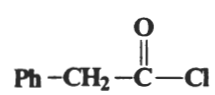


6pt a, no reaction
b. Br_2 decolorizes if a test); if rxn: adds to double bond
c. NaOI/ NaOH gives CHI_3 (yellow ppt)
d. 2,4-DNPH gives a yellow ppt R-C(CH_3)=NNHC_6H_3 (NO_2)$_2$
e. R-NH_2 : no rxn

f. Ag^+ no rxn

IR: C=O 1715 cm^{-1} ; no aromatic peaks 600-800

NMR δ 2.1 (s,3), vinyl Hs 5-6



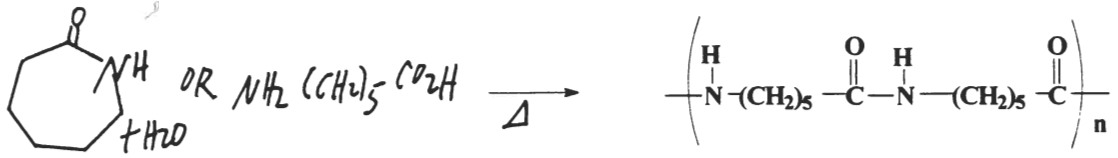
a. H_2O: gives $PhCH_2CO_2H$ + HCl
b. no color change (maybe slow reaction ⟶ $PhCH_2C(=O)Br$ + BrCl
no yellow ppt (rxn gives $PhCH_2CO_2$ Na)
no rxn
RNH_2 converts the acid chloride to an amide $PhCH_2C(=O)NHR$
Ag^+ gives AgCl white ppt (rxn or test)

C=O 1800; 2 peaks 600-800

no δ 5-6, no 2.1 but instead phenyl at 7.1 (s,5)

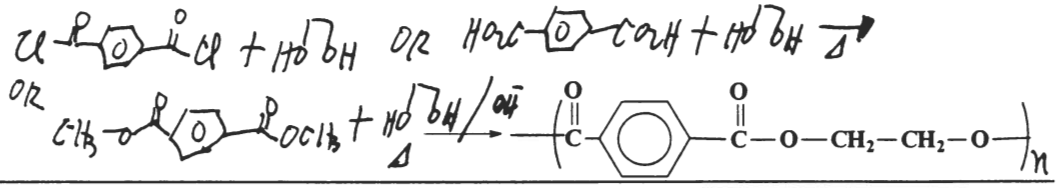
5. **(15)** a. Write the structures of the reactant(s) that are used to make each of the following polymers: Note that more than one reactant may or may not be necessary.

(1) :



3

(2) :



3

b. Accurately name the above polymers.

(1) **Nylon-6** (-0.5 pt for Nylon-66)

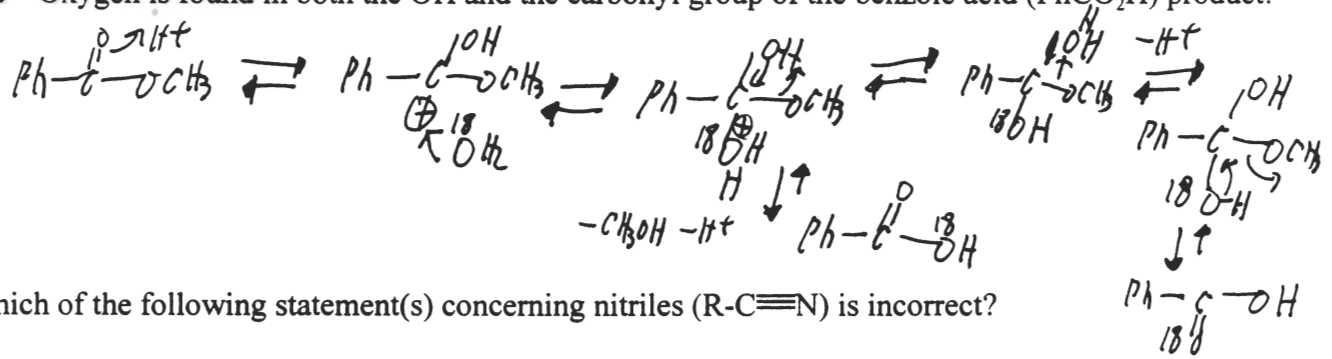
3Pt (1.5 pt x 2)

(2) **poly (ethylene terphthalate); Dacron** (-0.5 pt "polyester" OK

c. In the acid catalyzed hydrolysis of  with $H_2{}^{18}O$ where is the ^{18}O isotopic label found in the products? Explain by giving the mechanism and the products of the reaction.

3pt

The ^{18}Oxygen is found in both the OH and the carbonyl group of the benzoic acid ($PhCO_2H$) product:



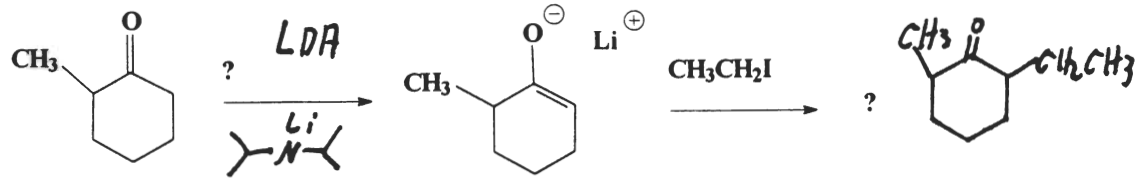
c. Which of the following statement(s) concerning nitriles (R-C≡N) is incorrect?

3pt

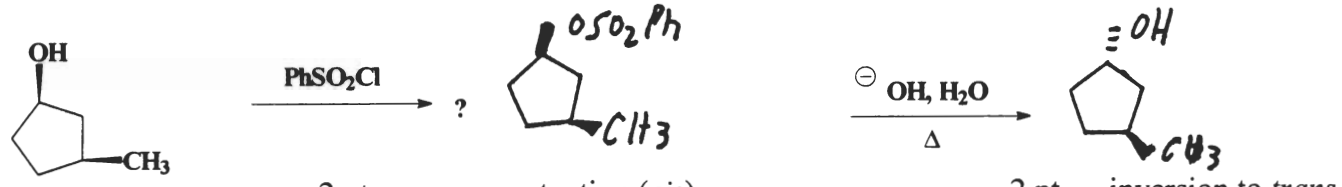
1. nitriles can be hydrolyzed to carboxylic acids
2. nitriles can be formed from (many) alkyl halides by nucleophilic substitution by cyanide ion
3. nitriles can be reduced with excess $LiAlH_4$ to primary amines RNH_2
4. nitriles react with RMgX (Grignard reagents) to form tertiary alcohols (incorrect ans.)**
5. nitriles can be made by dehydration of amides

6. **(19)** Do the following conversions. Fill in the missing inorganic/organic reagents, intermediates, and major products.

a.



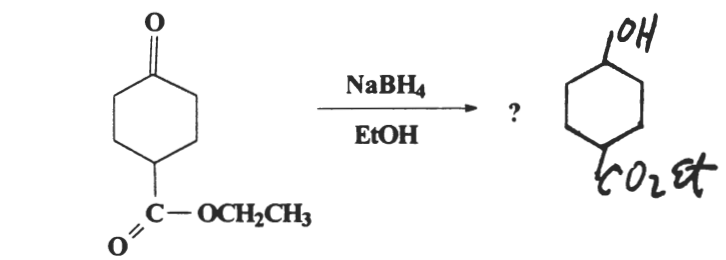
4



2 pt retention (*cis*) 2 pt inversion to *trans*

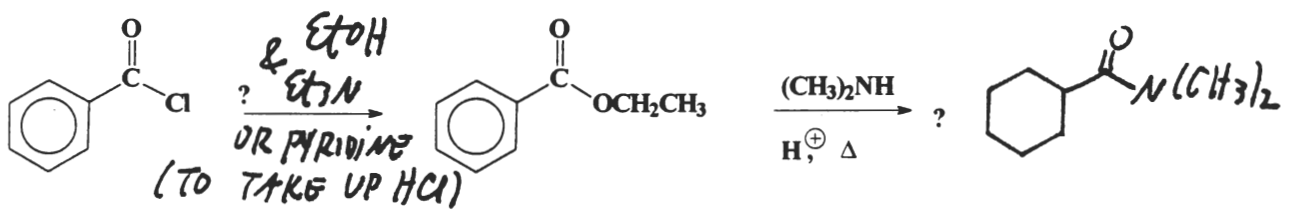
Show stereochemistry at each stage

4



(no stereochemistry implied)

3



4pt

should have a 3° amine (pyridine, Et_3N, etc) present to take up HCl

e. Circle the compound below which is the strongest acid?

2 pt

1. $CHCl_2CH_2CH_2CO_2H$
2. $ClCH_2CHClCH_2CO_2H$
3. $CH_3CCl_2CH_2CO_2H$
4. $CH_3CHClCHClCO_2H$

***5.** $CH_3CH_2CCl_2CO_2H$

f. (2 pt) Explain your answer to **2e** above using structures and words.

2,2-Dichloroacetic acid is the strongest acid because of the two electronegative chlorines alpha to the carboxyl group: