First	Mid	dterm	Exam
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Monday, January 24, 2022

F	O	rr	n	Δ

You may use model kits but no other material with chemical information without instructor approval.

Please do not use any electronic gadgets.

hydrogen	( I		1070	185	1(5)	6	16.5%	ē	1950	5(5)	151575	100	65%	700	(6)77	7(3)	1513 1	helium
1																		2
H																		He
1.0079																		4.0026
lithium	beryllium												boron	carbon	nitrogen	oxygen	fluorine	neon
3	_4												5	6		8	9	10
Li	Be												В	С	N	0	F	Ne
6.941	9.0122												10.811	12.011	14.007	15.999	18.998	20.180
sodium 11	magnesium 12												aluminium 13	silicon 14	phosphorus 15	sulfur 16	chlorine 17	argon 18
																		. 2550
Na	Mg												ΑI	Si	Р	S	CI	Ar
22.990	24.305			Winds		- towns town		Taxas .		and a fine f		in to be	26.982	28.086	30.974	32.065	35.453	39.948
potassium 19	calcium 20		scandium 21	titanium 22	vanadium 23	chromium 24	manganese 25	iron 26	cobalt 27	nickel 28	copper 29	zinc 30	gallium 31	germanium 32	arsenic 33	selenium 34	bromine 35	krypton 36
K				Ti	1/			Fe		Ni					_	Se		Kr
	Ca		Sc		V	Cr	Mn		Co		Cu	Zn	Ga	Ge	As		Br	
39,098 rubidium	40.078 strontium		44.956 yttrium	47.867 zirconium	50.942 niobium	51.996 molybdenum	54.938 technetium	55.845 ruthenium	58,933 rhodium	58,693 palladium	63,546 silver	65.39 cadmium	69.723 indium	72.61 tin	74.922 antimony	78.96 tellurium	79,904 lodine	83.80 xenon
37	38		39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr		V	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Λa	Cd	In	Sn	Sb	Te	1	Xe
			00.000								Ag							
85.468 caesium	87.62 barium		88.906 lutetium	91.224 hafnium	92.906 tantalum	95.94 tungsten	(98) rhenium	101.07 osmium	102.91 iridium	106.42 platinum	107.87 gold	112.41 mercury	114.82 thallium	118.71 lead	121.76 bismuth	127.60 polonium	126.90 astatine	131.29 radon
55	56	57-70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	*	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
132.91	137,33	, ,	174.97	178.49	180.95	183.84	186.21	190.23	192.22	195,08	196.97	200.59	204.38	207.2	208,98	[209]	12101	[222]
francium	radium		lawrencium	rutherfordium	dubnium	seaborgium	bohrium	hassium	meitnerium	ununnilium	unununium	ununbium	204.38	ununquadium	206.98	[209]	[210]	222
87	88	89-102	103	104	105	106	107	108	109	110	111	112		114				
Fr	Ra	* *	Lr	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq				
[223]	[226]		12621	[261]	12621	12661	[264]	[269]	[268]	[271]	[272]	[277]		[289]				

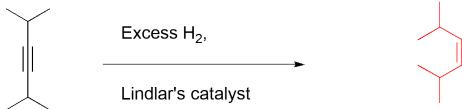
*	Lan	thanic	e ser	ies

<sup>\* \*</sup> Actinide series

	lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	europium 63	gadolinium 64	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	ytterbium 70
1	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb
-	138.91	140.12	140.91	144.24	[145]	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
ı	actinium	thorium	protactinium	uranium	neptunium	plutonium	americium	curium	berkelium	californium	einsteinium	fermium	mendelevium	nobelium
-	89	90	91	92	93	94	95	96	97	98	99	100	101	102
1	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
1	[227]	232.04	231.04	238.03	[237]	[244]	[243]	[247]	[247]	[251]	[252]	[257]	12581	[259]

1. (30 points) Write the expected products for each of the following reactions. Specify stereochemistry where appropriate (you may write "racemic" in place of drawing a second enantiomer).

Α.



В.

C.

E. 
$$CaC_2 + A$$
 Br (2.5 eq.)

## 2. (25 points) Write (over the arrow) the reagents needed to accomplish the following transformations.

A.

B.

1. BH<sub>3</sub>•THF or B<sub>2</sub>H<sub>6</sub>

D.

mCPBA (or any percarboxylic acid)

(racemic)

E.

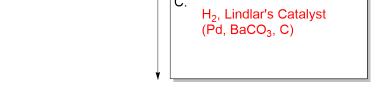
Na<sup>+</sup> : C≡CH (or CaC<sub>2</sub>, or HCCH/strong base)

F.

1. Strong base (NaNH<sub>2</sub>)--excess

 (20 points) Write mechanisms (using the correct electron-pushing formalism, and as many steps as needed) for each of the following transformations.
 A.

4. (16 points) Long-chain fatty alcohols are often observed to be chemical signaling agents in insect biochemistry. Fill in the boxes for intermediate structures or reagents in the following synthesis of (9S, 10R)-1,9,10-octadecanetriol. (You may abbreviate using the  $(CH_2)_n$  terminology).





\* This reagent reacts selectively with monosubstituted alkenes in the presence of more highly substututed alkenes

5. (9 points) The heat of hydrogenation for trans-cyclooctene, shown at the right) is -34.4 kcal/mol.

Explain why this is different from that for cis-cyclooctene (-23.0 kcal/mol).

$$H_2$$
, Pd/C
$$\Delta H^\circ = -34.4 \text{ kcal/mol}$$

Trans cyclooctene is a strained alkene. Placing the trans double bond in a ring imposes a force that slightly twists the C=C bond, decreasing the overlap between p orbitals and weakening the pi bond. Numerically, this effect is worth 11.4 kcal/mol.



$$H_2$$
, Pd/C
$$\Delta H^\circ = -23.0 \text{ kcal/mol}$$

(A secondary observation, not necessary to answer what was asked, is that cis cyclooctene gives a much lower than expected heat of hydrogenation. This is due to ring strain arising mostly from torsional eclipsing interactions in cyclooctane.)

## Bond strengths (kcal/mol):

F-F	38
Cl-Cl	58
Br-Br	46
I-I	36
H-F	136
H-Cl	103
H-Br	87
H-I	71
CH₃-H	105
CH <sub>3</sub> CH <sub>2</sub> -H	101
(CH <sub>3</sub> ) <sub>2</sub> CH-H	98.5
(CH <sub>3</sub> ) <sub>3</sub> C-H	96.5
CH₃-F	110
CH₃-Cl	85
CH₃-Br	70
CH₃-I	57
CH₃CH₂-F	111
CH₃CH₂-Cl	84
CH₃CH₂-Br	70
CH₃CH₂-I	56
(CH3)2CH-F	111
(CH₃)₂CH-Cl	84
(CH₃)₂CH-Br	71
$(CH_3)_2CH-I$	56
(CH <sub>3</sub> ) <sub>3</sub> C-F	110
(CH₃)₃C-Cl	85
(CH₃)₃C-Br	71
(CH <sub>3</sub> ) <sub>3</sub> C-I	55

## Typical Heats of Hydrogenation