

**Organic Chemistry: Chem 210****Practice Exam 3A**

There are **28** questions on this exam. Check that you have done all of the problems and filled in the first **28** bubbles on the scantron. Most questions are worth 4 points; there are several two-point questions clearly labeled in the text. The maximum score on this exam is 100 points.

*Instructions***Answer sheet**

- 1) On the scantron, you need to clearly fill:
  - your **name** and your **student number**,
  - **section number**: (it is 001)
  - **test form** (white = test form A; yellow = test form B).
- 2) Use a #2 pencil

**Exam policy**

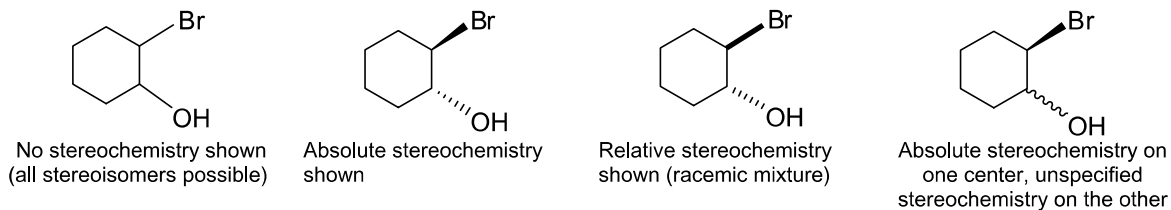
- 1) No electronic devices of any kind, such as calculators, cell phones, or even more advanced digital watches, are allowed. Possession of such devices during the exam, whether in use or not, is grounds for awarding a zero on the exam.
- 2) Molecular models are allowed (no instruction pages are permitted, however).
- 3) There are some blank pages at the end of the test that can be used as scratch paper.
- 4) Relevant tables, including the periodic table, are attached at the end of this exam.
- 5) Numerical values given in one question apply only to that question, and should not be used in other questions, unless there is a specific instruction to do so. If necessary, the values from the provided tables should be used, even if they differ from values that you may remember from different sources.
- 6) The exam results are based strictly on scantron's marks. No extraneous information is used to adjust the scores. Mark your choices with extra care.
- 7) Feel free to take this copy of the exam with you. The answer key will be posted on the web after the exam (under "News").

**Hints**

- 1) As you read the question, underline or circle key words to highlight them for yourself.
- 2) Questions have only one correct answer, unless indicated otherwise. No partial credit will be given.
- 3) There is no penalty for guessing.

**Notes:** I. When listing reagents, a slash (/) is used between reagents that are employed simultaneously, and a semicolon (;) is used between reagents that are employed in a stepwise fashion.

II. The stereochemistry conventions are illustrated below:

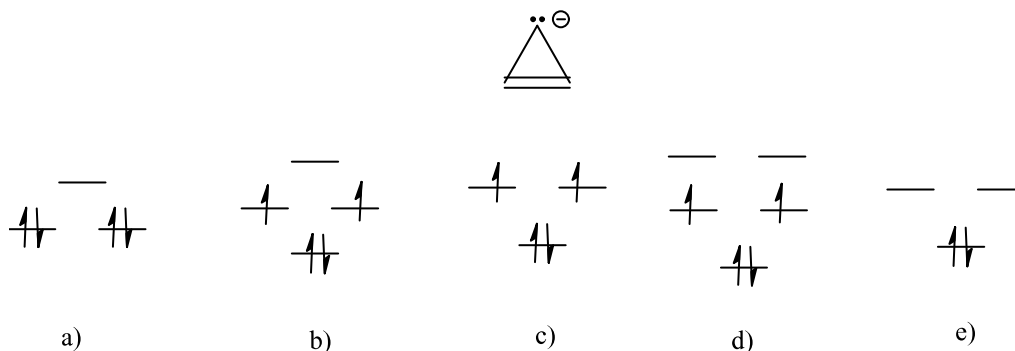


III. Abbreviations: Me = methyl, Et = ethyl, Pr = propyl, Bu = butyl, Pe = pentyl, Ph = phenyl (i.e. benzene as a substituent), AcO = acetate ( $\text{H}_3\text{CCOO}$ ), MCPBA = m-chloroperbenzoic acid., TosO = TsO = tosylate

1. (4 pts) Radicals can be compared according to their selectivity in hydrogen abstractions based on the reactivity-selectivity principle. Which of the following radicals would be expected to have selectivity very similar to that of the  $\text{H}\cdot$  radical?

- a)  $\text{Cl}\cdot$     b)  $\text{F}\cdot$     c)  $\text{HO}\cdot$     d)  $\text{Br}\cdot$     e)  $\text{I}\cdot$

2. (4 pts) Which of the following  $\pi$  MO energy diagrams corresponds to the cyclopropenyl anion?

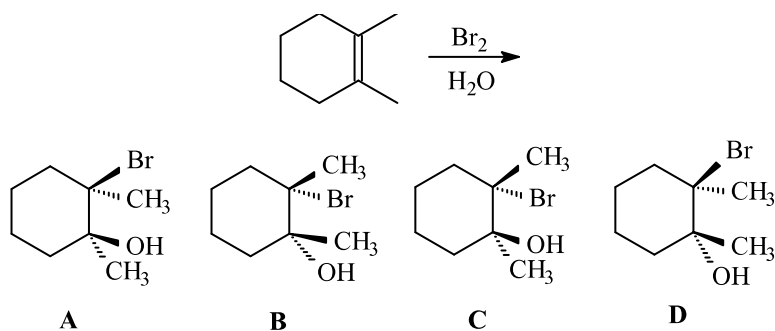


3. (4 pts) Which of the following is the best characterization of the cyclopentadienyl cation?



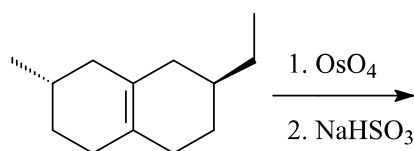
- a) antiaromatic    b) non-aromatic    c) carbocationic    d) aromatic    e) hyperconjugated

4. (4 pts) Which of the following is (are) the product(s) of the reaction shown below?



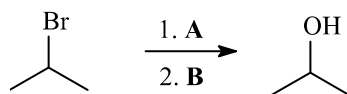
- a) **A**      b) **B**      c) **C**      d) **D**      e) **A and B**      f) **C and D**

5. (4 pts) How many **stereoisomers** of the product will form in this reaction?



- a) 1      b) 2      c) 3      d) 4      e) 5

6. (4 pts) Which of the reagents shown below would accomplish the following transformations?

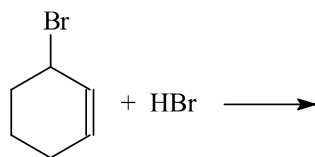


**A**

**B**

- |                             |   |
|-----------------------------|---|
| a) $\text{H}_3\text{O}^+$   | $\text{BH}_3\text{-THF}; \text{H}_2\text{O}_2/\text{NaOH}$  |
| b) $\text{NaOH}$            | $\text{BH}_3\text{-THF}; \text{H}_2\text{O}_2/\text{NaOH}$  |
| c) $\text{HBr}$ in ether    | $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}; \text{NaBH}_4$ |
| d) $\text{NaNH}_2$          | $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}; \text{NaBH}_4$ |
| e) $\text{H}_2/\text{Pd/C}$ | $\text{NBS/DMSO}/\text{H}_2\text{O}$                        |

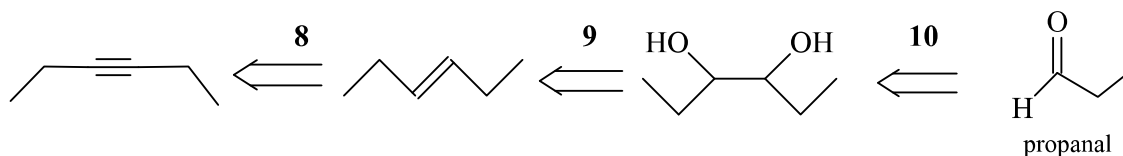
7. (4 pts) Surprisingly, the reaction shown below goes through a bromonium ion. What is (are) the major product(s) of this reaction?



- A:** *trans*-1,3-dibromocyclohexane  
**B:** *cis*-1,3-dibromocyclohexane  
**C:** *trans*-1,2-dibromocyclohexane  
**D:** *cis*-1,2-dibromocyclohexane

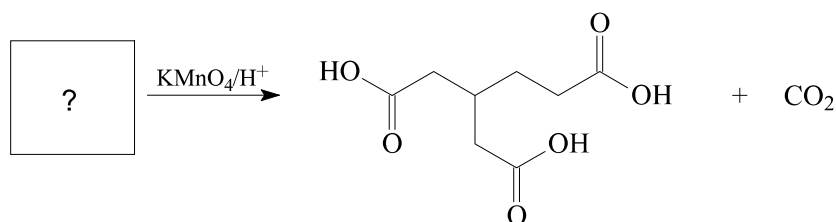
a) **A**    b) **B**    c) **C**    d) **D**    e) **A and B**    f) **C and D**    g) **A and C**    h) **B and D**

8-10. (2 pts each) Here is a retro-synthetic analysis for the preparation of propanal from 3-hexyne. What are the most appropriate reagents to accomplish each step of the **synthesis** of propanal?



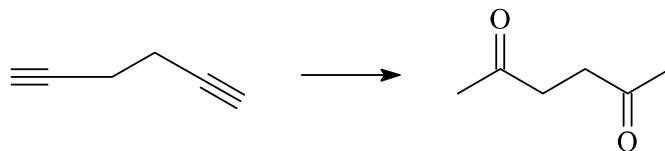
- a) Li/liquid NH<sub>3</sub>    b) BH<sub>3</sub>-THF; H<sub>2</sub>O<sub>2</sub>/NaOH    c) Hg(OAc)<sub>2</sub>/H<sub>2</sub>O; NaBH<sub>4</sub>    d) OsO<sub>4</sub>; NaHSO<sub>3</sub>  
 e) Br<sub>2</sub>/AcOH; NaNH<sub>2</sub>    f) O<sub>3</sub>; Zn/AcOH    g) KMnO<sub>4</sub>/H<sup>+</sup>    h) H<sub>3</sub>O<sup>+</sup>  
 i) H<sub>2</sub>/Lindlar    j) HIO<sub>4</sub>/THF/H<sub>2</sub>O

11. (4 pts) Which of the following compounds was the starting material for the oxidation shown below?



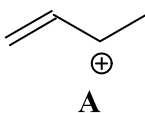
- a)    b)    c)    d)

12. (4 pts) How is the following transformation best carried out?



- a)  $\text{BH}_3\text{-THF}; \text{H}_2\text{O}_2/\text{NaOH}$       b)  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$       c)  $\text{HgSO}_4/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$   
 d)  $\text{OsO}_4; \text{NaHSO}_3$                       e)  $\text{O}_3; \text{Zn}/\text{AcOH}$                       f)  $\text{HIO}_4/\text{H}_2\text{O}/\text{THF}$

13. (4 pts) Carbocation **A** can be an intermediate in many reactions studied in Chem 210. Which of the following reactions **does not** involve **A** as an intermediate?



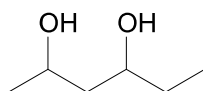
- a) electrophilic addition of HBr to 2-butyne  
 b) electrophilic addition of HCl to 1,2-butadiene  
 c) electrophilic addition of HI to 1,3-butadiene  
 d) rearrangement of 3-bromo-1-butene (the kinetic product) to 1-bromo-2-butene (the thermodynamic product)  
 e) reaction of 3-hydroxy-1-butene with  $\text{H}_2\text{SO}_4$  to yield 1,3-butadiene

14-16. (2 pts each) An unknown hydrocarbon **A**, with formula  $\text{C}_6\text{H}_{12}$ , reacts with 1 molar equivalent of  $\text{H}_2$  over a Pd catalyst. Hydrocarbon **A** also reacts with  $\text{OsO}_4$  to give a diol, **B**. When oxidized with  $\text{KMnO}_4$  in acidic solution, **A** gives 2 fragments. One fragment is propanoic acid,  $\text{CH}_3\text{CH}_2\text{COOH}$ , and the other is a ketone, **C**. From the structures (a)-(j) below, select the correct answers for questions 14-16.

14. What is the structure of **A**?

15. What is the structure of **B**?

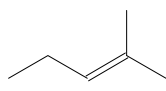
16. What is the structure of **C**?



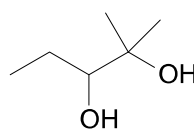
a)



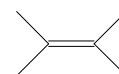
b)



c)



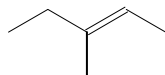
d)



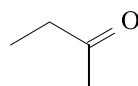
e)



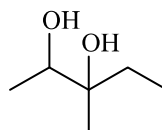
f)



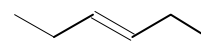
g)



h)

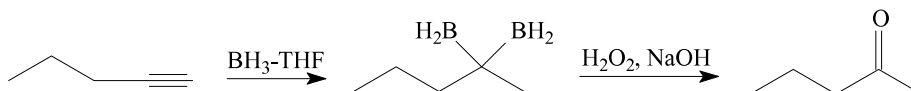


i)



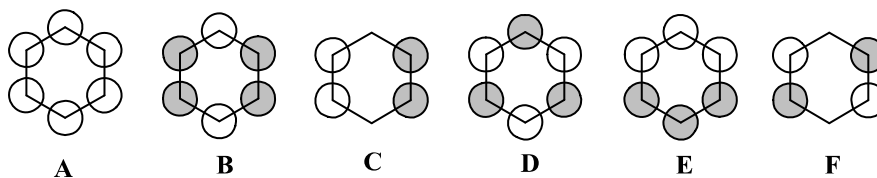
j)

17. (4 pts) Consider the following synthesis. What is **wrong** with these transformations?



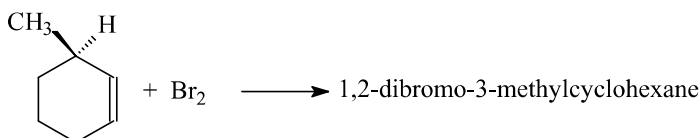
- $\text{BH}_3$  in THF is actually unreactive toward alkynes.
- $\text{BH}_3$  should add to adjacent carbons, rather than the same carbon.
- The oxygen in THF is responsible for oxidation;  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$  are not required.
- Borane can be used as an electrophile only with non-terminal alkynes.
- The borane addition follows regiochemistry opposite to that shown.

18. (4 pts) All six  $\pi$  MOs of benzene are shown below in a random order, in a view from the top (i.e. only top lobes of p orbitals on carbon atoms are visible). Which of the following electronic transitions will correspond to the absorption band with the shortest wavelength?



- $\text{E} \rightarrow \text{F}$
- $\text{A} \rightarrow \text{B}$
- $\text{E} \rightarrow \text{B}$
- $\text{C} \rightarrow \text{F}$
- $\text{C} \rightarrow \text{B}$

19. (4 pts) What is the absolute configuration of the stereogenic centers in the product(s) of the following reaction?



- 1*R*, 2*R*, 3*R*
- 1*S*, 2*S*, 3*S*
- 1*R*, 2*S*, 3*R*
- 1*R*, 2*R*, 3*S*
- 1*R*, 2*S*, 3*S*
- 1*S*, 2*R*, 3*R*
- 1*S*, 2*S*, 3*R*
- 1*R*, 2*R*, 3*R* and 1*S*, 2*S*, 3*R*
- 1*R*, 2*S*, 3*S*
- 1*R*, 2*S*, 3*R* and 1*S*, 2*R*, 3*R*

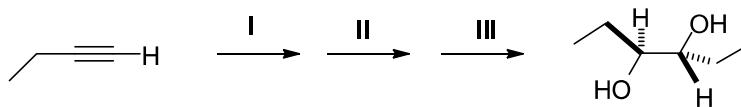
20. (4 pts) In which of the following **solvents** is it possible to create acetylide anions?

- $\text{AcOH}$
- $\text{H}_2\text{O}$
- $\text{H}_3\text{COH}$
- $(i\text{-Pr})_2\text{NH}$
- $t\text{-BuOH}$

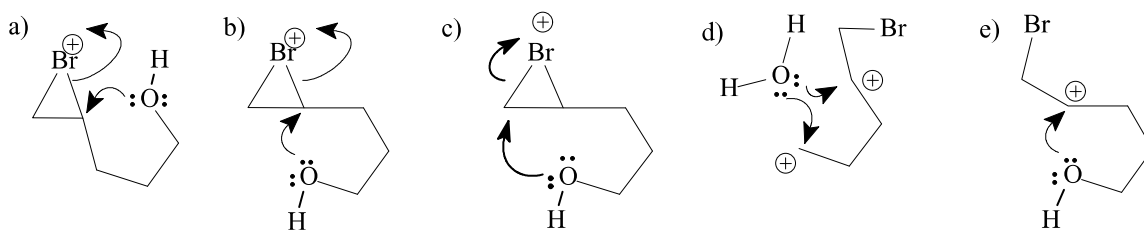
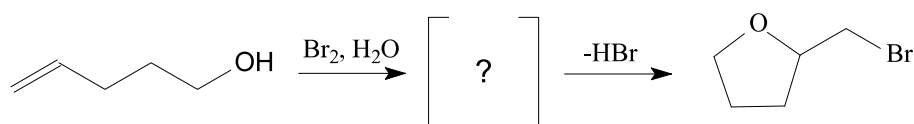
21. (4 pts) (*R*)-2-fluorobutane undergoes free-radical chlorination with  $\text{Cl}_2$ . Including **stereoisomers**, how many monochlorinated substitution products will form?

- 3
- 4
- 5
- 6
- 7
- 8

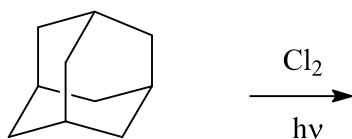
22. (4 pts) The following transformation is carried out in three steps. What are the appropriate reagents for the **first** (I) step?



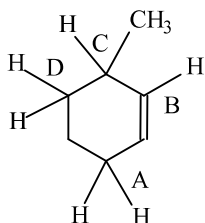
- a)  $\text{H}_2$ /Lindlar catalyst  
 b)  $\text{NaNH}_2/\text{NH}_3$  (liquid);  $\text{CH}_3\text{CH}_2\text{Br}$   
 c)  $\text{O}_3$ ;  $\text{Zn}/\text{AcOH}$   
 d)  $\text{KMnO}_4/\text{NaOH}$   
 e)  $\text{HCCH}/\text{NaNH}_2/\text{THF}/\text{CH}_3\text{I}$   
 f)  $\text{H}_2/\text{Pd}/\text{C}$   
 g)  $\text{Li}/\text{NH}_3$  (liquid)  
 h)  $\text{NBS}/\text{DMSO}/\text{H}_2\text{O}$
23. (4 pts) Consider the following transformation in which a cyclic bromoether is formed, rather than the expected bromohydrin. Which of the electron-pushing scheme **best** represents the mechanism of this reaction?



24. (4 pts) Assuming that only monosubstitution products are formed in the reaction shown below, what would be the expected ratio of 2° to 3° chlorides?

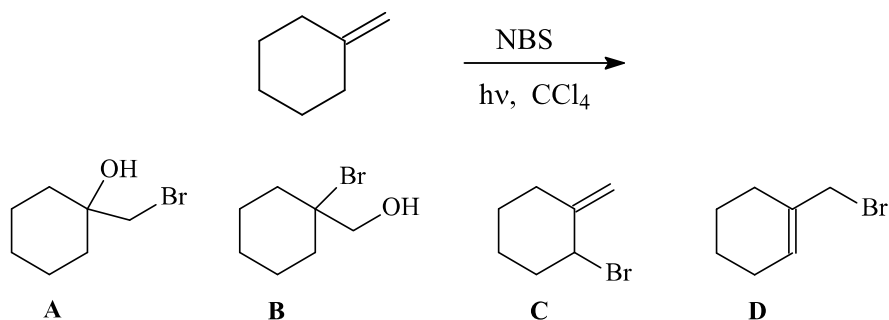


- a) 3/1  
 b) 6/7  
 c) 3/2  
 d) 21/10  
 e) 15/17
25. (4 pts) In the molecule shown below selected C-H bonds are labeled with capital letters. Arrange these bonds according to the difficulty with which they would be broken in radical-forming reactions, starting with the strongest.



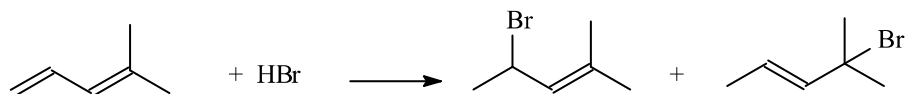
- a)  $\text{B} > \text{D} > \text{A} > \text{C}$   
 b)  $\text{D} > \text{A} > \text{C} > \text{B}$   
 c)  $\text{A} > \text{D} > \text{C} > \text{B}$   
 d)  $\text{B} > \text{C} > \text{A} > \text{D}$   
 e)  $\text{D} > \text{B} > \text{A} > \text{C}$   
 f)  $\text{C} > \text{B} > \text{A} > \text{D}$   
 g)  $\text{A} > \text{C} > \text{B} > \text{D}$   
 h)  $\text{C} > \text{A} > \text{D} > \text{B}$

26. (4 pts) What is(are) the product(s) of the following reaction?



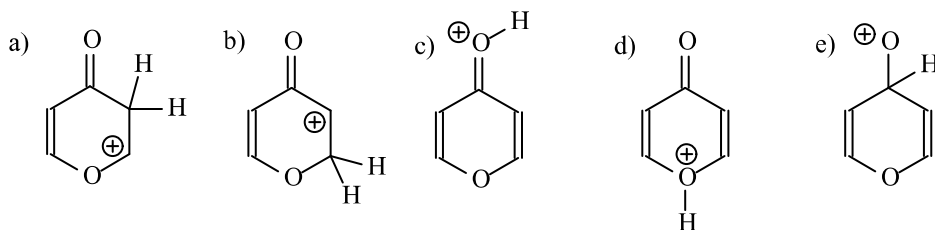
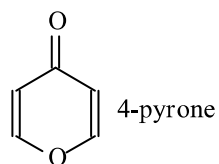
- a) **A**      b) **B**      c) **C**      d) **D**      e) **A and B**      f) **C and D**

27. (4 pts) Consider only the following two major products of the addition reaction shown below. Which statement is true about this reaction?



- a) The major product formed under thermodynamic control is 4-bromo-4-methyl-2-pentene.  
 b) The major product formed under kinetic control is 4-bromo-2-methyl-2-pentene.  
 c) The major product formed under thermodynamic control is 4-bromo-2-methyl-2-pentene.  
 d) The 1,2-adduct is the kinetic product and the 1,4-adduct is the thermodynamic product.  
 e) There is no thermodynamic or kinetic control in this reaction.

28. (4 pts) On reaction with acid, 4-pyrone is protonated to give a very stable cationic product. Which of the following structures shows the protonation site in that product?



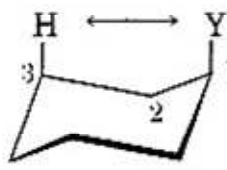
End of the exam



Total Strain Energies in Cycloalkanes		
ring size	kJ/mol	kcal/mol
3	115	27.6
4	110	26.4
5	27	6.5
6	0	0
7	26	6.3
8	40	8.6

Energy Costs for Interactions in Alkane Conformers		
Interaction	kJ/mole	kcal/mole
H-H eclipsed	4.0	1.0
H-CH <sub>3</sub> eclipsed	6.0	1.4
CH <sub>3</sub> -CH <sub>3</sub> eclipsed	11.0	2.6
CH <sub>3</sub> -CH <sub>3</sub> gauche	3.8	0.9

### Steric Strain Due to 1,3-Diaxial Interactions

Y	Strain of one H-Y 1,3-diaxial interaction		
	(kcal/mol)	(kJ/mol)	
—F	0.12	0.5	
—Cl	0.25	1.0	
—Br	0.25	1.0	
—OH	0.5	2.1	
—CH <sub>3</sub>	0.9	3.8	
—CH <sub>2</sub> CH <sub>3</sub>	0.95	4.0	
—CH(CH <sub>3</sub> ) <sub>2</sub>	1.1	4.6	
—C(CH <sub>3</sub> ) <sub>3</sub>	2.7	11.3	
—C <sub>6</sub> H <sub>5</sub>	1.5	6.3	
—COOH	0.7	2.9	
—CN	0.1	0.4	

MAIN GROUPS												MAIN GROUPS						
1A	2A		TRANSITION METALS										3A	4A	5A	6A	7A	8A
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
1 H 1.008	2 He 4.003	3 Li 6.941	4 Be 9.012	5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.180	11 Na 22.990	12 Mg 24.305	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.066	17 Cl 35.453	18 Ar 39.948	
19 K 39.098	20 Ca 40.078	21 Sc 44.956	22 Ti 47.887	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.992	34 Se 78.96	35 Br 79.904	36 Kr 83.80	
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc 98	44 Ru 101.07	45 Rh 102.90	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90	54 Xe 131.29	
55 Cs 132.91	56 Ba 137.33	57 La* 138.91	58 Hf 178.49	59 Ta 180.95	60 W 183.84	61 Re 186.21	62 Os 190.23	63 Ir 192.22	64 Pt 195.08	65 Au 196.97	66 Hg 200.59	67 Tl 204.38	68 Pb 207.2	69 Bi 208.98	70 Po [209]	71 At [210]	72 Rn [222]	
87 Fr [223]	88 Ra [226]	89 Ac** [227]	90 Rf [261]	91 Db [262]	92 Sg [266]	93 Bh [264]	94 Hs [265]	95 Mt [268]	100 [269]	101 [272]	102 [277]	103 [285]	104 [289]	105 [289]	106 [289]	107 [289]	108 [293]	
* LANTHANOIDS		58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm [145]	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97			
** ACTINOIDS		90 Th 232.04	91 Pa 321.04	92 U 238.03	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]			

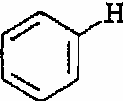
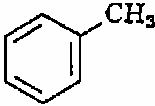
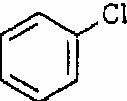
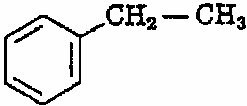
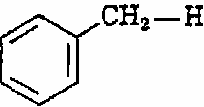
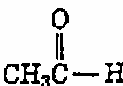
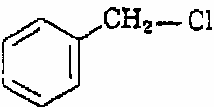
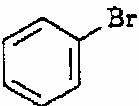
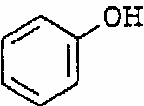
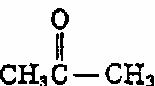
TABLE 22.1 Acidity Constants for Some Organic Compounds

Compound type	Compound	pK <sub>a</sub>
Carboxylic acid	CH <sub>3</sub> COOH	5
1,3-Diketone	CH <sub>2</sub> (COCH <sub>3</sub> ) <sub>2</sub>	9
1,3-Keto ester	CH <sub>2</sub> COCH <sub>2</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	11
1,3-Dinitrile	CH <sub>2</sub> (CN) <sub>2</sub>	11
1,3-Diester	CH <sub>2</sub> (CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	13
Water	HOH	16
Primary alcohol	CH <sub>3</sub> CH <sub>2</sub> OH	16
Acid chloride	CH <sub>3</sub> COCl	16
Aldehyde	CH <sub>3</sub> CHO	17
Ketone	CH <sub>3</sub> COCH <sub>3</sub>	19
Ester	CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	25
Nitrile	CH <sub>3</sub> CN	25
Dialkylamide	CH <sub>3</sub> CON(CH <sub>3</sub> ) <sub>2</sub>	30
Ammonia	NH <sub>3</sub>	35
Dialkylamine	HN( <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	40
Alkyne	HC≡CH	25
Alkene	CH <sub>2</sub> =CH <sub>2</sub>	49
Alkane	CH <sub>3</sub> CH <sub>3</sub>	60

## Selectivity of halogen radicals (per H)

	3°	2°	1°
F•	2	1	1
Cl•	5	3.5	1
Br•	1600	80	1
I•	97000	1100	1

TABLE 5.4 Bond Dissociation Energy Data for the Reaction  $A-B \rightarrow A\cdot + B\cdot$ 

Bond	$\Delta H^\circ$ (kcal/mol)	Bond	$\Delta H^\circ$ (kcal/mol)	Bond	$\Delta H^\circ$ (kcal/mol)
H—H	104	$(CH_3)_3C-I$	50	$CH_3-CH_3$	88
H—F	136	$H_2C=CH-H$	108	$C_2H_5-CH_3$	85
H—Cl	103	$H_2C=CH-Cl$	88	$(CH_3)_2CH-CH_3$	84
H—Br	88	$H_2C=CHCH_2-H$	87	$(CH_3)_3C-CH_3$	81
H—I	71	$H_2C=CHCH_2-Cl$	69	$H_2C=CH-CH_3$	97
Cl—Cl	58		112		102
Br—Br	46		97		72
I—I	36		85		86
$CH_3-H$	104		70	HO—H	119
$CH_3-Cl$	84		82	HO—OH	51
$CH_3-Br$	70		112	$CH_3O-H$	102
$CH_3-I$	56	$HC\equiv C-H$	125	$CH_3S-H$	88
$CH_3-OH$	91	$HC\equiv CH$	210	$C_2H_5O-H$	103
$CH_3-NH_2$	80	$H_2C=CH_2$	150		77
$C_2H_5-H$	98			$CH_3CH_2O-CH_3$	81
$C_2H_5-Cl$	81			NH <sub>2</sub> —H	103
$C_2H_5-Br$	68			H—CN	130
$C_2H_5-I$	53				
$C_2H_5-OH$	91				
$(CH_3)_2CH-H$	95				
$(CH_3)_2CH-Cl$	80				
$(CH_3)_2CH-Br$	68				
$(CH_3)_3C-H$	91				
$(CH_3)_3C-Cl$	79				
$(CH_3)_3C-Br$	65				