Chemistry 232, Final Exam

Instructor: Bergdahl

Summer 2014

Name:_____

Be prepared to show ID upon request.

****No cellular phones or calculators are allowed during the test****

My laboratory instructor (TA) is (Please circle):

David Schmit

Arielle Kanner

Tim Montgomery

I do not take the 232L this summer

Before you start the exam, make sure that you have 13 problems!!

My student I.D. (red I.D.) number is:

A very Good Luck

For graders only:

Problem: #1_____/12p

#2_____/24p

#3_____/27p

#4_____/16p

#5_____/10p

#6_____/12p

#7_____/16p

#8_____/15p

#9_____/10p

#10_____/20p

#11_____/25p

#12_____/13p

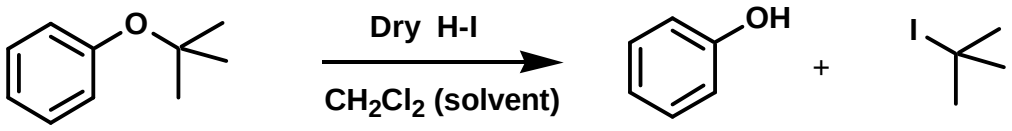
#13_____/18p

Total:_____/218p

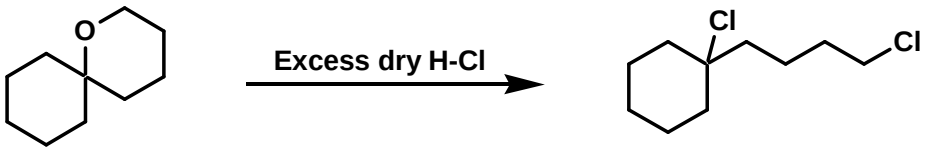
Grand Total:_____/Max 200p

Problem 1. Propose mechanisms for the following two reactions showing structures of possible intermediates and using curved arrows to indicate the electron flows in every step. (5 + 7p)

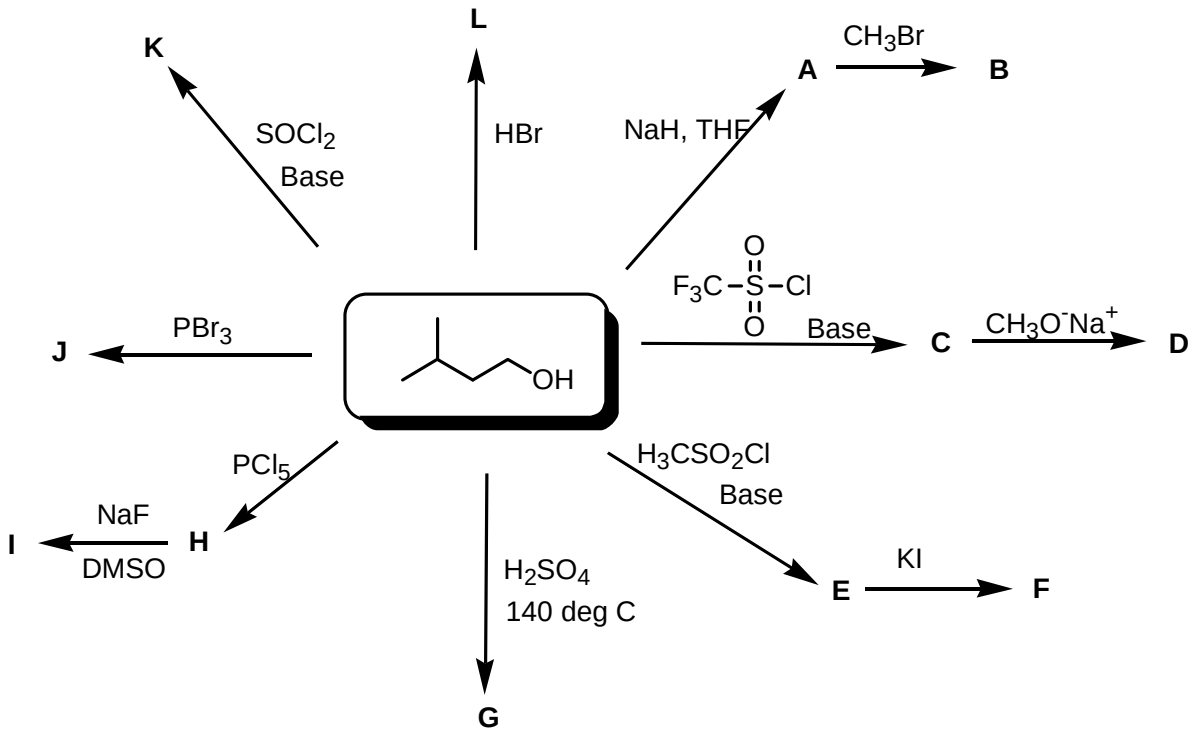
A)



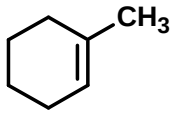
B)



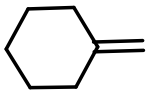
Problem 2. Considering **A-L** to represent the major products formed in each of the following reactions. Provide a structure for each of **A** through **L**. (24p)

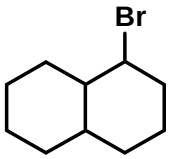


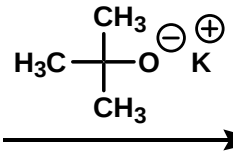
Problem 3. Indicate the major product formed in the following reactions. (27p)

A) 

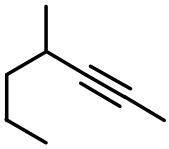
1) $HBSia_2$, THF
2) H_2O_2, NaOH

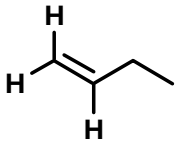
B) 
1) $Hg(OAc)_2$, H_2O
2) $NaBH_4$, EtOH

C) 



DMSO (Solvent)

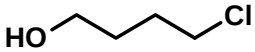
D) 
Br_2 (excess)

E) 

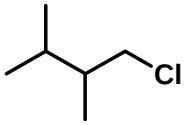
1) O_3, -78 deg C
2) H_3CSCH_3

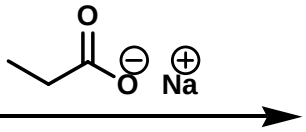
F) 

H_2, Excess
$Pd/CaSO_4$,
"Lindlar cat."

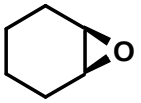
G) 

NaH, THF

H) 



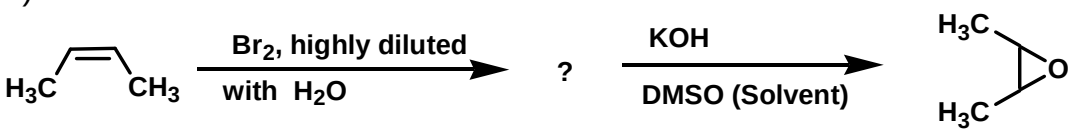
DMF (Solvent)

I) 

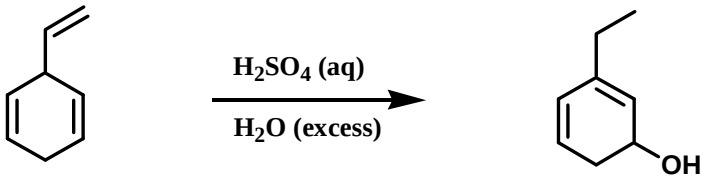
H_2SO_4 (cat)
H_2O, excess

Problem 4. Provide detailed mechanisms for the two reactions below. (16p)

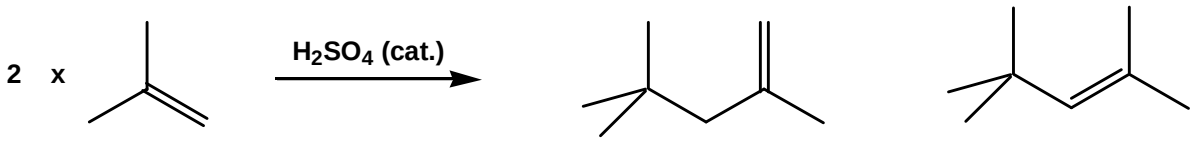
A)



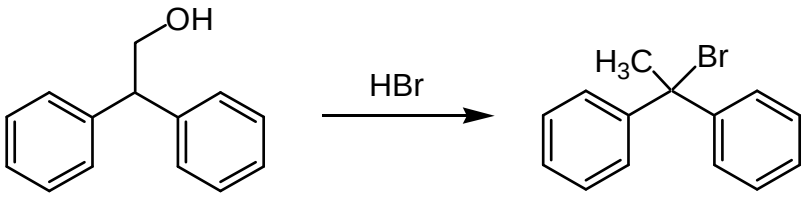
B)



Problem 5. Propose a mechanism that explains formation of the two products from the following reaction. (10p)

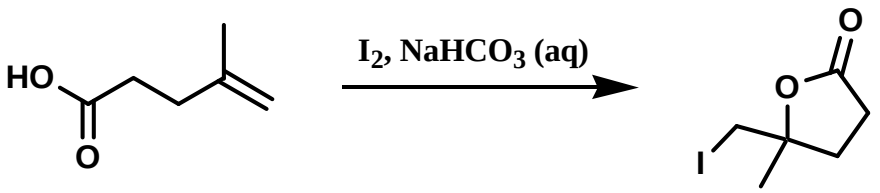


Problem 6. Propose a mechanism that accounts for the following reaction. (12p)

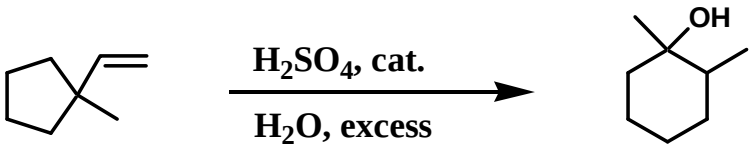


Problem 7. Provide reaction mechanisms for the following two reactions. (16p)

A)

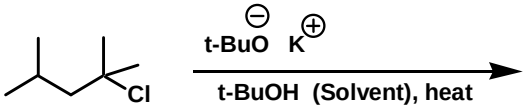


B)

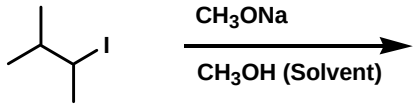


Problem 8. Predict the reaction pathways for the following reactions. Will it be substitution (S_N2 or S_N1) or elimination (*E1* or *E2*)? Write the structural formulas for the major organic products. (15p)

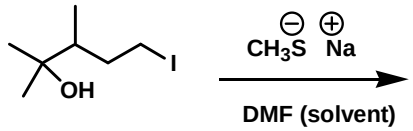
A)



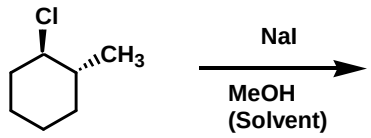
B)



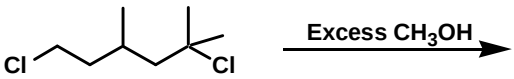
C)



D)

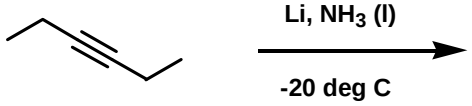


E)

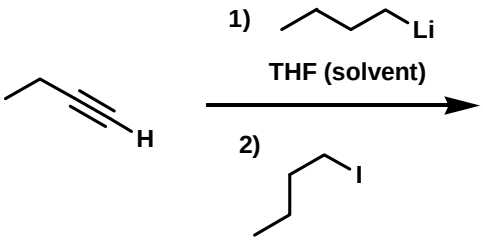


Problem 9 Indicate the products formed in the following reactions. For full credit, correct stereochemical/constitutional isomer must be depicted (if appropriate). (10p)

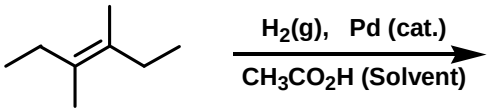
A)



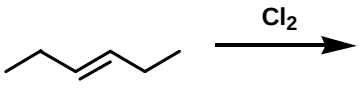
B)



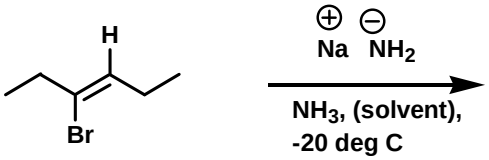
C)



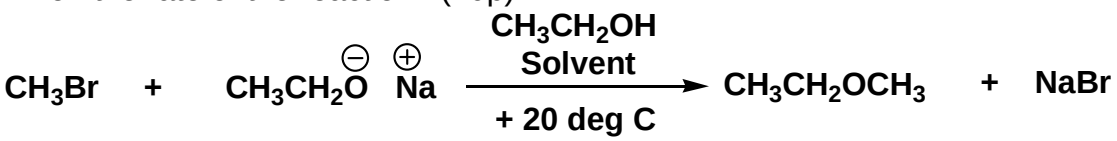
D)



E)



Problem 10. Consider the reaction below. Predict and explain the effect of the changes given on the rate of the reaction. (20p)



A) Change the solvent from CH_3CH_2OH to DMSO.

B) Change the starting material from CH_3Br to $CH_3CH_2CH_2Br$.

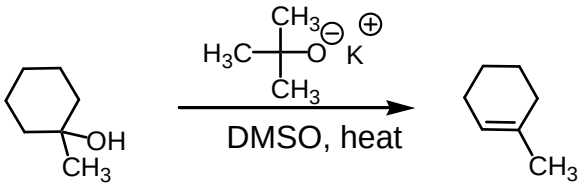
C) Change the starting material from CH_3Br to CH_3F.

D) Change the solvent system by adding H_2O to the CH_3CH_2OH.

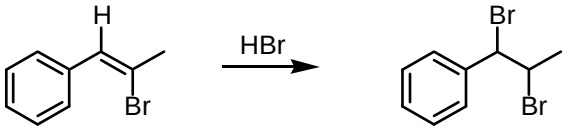
E) Increase the concentration of nucleophile in the CH_3CH_2OH and increase at the same time the temperature from +20deg C to +40deg C.

Problem 11. The reactions shown below are unlikely to occur as described. Tell what is wrong and predict the true product. (25p)

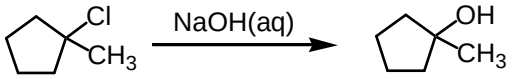
A)



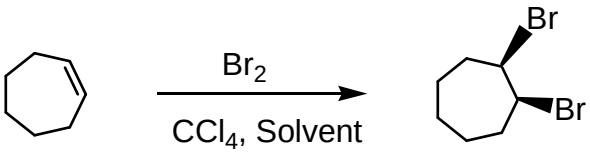
B)



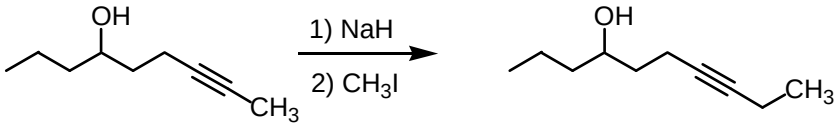
C)



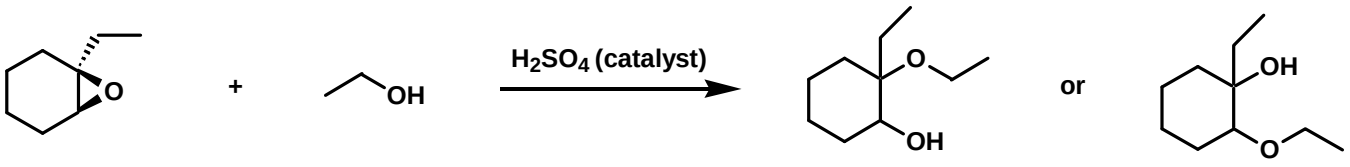
D)



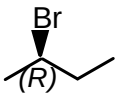
E)



Problem 12. Predict which of these two products would form in this reaction and explain your choice showing ALL of the steps in the mechanisms. Include correct stereochemistry to the product. (13p)

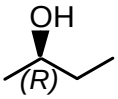


Problem 13. Optically active *R*-bromobutane and *R*-butanol have the optical rotations given:



(*R*)-(-)-2-Bromobutane

[α] = - 23°



(*R*)-(-)-2-Butanol

[α] = - 13°

Treatment of the bromide with NaOH in H_2O yields 2-butanol with an optical rotation of [α] = +6.5°.

A) Is the outcome of this reaction consistent with an S_N2, S_N1 reaction or both? (8p)

B) What is the optical purity of the alcohol in A) after the reaction? (3p)

C) In a different flask, changing the solvent from H_2O to DMSO gave [α] = +13° of the 2-butanol.

Is the outcome in this case consistent with an S_N2, S_N1 reaction or both? (5p)
What is the ratio of R/S in this case? (2p)

Scratch paper

Scratch paper

Scratch paper

Periodic Table of the Elements

1 IA																	18 VIIIA
1 H Hydrogen 1.0079	2 IIA											13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	2 He Helium 4.0026
3 Li Lithium 6.941	4 Be Beryllium 9.0122											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.065	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.409	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.922	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.41	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xeno 131.29
55 Cs Caesium 132.91	56 Ba Banum 137.33	57 *La Lanthanum 138.91	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.97	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 #Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (266)	107 Bh Bohrium (264)	108 Hs Hassium (277)	109 Mt Meitnerium (268)	110 Uun (281)	111 Uuu (272)	112 Uub (285)		114 Uuq (289)				

Atomic number → 6
Symbol → C
Name (IUPAC) → Carbon
Atomic mass → 12.011

IUPAC recommendations →
Chemical Abstracts Service group notation →

*Lanthanide Series	58 Ce Cerium 140.12	59 Pr Praseodymium 140.91	60 Nd Neodymium 144.24	61 Pm Promethium (145)	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.93	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.97
# Actinide Series	90 Th Thorium 232.04	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

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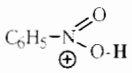
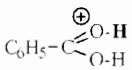
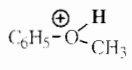
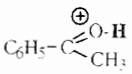
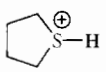
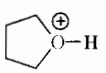
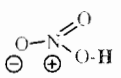
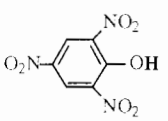
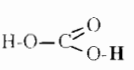
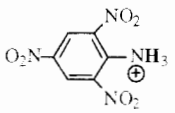
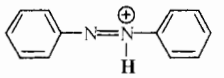
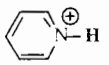
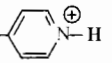
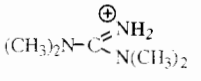
pKa Table (H_2O Reference)

Oxygen Acids

$CF_3SO_2\mathbf{H}$	-14
	-12.4
	-7.8
	-6.5
	-6.2
$(CH_3)_2S^+—\mathbf{H}$	-5.4
	-4.4
$(CH_3)_2O^+—\mathbf{H}$	-3.8
$CH_3SO_2\text{-}\mathbf{OH}$	-2.6
$CH_3O\mathbf{H}_2^+$	-2.2
	-2.05
$(CH_3)_2S{=}O^+—\mathbf{H}$	-1.8
	-1.37
$CF_3CO_2\mathbf{H}$	-0.25
	0.3
$C_6H_5\text{-}CO_2\mathbf{H}$	4.2
$CH_3\text{-}CO_2\mathbf{H}$	4.76
$C_6F_5\text{-}\mathbf{OH}$	5.5
	6.3
$C_6H_5\text{-}\mathbf{SH}$	6.5
$C_6H_5\text{-}\mathbf{OH}$	9.95
$\mathbf{H}CO_3^-$	10.3
R-S-**H**	10.5
HO-**H**	15.7
$CH_3\text{-}\mathbf{OH}$	16
$(CH_3)_3C\text{-}\mathbf{OH}$	20
[t-BuO**H**]	

All compounds shown in this Table are acids herein; the acidic H for which the pKa value is provided is indicated in **bold red**. All acids shown here are monoprotic; that is, only one of the bolded **H**'s will be lost.

Nitrogen Acids

$^+\mathbf{P}H_4$	-14
$C_6H_5\text{-}C{\equiv}N^+—\mathbf{H}$	-10.5
$CH_3\text{-}C{\equiv}N^+—\mathbf{H}$	-10
	-9.3
	-2.9
$(C_6H_5)_2N\mathbf{H}_2^+$	0.78
$CH_3\text{-}P\mathbf{H}_3^+$	2.7
$C_6H_5\text{-}N\mathbf{H}_3^+$	4.6
	5.21
$N{\equiv}C\text{-}CH_2\text{-}CH_2\text{-}N\mathbf{H}_3^+$	7.87
$(CH_3CH_2)_3\text{-}P\mathbf{H}^+$	9.1
	9.2
$^+N\mathbf{H}_4$	9.2
$CH_3CH_2\text{-}N\mathbf{H}_3^+$	10.6
$(CH_3CH_2)_2\text{-}N\mathbf{H}_2^+$	11.0
$(CH_3CH_2)_3\text{-}N\mathbf{H}^+$	10.75
	13.6
$C_6H_5\text{-}N\mathbf{H}_2$	28
$N\mathbf{H}_3$	33

Remember that acidity is defined as follows:

$$\mathbf{H}A \Leftrightarrow \mathbf{H}^+ + A^-$$

Thus:

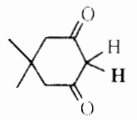
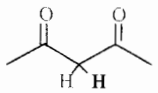
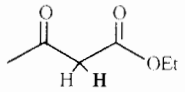
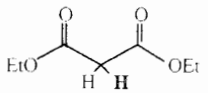
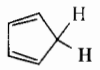
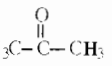
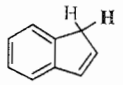
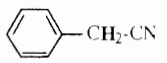
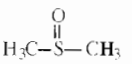
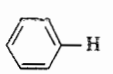
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Taking the log of both sides and multiplying through by -1, we get:

$$pK_a = pH - \log\frac{[A^-]}{[HA]}$$

Leading to this relationship, pKa is defined as -log Ka; as such the more NEGATIVE the value (or the SMALLER the value) the more acidic the compound is.

Carbon Acids

$(NO_2)_2CH_2$	3.6
	5.2
	9
$N{\equiv}C\text{-}\mathbf{H}$	9.1
$O_2N\text{-}CH_3$	10.2
	10.7
$(CF_3)_3C\mathbf{H}$	11
$(N{\equiv}C)_2CH_2$	11.2
	13
	15
	20
	20
	20.8
$C_6H_5\text{-}C{\equiv}C\text{-}\mathbf{H}$	23
$CH_3\text{-}CO_2Et$	24
$CH_3\text{-}SO_2\text{-}CH_3$	33
$CH_3\text{-}C{\equiv}N$	25
$H\text{-}C{\equiv}C\text{-}\mathbf{H}$	24
	29
$CF_3\text{-}\mathbf{H}$	32
$(C_6H_5)_3C\mathbf{H}$	31.5
	33.5
$C_6H_5\text{-}CH_3$	41
$CH_2{=}CH_2$	44
	43
	46
$CH_3\text{-}CH_3$	50