CHE321 Exam 3 11/21/2006

The first 12 questions are 5 point multiple choice questions and should be answered by filling in the appropriate bubble for each question.

Questions 13-16 are 10 point short answer questions and should be answered in the space provided on the front and back of the answer form.

Bond ΔH^0		Bond	ΔH^0	Bond	ΔH^0	
H—H bonds		C—C multiple bonds		C-Br bonds		
н—н	435 (104)	CH ₂ =CH ₂	727 (174)	CH ₃ —Br	301 (72)	
D—D	444 (106)	HC≡СН	966 (231)	C ₂ H ₅ —Br	301 (72)	
				(CH ₃) ₉ CH—Br	309 (74)	
X—X bonds		C—H bonds		(CH ₃) ₃ C—Br	305 (73)	
F—F	159 (38)	CH ₃ —H	439 (105)	CH ₉ =CHCH ₉ -Br	247 (59)	
Cl—Cl	247 (59)	C ₂ H ₅ —H	422 (101)	C ₆ H ₅ —Br	351 (84)	
Br—Br	192 (46)	(CH ₃) ₂ CH—H	414 (99)	C ₆ H ₅ CH ₂ —Br	263 (63)	
I—I	151 (36)	(CH ₃) ₃ C—H	405 (97)			
		CH ₉ =CH-H	464 (111)	C—I bonds		
H—X bonds		CH ₂ =CHCH ₂ -H	372 (89)	CH ₃ —I	242 (58)	
H—F	568 (136)	C ₆ H ₅ —H	472 (113)	C ₂ H ₅ —I	238 (57)	
H—Cl	431 (103)	C ₆ H ₅ CH ₉ —H	376 (90)	(CH ₃) ₉ CH—I	238 (57)	
H—Br	368 (88)	нс≡с−н	556 (133)	(CH ₃) ₃ C—I	234 (56)	
н—і	297 (71)			CH ₂ =CHCH ₂ -I	192 (46)	
	1. 1	C-F bonds		C ₆ H ₅ —I	280 (67)	
O—H bonds		CH ₃ —F	481 (115)	C ₆ H ₅ CH ₉ —I	213 (51)	
но—н	497 (119)	C ₂ H ₅ —F	472 (113)			
CH ₃ O—H	439 (105)	(CH ₃) ₂ CH—F	464 (111)	C-N single bonds		
C ₆ H ₅ O—H	376 (90)	C ₆ H ₅ —F	531(127)	CH ₃ —NH ₂	355 (85)	
				C ₆ H ₅ —NH ₉	435 (104	
O—O bonds		C—Cl bonds				
но-он	213 (51)	CH ₃ —Cl	351 (84)	C-O single bonds		
CH ₃ O—OCH ₃	159 (38)	C ₂ H ₅ −Cl	355 (85)	CH ₃ —OH	385 (92)	
(CH ₃) ₃ CO-OC(CH ₃) ₃	159 (38)	(CH ₃) ₉ CH—Cl	355 (85)	C ₆ H ₅ —OH	468 (112	
		(CH ₃) ₃ C—Cl	355 (85)			
C—C single bonds		CH ₂ =CHCH ₂ -Cl	288 (69)			
CH ₃ —CH ₃	376 (90)	C ₆ H ₅ —Cl	405 (97)			
C ₀ H ₅ —CH ₃	372 (89)	C ₆ H ₅ CH ₉ —Cl	309 (74)			
CH ₉ =CH-CH ₃	422 (101)					
CH ₉ =CHCH ₉ -CH ₃	322 (77)					
C ₆ H ₅ —CH ₃	435 (104)					
C ₆ H ₅ CH ₉ —CH ₃	326 (78)					

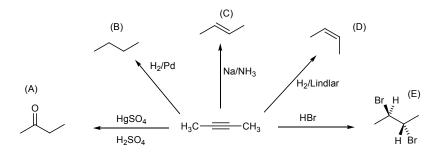
Class and Example	Typical p K_a	Class and Example	Typical pK,
Sulfonic acid		β-Ketoester	
		O H O	
√ SO−H	0-1	CH ₃ —CH—COCH₂CH ₃	11
<u></u>		Water	
Carboxylic acid		HO—H	15.7
P		Alcohol	
CH ₅ CO—H	3-5	CH₃CH₂O— <mark>H</mark>	15-19
Arylammonium ion		Amide	
/=\ H		Ŷ	
⟨	4-5	CH₃CŅ—H	15-19
H		H	
Imide		Cyclopentadiene	
O		H	16
	8-9	X _H	.10
N—H			
~ 1		α-Hydrogen of an aldehyde or keton O	ic
Thiol		∥ CH _* CCH _° — <mark>H</mark>	18-20
CH ₃ CH ₂ S—H	8-12		18-20
Phenol	0-12	α-Hydrogen of an ester Ο	
rnenoi		1	
√	9-10	CH₃CH₂OCCH₂—H	23-25
		Alkyne	
Ammonium ion NH ₃ —H ⁺	9.24	HC≡C— <mark>H</mark>	25
β-Diketone	J.4.1	Ammonia	1122
О Н О		NH ₂ —H	38
CH ₂ —C—CH—CCH ₂	10	Amine	
Nitroalkane	10	[(CH ₃) ₂ CH] ₂ N—H	40
H—CH ₉ NO ₉	10	Alkene	
Alkylammonium ion	0.770	CH₂=CH−H	44
		Alkane	**
(CH ₃ CH ₂) ₃ N—H	10-12	CH₃CH₂— <mark>H</mark>	51

	1	II											Ш	IV	٧	VI	VII	VIII
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8	9 F	10 Ne
	11 Na	12 Mg				Tra	nsition	eleme	ents				13 Al	14 Si	15 P	16 S	17 CI	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
5	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
6	55 Cs																85 At	86 Rn

$ \begin{array}{c c} & H_2 \\ \hline & Pd/C \end{array} $ Br	Selected Reactions of CHE 321	O H Na O Na O Na
Br_2 Br	Note: This list is not complete. You are responsible for the limitations,	O H PBr ₃ Br
HBr H	regiochemstry and stereochemistry of $H_3C \xrightarrow{\qquad} CH_3 \xrightarrow{\qquad} Lindlar$	O H SOCI ₂ CI
1. BH ₃ OH	H ₃ C ————————————————————————————————————	O H 85% H ₃ PO ₄ ==
2. H ₂ O ₂ ,NaOH	H_3C \longrightarrow H_2SO_4 O	PCC O
1. Hg(OAc) ₂ BH ₄	H_3C — H 1. $\underbrace{(sia)_2BH}_{2. H_2O_2, NaOH}$ O	H H ₂ CrO ₄ O
1. OsO ₄ OH	H_3C \longrightarrow H $1. NaNH_2$ \longrightarrow H_3C \longrightarrow	H ₂ O
2. NaHSO ₃ 1. O ₃ H O H	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$0 \xrightarrow{\text{H}} \frac{\text{CI-SiR}_3}{\text{pyridine}} 0 \xrightarrow{\text{SiR}_3}$
1. O ₃ 2. (CH ₃) ₂ S	2. j 3. H*	$O^{SiR_3} \xrightarrow{F^-} O^{H}$
Br Li	X $S_{N1} \text{ or } S_{N2}$ Y	RCO ₃ H O
Li 2. H ⁺ OH	$\begin{array}{c} X \\ B \\ \hline E1 \text{ or } E2 \end{array}$	

Multiple Choice Questions. 60 points Select the best answer to each of the questions.

1. Choose the *incorrect* reaction.



2. Choose the species that could not be used as the base in the following reaction.

3. Professor Lee proposed the following reaction for the preparation of 3-iodo-1-propene from propene.

$$H$$
 + I-I $\frac{1}{h_{V}}$ or heat $\frac{1}{h_{V}}$ + H-

The following two propagation steps were hypothesized. The relevant bond energies in kcal/mole are shown.

Choose the incorrect statement.

(A) The first reaction is endothermic.

- (B) The second reaction is exothermic.
- (C) The overall reaction is exothermic.
- (D) The I–I bond is weaker than the H–I bond.
- (E) The proposed reaction is not a good method for the preparation of 3-iodo-1-propene from propene.

4. Here is a reaction that we did not cover in the lectures.

$$\begin{array}{c} & & Br_2 \\ \hline & & \\ H & & H_2O \end{array}$$

Use your knowledge of mechanisms to choose the most likely product from among the following compounds.

5. On the final exam in CHE 321 a student was asked to propose a synthesis of compound X and came up with the scheme shown below.

The TA grading the problem thought most of the steps were just fine, but she took off a couple of points because she knew that one step would not work. Choose the reaction of the proposed synthesis that is least likely to be successful.

6. The NBS bromination of the compound shown below gives a mixture of products.

Choose the compound that should be the main product of this reaction.

7. Which of the following schemes will proceed to give the compound indicated as the major product.

(1)
$$\begin{array}{c} H \\ O \\ \end{array}$$

$$\begin{array}{c} 1. \text{ NaNH}_2 \\ \hline 2. \\ \text{Br} \end{array}$$

(3)
$$_{\text{H}}^{\oplus}$$
 $_{\text{Na}}^{\oplus}$ $_$

8. Choose the *incorrect* statement about the following two reactions.

(1)
$$CH_3 - \stackrel{H}{C} - H + \cdot CI \longrightarrow CH_3 - \stackrel{H}{C} \cdot + H - CI \qquad \Delta H^\circ = -2 \text{ kcal/mol}$$

(2) $CH_3 - \stackrel{H}{C} - H + \cdot Br \longrightarrow CH_3 - \stackrel{H}{C} \cdot + H - Br \qquad \Delta H^\circ = +13 \text{ kcal/mol}$

- (A) Reaction (1) would be expected to be faster than reaction (2).
- (B) According to Hammond's postulate the transition state of reaction (2) resembles the product.
- (C) According to Hammond's postulate the transition state of reaction (1) resembles the reactant.
- (D) The C-H bond of reaction (2) is completely broken in the transition state.
- (E) The reaction of ethane with the fluorine radical (•F) would be expected to be faster than either (1) or (2).
- 9. Choose the answer that has the following nucleophiles correctly arranged with respect to increasing reactivity.

$$CH_{3}-\overset{..}{\bigcirc}H \qquad CH_{3}-\overset{..}{\bigcirc}\overset{..}{\bigcirc} \qquad CH_{3}-\overset{..}{\bigcirc} \qquad CH_{3}-\overset{..}{\bigcirc} \qquad CH_{3}-\overset{..}{$$

- 10. Choose the *incorrect* statement about organohalogen compounds.
 - A) Organohalogen compounds, such as the polychlorinated biphenyls (PCBs), are persistent in our environment and are often found in the hydrophobic lipid bilayers of our cell membranes.
 - (B) Organohalogen compounds are also produced by living organisms, particularly in the marine environment.
 - (C) Technology has produced commonly used materials containing organohalogen compounds.
 - (D) Based upon periodic table considerations, the C-Cl bond is predicted to be stronger than the C-I bond.
 - (E) Based upon periodic table considerations, the C-Cl bond is predicted to be longer than the C-I bond.
- 11. Choose the order that has the following alkyl bromides correctly arranged with respect to increasing reactivity in a $S_N 2$ reaction.

12. Choose the order that has the following alkyl bromides correctly arranged with respect to increasing reactivity in a S_N1 reaction.

increasing reactivity

(A)
$$CH_3 - Br$$
 $H - \overset{C}{C} - Br$ $CH_3 - \overset{C}{C} - Br$ (B) $CH_3 - \overset{C}{C} - Br$ $CH_$

Short Answer Questions. 40 points.

13. Propose a synthesis of the following compound from compounds containing four carbons or less. (10 points)

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14. Consider the following reaction.

- (a) Give an acceptable name for the product of the above reaction.
- (b) Give the best reactant(s) and reagent(s) that could be used to perform the above transformation in one step using the reactions we have covered in CHE 321.
- 15. (a) Predict the product of the following reaction.

(b) Using the curved arrow formalism, give a reaction mechanism that explains why the following substitution reaction proceeds with retention of configuration.

16. The following reaction of toluene with bromotrichloromethane proceeds via a radical chain mechanism.

- (a) Give the initiating reaction.
- (b) Give the two propagating reactions of this reaction mechanism.
- (c) Give one of the several possible termination reactions.