CHM 2120
SAMPLE MIDTERM 2
ANSWERS

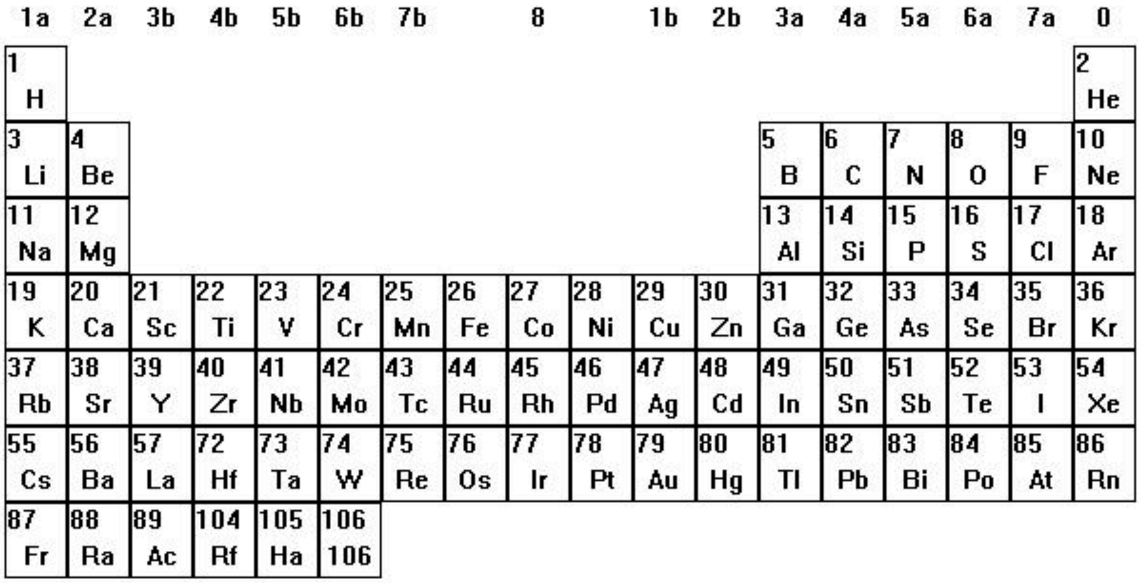
First Name: ______________________ Last Name: ______________________________

Student Number: _______________________

Approximate total number of marks:
(subject to minor changes)

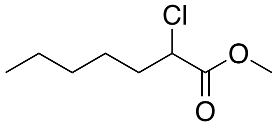
Notes:

- Molecular models are permitted
- Rulers and non-programmable calculators are permitted
- There is an IR absorbance table and a ^{1}H NMR table on the last page.



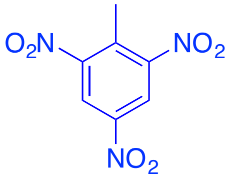
1a	2a	3b	4b	5b	6b	7b	8			1b	2b	3a	4a	5a	6a	7a	0
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Ha	106 106												

1. Name or draw the structure of the following molecules, as appropriate. **(4 points)**
   a.

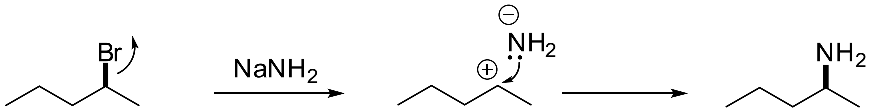


methyl 2-chloroheptanoate

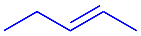
   b. 2,4,6-trinitrotoluene (TNT)



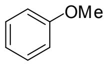
2.
   a. Explain why the following reaction will not work as shown. **(3 points)**
   b. Give the true product of the reaction. **(1 point)**

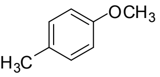


E2 reaction is favoured with a strong base and a good leaving group. The high energy carbocation will not form.

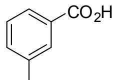


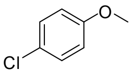
3. Which of the following aromatics would react most rapidly and which would react most slowly with $Br_2/FeBr_3$? Justify your answer and predict the structure of the major product for the fastest reacting substrate.

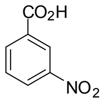




fastest

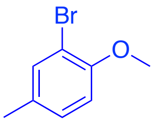




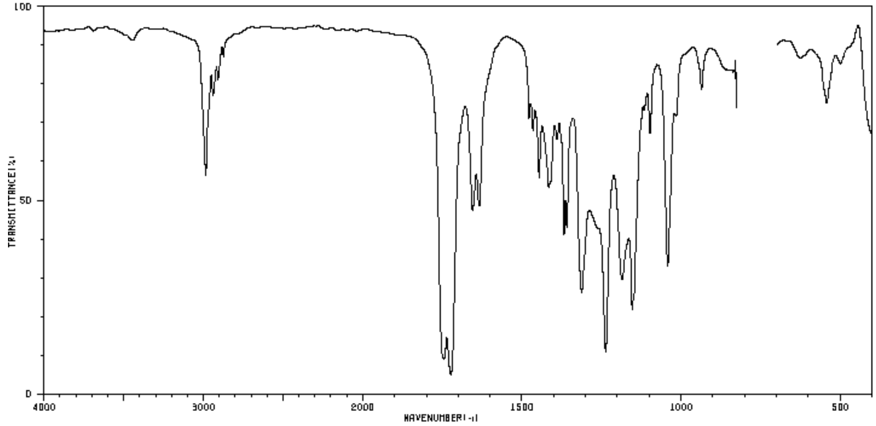


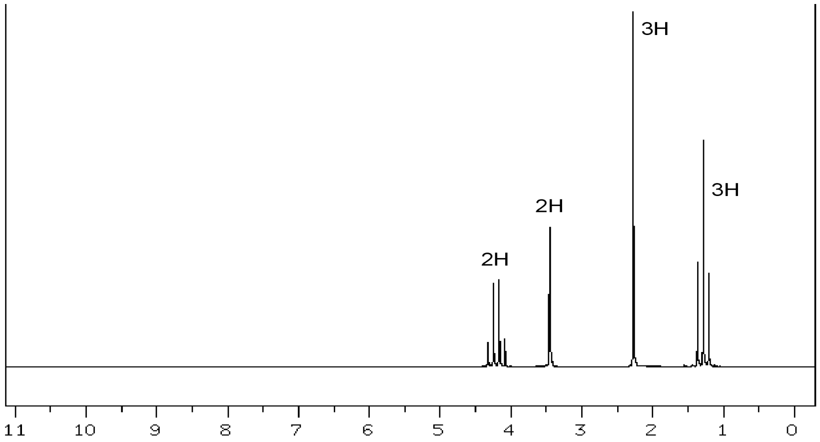
slowest

For the fastest-reacting: 2 EDGs can stabilize the transition state that leads to the formation of the arenium intermediate, lowering the activation energy of the rds and speeding up the reaction (relatvie to the other compounds).
For the slowest-reacting: the 2 EWGs destabilize the transition state that leads to the formation of the arenium intermediate, raising the activation energy of the rds and slowing down the reaction.



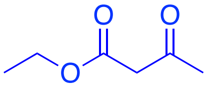
4. Draw the structure represented by the following IR and ^{1}H NMR spectra, with a molecular formula $C_6H_{10}O_3$.



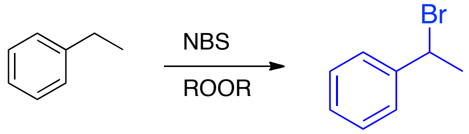


Peak	Chemical shift (ppm)	Integration	Multiplicity	Comments/Ideas
A	~4.2	2	q	CH_3-CH_2-O
B	~3.5	2	s	CH_2-O or between 2 carbonyls. Not between O and C=O (it would be more deshielded (shifted left) than 3.5.
C	~2.2	3	s	CH_3-C=O
D	~1.3	3	t	CH_3-CH_2

DU = 2, IR: 2 carbonyls



5.
   a. What is the major product of the following reaction? **(1 point)**
   b. How would you distintinguish between this product and the starting material by ^{1}H NMR? **(2 points)**

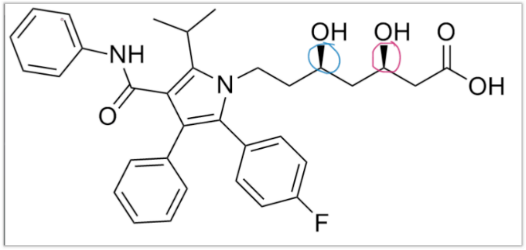


Integration: 10 Hs in the SM, 9 Hs in the product (Note: don't just say "integration" or "multiplity"—be specific and compare/discuss BOTH SM and product).

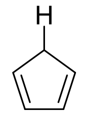
OR

Multiplicity: a triplet and a quartet for the CH3 and CH2, respectively, in the SM, a doublet and a quartet for the CH3 and CH, respectively, in the product

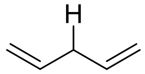
6. Circle **one** bond in Lipitor, a cholesterol-lowering drug in the "statin" class, that could be made by an S_N2 reaction. The drug works by inhibiting cholesterol production in the liver.
   Note: the competing E2 reaction would be a concern if making those bonds by S_N2.



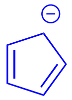
7. The pK_a of the indicated proton on the sp^3-hybridized carbon in cyclopentadiene is 15, while the pK_a of the proton on the sp^3-hybridized carbon in 1,4-pentadiene is 40. Explain why is one proton so much more acidic than the other. **(5 points)**



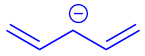
pK_a = 15



pK_a = 40

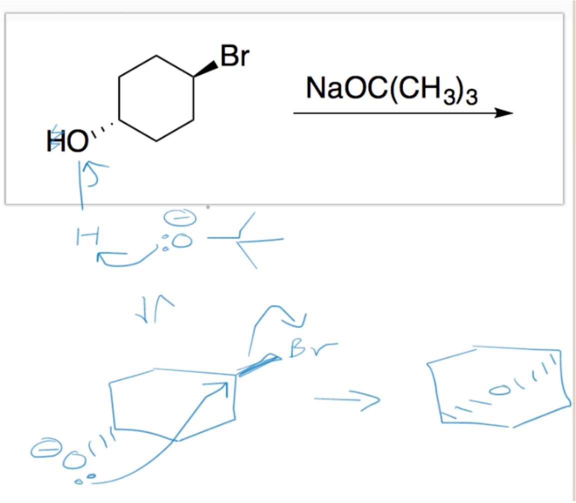


Aromatic therefore extra stabilized
Planar ring
all atoms sp^2
6 π electrons (satisfies 4n+2 rule)

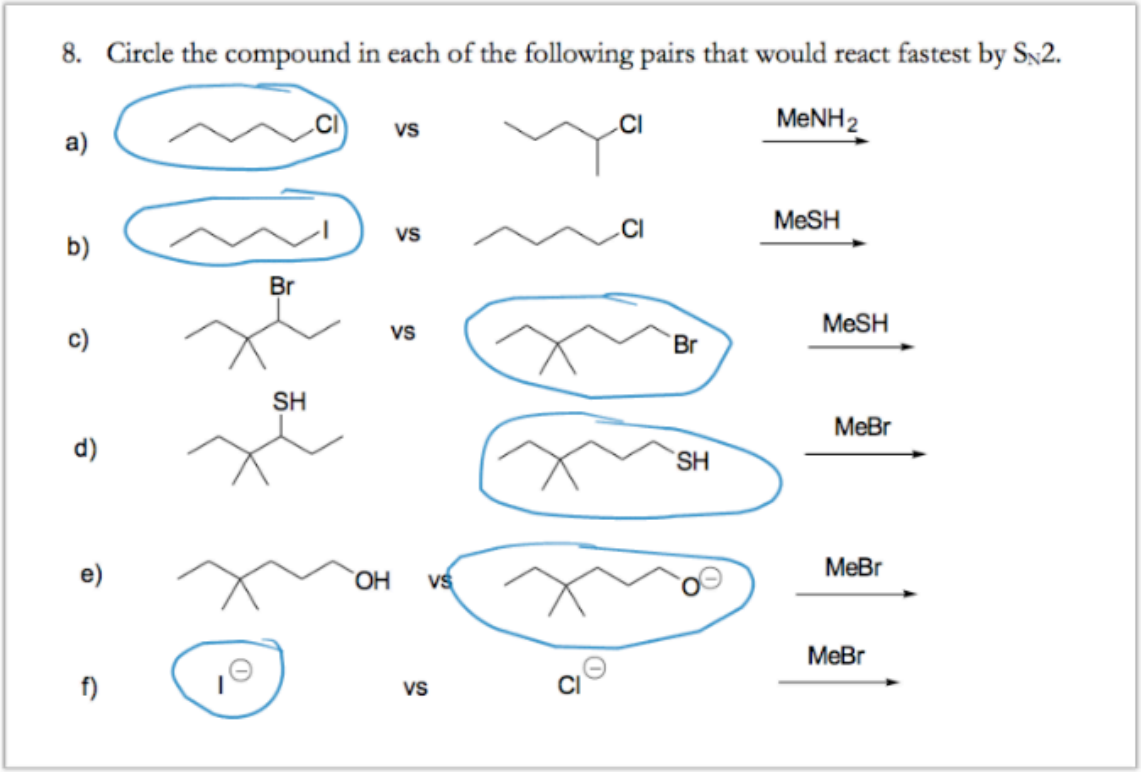


Non-aromatic, therefore stabilized only by resonance (not a ring)

8. Give the full detailed mechanism for the formation of the major product. **(6 pts)**

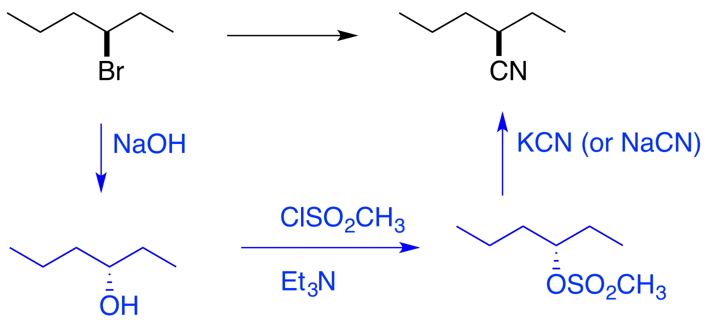


9. Circle the compound in each of the following pairs that would react fastest by S_N2.



8. Circle the compound in each of the following pairs that would react fastest by S_N2.

9. Propose a synthesis of the following compound Show all required reagents and intermediates. A retrosynthesis and mechanisms are not required. **(10 points)**

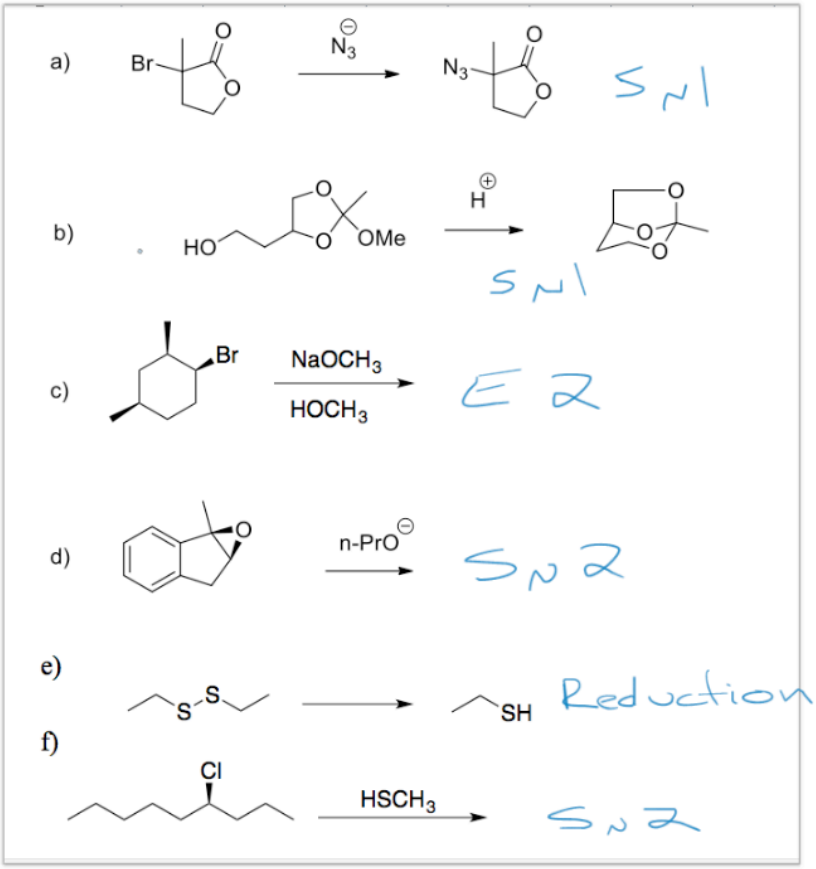


Note: you could use TsCl or TfCl instead of MsCl

It's ok to use another non-nucleophilic base, such as pyridine. Don't use too strong a base, or an E2 reaction will occur

10. State what type of reaction is operative in each case. **(4 points)**

Note: Part a is actually an unusual case of S_N2 on a tertiary C, possible because of overlap of the nucleophile with the nearby π^* orbitals of the carbonyl. This would be the type of question where I'd give you the question and the answer/mechanism, and ask you to explain the outcome



a) S_N1

b) S_N1

c) E2

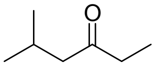
d) S_N2

e) Reduction

f) S_N2

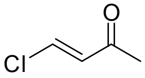
11. How many unique proton signals would be expected in the ^{1}H NMR spectrum of the following molecules? **(3 points)**

a.



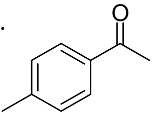
5

b.



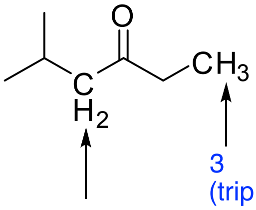
3

c.



4

12. Give the number of peaks (multiplicity) expected in the ^{1}H NMR spectrum for the indicated protons in the following structure: **(2 points)**



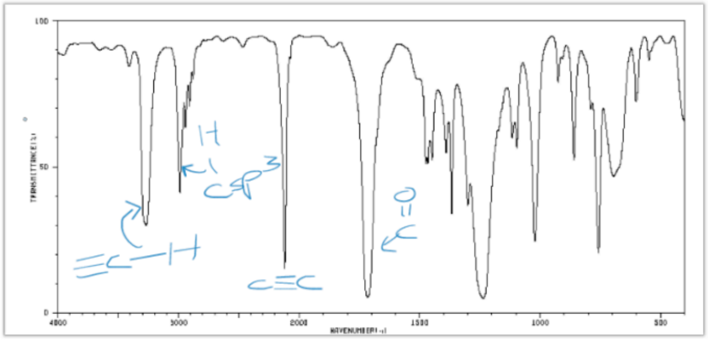
2
(doublet)

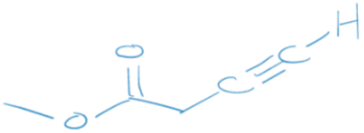
3
(triplet)

13.

a. Identify the key absorbances in the following IR spectrum. **(5 points)**
b. Propose a structure for the molecule given that its formula is $C_5H_6O_2$. **(2 points)**

$C_5H_6O_2$





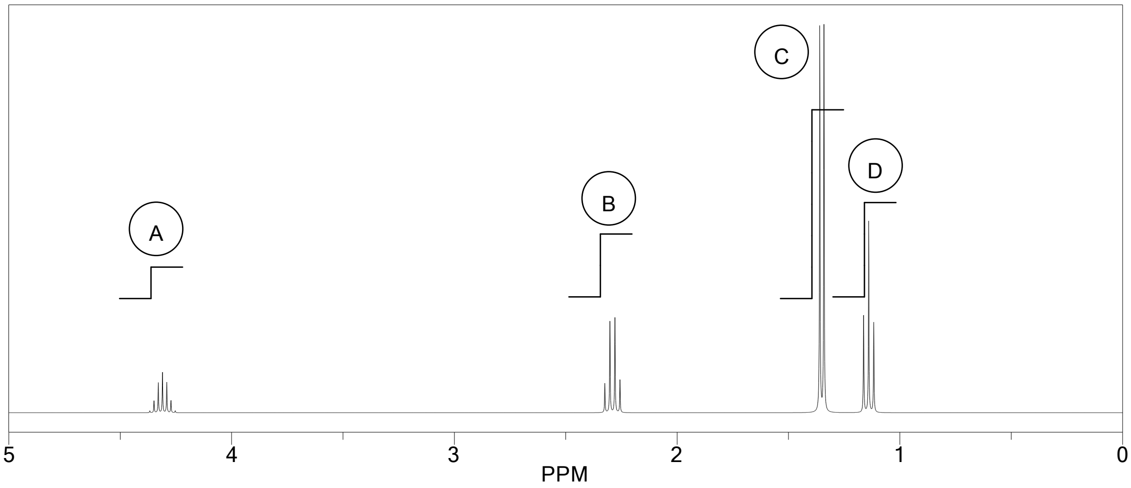
Other structures are possible. Make sure to have all the functional groups indicated in the IR, and the right formula.

14.

a. What is the structure of the unknown compound whose molecular formula is **$C_6H_{12}O_2$**? The ^{1}H NMR spectrum of this compound is below. **(2 points)**

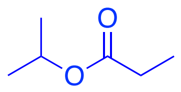
b. Justify your answer by accounting for all information given. **(10 points)**

Note: the infrared spectrum showed a number of absorbances from 2879 – 2960 cm^{-1}, and a strong absorbance at 1734 cm^{-1}.



Peak	Chemical shift	Integration	Multiplicity	Comments/Ideas
A	~4.3	1	m	CH-O
B	~2.3	2	q	$O=C-CH_2-CH_3$
C	~1.4	6	d	2 x CH_3-CH A and C are a fragment (O-isopropyl)
D	~1.1	3	t	CH_3-CH_2 B and D are a fragment (O=C-ethyl)

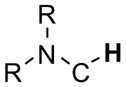
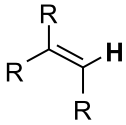
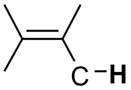
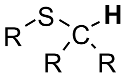
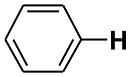
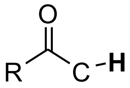
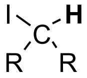
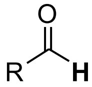
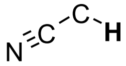
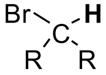
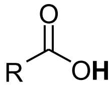
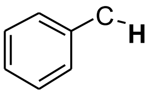
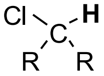
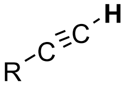
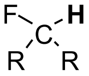
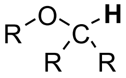
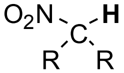
DU = 1, IR: C=O



IR: **Key Absorptions (cm^{-1}):**

C-H	Alkyl	C-H	2850-2960	m-s, sharp
C-H	sp^2	C-H	just >3000	m-s, sharp
Alcohol		R**O-H**	3200-3650	s, broad
Carboxylic acid		RC(=O)**O-H**	2500-3300	s, broad
Amine		R_2**N-H**	3300-3500	s, broad
Carbonyl		R_2**C=O**	1650-1780	s, sharp
Nitrile		R**C≡N**	2220-2260	v, sharp
Alkynyl		C≡**C-H**	~3300	m-s, sharp
Alkynyl		**C≡C**	2100-2260	v, sharp

^{1}**H NMR – Key APPROXIMATE chemical shifts (ppm):**

R-C-CH$_n$	0.7 - 1.7		2.2 - 2.9		4.5 - 7.0
	1.6 - 2.6		2.0 - 3.0		6.5 - 8.0
	2.1-2.5		2.0 - 4.0		9.0 - 10.0
	2.1 - 3.0		2.7 - 4.1		11.0 - 12.0
	2.3 - 2.7		3.1 - 4.1		
	1.7 - 2.7		4.2 - 4.8		
			3.0 - 5.0		
			4.1 - 4.3		

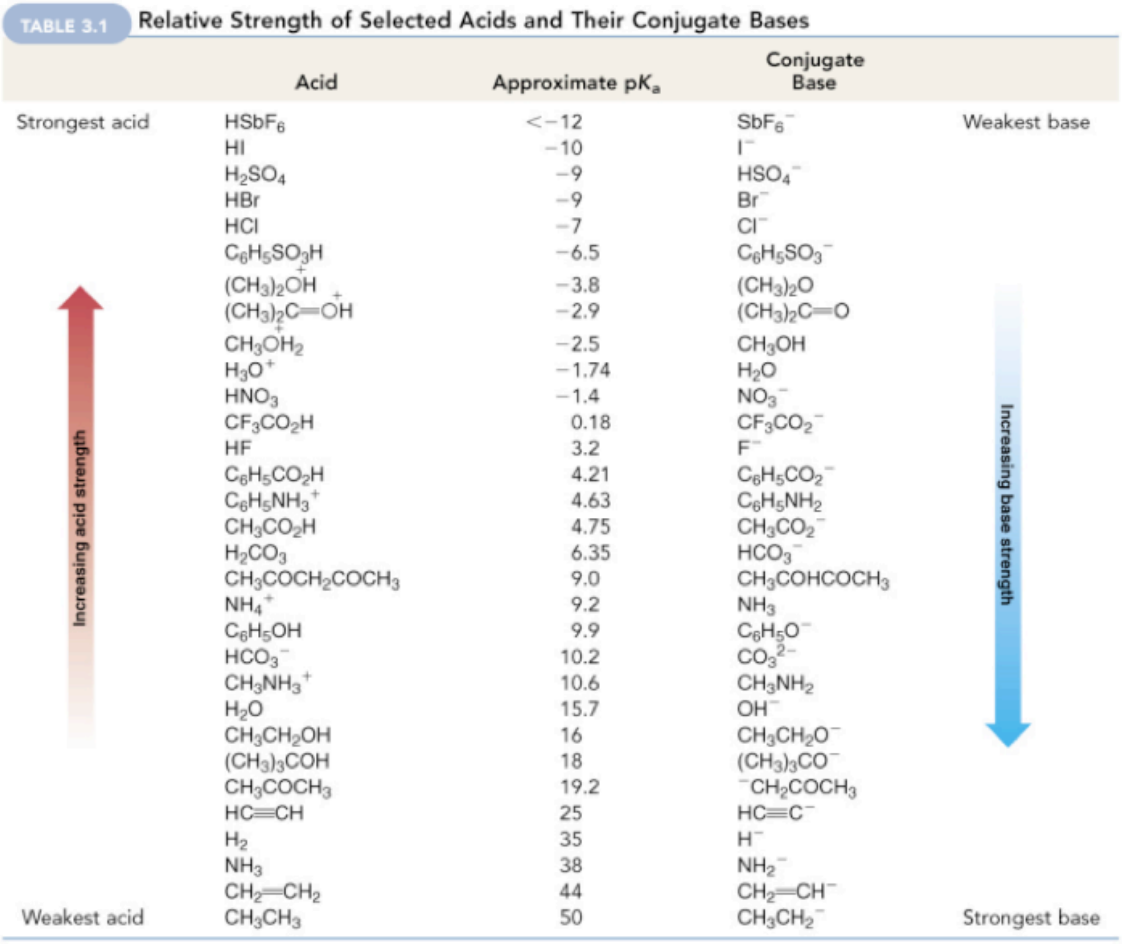


TABLE 3.1 **Relative Strength of Selected Acids and Their Conjugate Bases**

	Acid	Approximate pK_a	Conjugate Base	
Strongest acid	$HSbF_6$	<-12	SbF_6^-	Weakest base
	HI	-10	I^-	
	H_2SO_4	-9	HSO_4^-	
	HBr	-9	Br^-	
	HCl	-7	Cl^-	
	$C_6H_5SO_3H$	-6.5	$C_6H_5SO_3^-$	
	$(CH_3)_2\overset{+}{O}H$	-3.8	$(CH_3)_2O$	
	$(CH_3)_2C{=}\overset{+}{O}H$	-2.9	$(CH_3)_2C{=}O$	
	$CH_3\overset{+}{O}H_2$	-2.5	CH_3OH	
	H_3O^+	-1.74	H_2O	
	HNO_3	-1.4	NO_3^-	
	CF_3CO_2H	0.18	$CF_3CO_2^-$	
	HF	3.2	F^-	
	$C_6H_5CO_2H$	4.21	$C_6H_5CO_2^-$	
	$C_6H_5NH_3^+$	4.63	$C_6H_5NH_2$	
	CH_3CO_2H	4.75	$CH_3CO_2^-$	
	H_2CO_3	6.35	HCO_3^-	
	$CH_3COCH_2COCH_3$	9.0	$CH_3COHCOCH_3$	
	NH_4^+	9.2	NH_3	
	C_6H_5OH	9.9	$C_6H_5O^-$	
	HCO_3^-	10.2	CO_3^{2-}	
	$CH_3NH_3^+$	10.6	CH_3NH_2	
	H_2O	15.7	OH^-	
	CH_3CH_2OH	16	$CH_3CH_2O^-$	
	$(CH_3)_3COH$	18	$(CH_3)_3CO^-$	
	CH_3COCH_3	19.2	$^-CH_2COCH_3$	
	$HC{\equiv}CH$	25	$HC{\equiv}C^-$	
	H_2	35	H^-	
	NH_3	38	NH_2^-	
	$CH_2{=}CH_2$	44	$CH_2{=}CH^-$	
Weakest acid	CH_3CH_3	50	$CH_3CH_2^-$	Strongest base