

# CHEM 3331 (Richardson) Second Midterm Exam – Mar. 13, 2018

Your Name: Key

Student ID: \_\_\_\_\_

- Recitation (check one)      O 8:00 Wed (Rachel Weintraub)  
 O 12:00 Wed (Patrick Li)      O 2:00 Wed (Patrick Li)  
 O 4:00 Wed (Michael Ortiz)      O 9:00 Thu (Josh Kamps)  
 O 11:00 Thu (Josh Kamps)      O 1:00 Thu (Aaron Hinds)  
 O 3:00 Thu (Rachel Weintraub)      O 5:00 Thu (Rachel Weintraub)

Question	Score	Out of
1		30
2		15
3		5
4		30
5		15
6		5
7		10 e.c.
<b>Total</b>		<b>100</b>

This is a closed-book exam. The use of notes, calculators, or cell phones will not be allowed during the exam. You may use models sets brought in a clear ziplock bag. Use the backs of the pages for scratch work. If your final answer is not clearly specified, you will lose points. For mechanisms, show all intermediates including correct formal charges, but do not show transition states. For synthesis, show the product of each synthetic step, but do not show mechanisms. You do not need to show the exact structure of transition metal catalysts.

Hydrogen																Helium																			
1 <b>H</b> 1.0079																2 <b>He</b> 4.0026																			
Lithium				Beryllium				Boron				Carbon				Nitrogen				Oxygen				Fluorine				Neon							
3 <b>Li</b> 6.941				4 <b>Be</b> 9.0122				5 <b>B</b> 10.811				6 <b>C</b> 12.011				7 <b>N</b> 14.007				8 <b>O</b> 15.999				9 <b>F</b> 18.998				10 <b>Ne</b> 20.180							
Sodium				Magnesium				Aluminum				Silicon				Phosphorus				Sulfur				Chlorine				Argon							
11 <b>Na</b> 22.990				12 <b>Mg</b> 24.305				13 <b>Al</b> 26.982				14 <b>Si</b> 28.086				15 <b>P</b> 30.974				16 <b>S</b> 32.065				17 <b>Cl</b> 35.453				18 <b>Ar</b> 39.948							
Potassium		Calcium		Scandium		Titanium		Vanadium		Chromium		Manganese		Iron		Cobalt		Nickel		Copper		Zinc		Gallium		Germanium		Arsenic		Selenium		Bromine		Krypton	
19 <b>K</b> 39.098		20 <b>Ca</b> 40.078		21 <b>Sc</b> 44.956		22 <b>Ti</b> 47.867		23 <b>V</b> 50.942		24 <b>Cr</b> 51.996		25 <b>Mn</b> 54.938		26 <b>Fe</b> 55.845		27 <b>Co</b> 58.933		28 <b>Ni</b> 58.693		29 <b>Cu</b> 63.546		30 <b>Zn</b> 65.38		31 <b>Ga</b> 69.723		32 <b>Ge</b> 72.61		33 <b>As</b> 74.922		34 <b>Se</b> 78.96		35 <b>Br</b> 79.904		36 <b>Kr</b> 83.80	
Rubidium		Strontium		Yttrium		Zirconium		Niobium		Molybdenum		Technetium		Ruthenium		Rhodium		Palladium		Silver		Cadmium		Indium		Tin		Antimony		Tellurium		Iodine		Xenon	
37 <b>Rb</b> 85.468		38 <b>Sr</b> 87.62		39 <b>Y</b> 88.906		40 <b>Zr</b> 91.224		41 <b>Nb</b> 92.906		42 <b>Mo</b> 95.94		43 <b>Tc</b> 98		44 <b>Ru</b> 101.07		45 <b>Rh</b> 102.91		46 <b>Pd</b> 106.42		47 <b>Ag</b> 107.87		48 <b>Cd</b> 112.41		49 <b>In</b> 114.82		50 <b>Sn</b> 118.71		51 <b>Sb</b> 121.76		52 <b>Te</b> 127.60		53 <b>I</b> 126.90		54 <b>Xe</b> 131.29	
Cesium		Barium		Lanthanum		Hafnium		Tantalum		Tungsten		Rhenium		Osmium		Iridium		Platinum		Gold		Mercury		Thallium		Lead		Bismuth		Polonium		Astatine		Radon	
55 <b>Cs</b> 132.91		56 <b>Ba</b> 137.33		* <b>* Lu</b> 174.97		71 <b>Hf</b> 178.49		72 <b>Ta</b> 180.95		73 <b>W</b> 183.84		74 <b>Re</b> 186.21		75 <b>Os</b> 190.23		76 <b>Ir</b> 192.22		77 <b>Pt</b> 195.08		78 <b>Au</b> 196.97		79 <b>Hg</b> 200.59		80 <b>Tl</b> 204.39		81 <b>Pb</b> 207.2		82 <b>Bi</b> 208.98		83 <b>Po</b> [209]		84 <b>At</b> [210]		85 <b>Rn</b> [222]	
Francium		Radium		* <b>* Lr</b>		103 <b>Rf</b>		104 <b>Db</b>		105 <b>Sg</b>		106 <b>Bh</b>		107 <b>Hs</b>		108 <b>Hs</b>		109 <b>Mt</b>		110 <b>Uun</b>		111 <b>Uuu</b>		112 <b>Uub</b>		113 <b>Uuq</b>									

\* Lanthanide series

57	58	59	60	61	62	63	64	65	66	67	68	69	70
<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>	<b>Tm</b>	<b>Yb</b>
138.91	140.12	140.91	144.24	144.91	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.04
89	90	91	92	93	94	95	96	97	98	99	100	101	102
<b>Ac</b>	<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>	<b>Md</b>	<b>No</b>
[227]	232.04	231.04	238.03	237.04	244	[243]	[247]	[247]	[251]	[252]	[257]	[258]	[259]

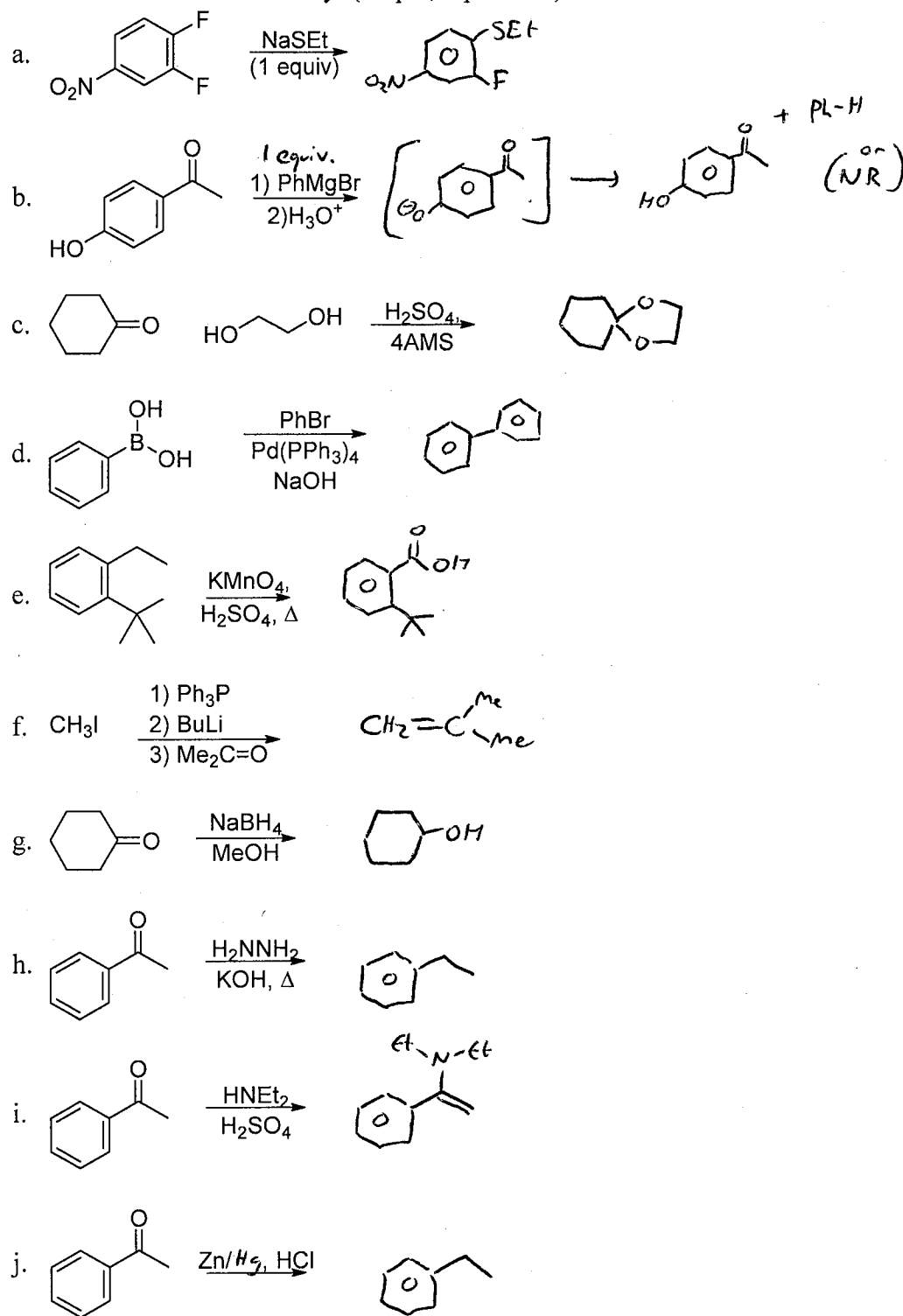
\*\* Actinide series

## pKa Values

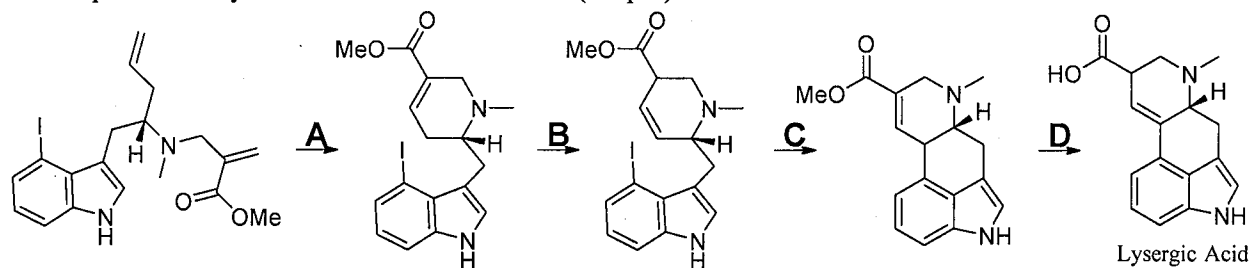
HI	-10	CH <sub>3</sub> COOH	4.7	ArOH	10	H <sub>2</sub>	35
HBr	-8	HN <sub>3</sub>	4.7	RSH	10-12	NH <sub>3</sub>	36
HCl	-6	H <sub>2</sub> S	7.0	H <sub>2</sub> O	15.7	H <sub>2</sub> C=CH <sub>2</sub>	45
H <sub>3</sub> O <sup>+</sup>	-1.7	NH <sub>4</sub> <sup>+</sup>	9.3	ROH (R=alkyl)	16-18	CH <sub>4</sub>	60
HF	3.2	HCN	9.4	HC≡CH	26		

Average: 80  
 St Dev: 19  
 Max: 108  
 Min: 15

1) Predict the major product of the following reactions. If no reaction occurs, then write NR. Do not show stereochemistry. (30 pts; 3 pts each)

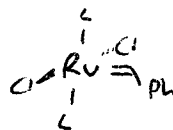


- 2) Lysergic acid is a precursor for a wide range of psychoactive compounds including LSD (lysergic acid diethylamide). A new synthesis of lysergic acid was recently published; a few steps of this synthesis are shown below. (15 pts)



- a. What reaction is happening in step A? What reagents are used for this step? (5 pts)

Grubbs metathesis  $\rightarrow$   $\text{C}_2$ , or Grubbs, or

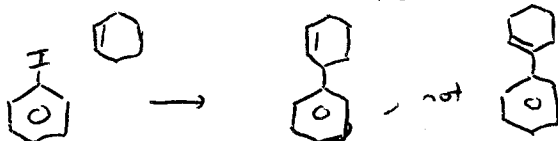


- b. What reaction is happening in step C? What reagents are used for this step? (5 pts)

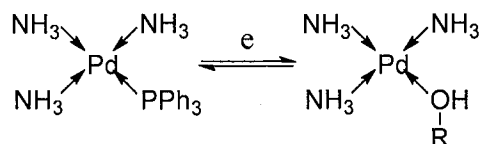
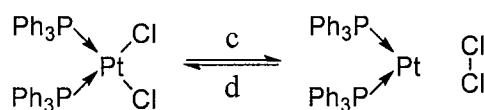
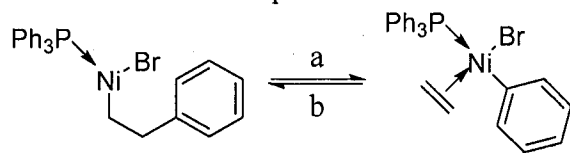
Heck rxn  $\rightarrow$   $\text{Pd}(\text{PAr}_3)_4 + \text{Et}_3\text{N}$

- c. What changes occur to the molecule during step D? Given the regiochemical outcome of step C, why is step D necessary? (5 pts)

Heck rxn on cycloalkenes products alkene in wrong location, compared to where it needs to be in D. (Also in D, ester at top left has become an acid).



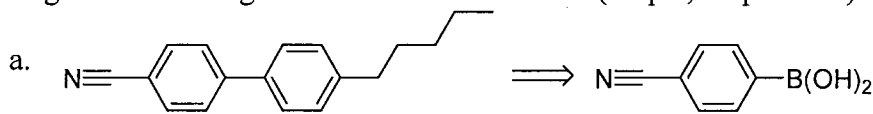
- 3) Label each of the steps in terms of basic transition metal-ligand reaction steps. (5 pts)



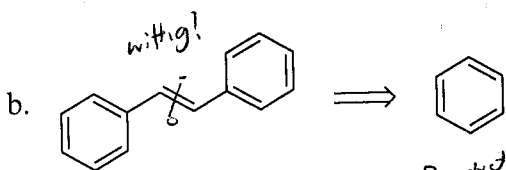
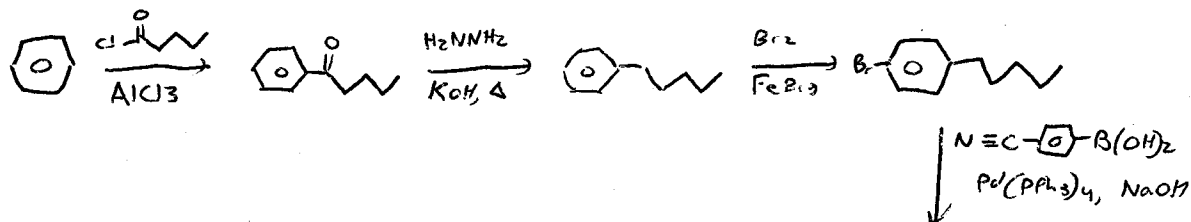
**Describe each step:**

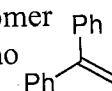
- a.  $\beta$ -elimination  
 b. ligand insertion  
 c. reductive elimination  
 d. oxidative addition  
 e. ligand substitution

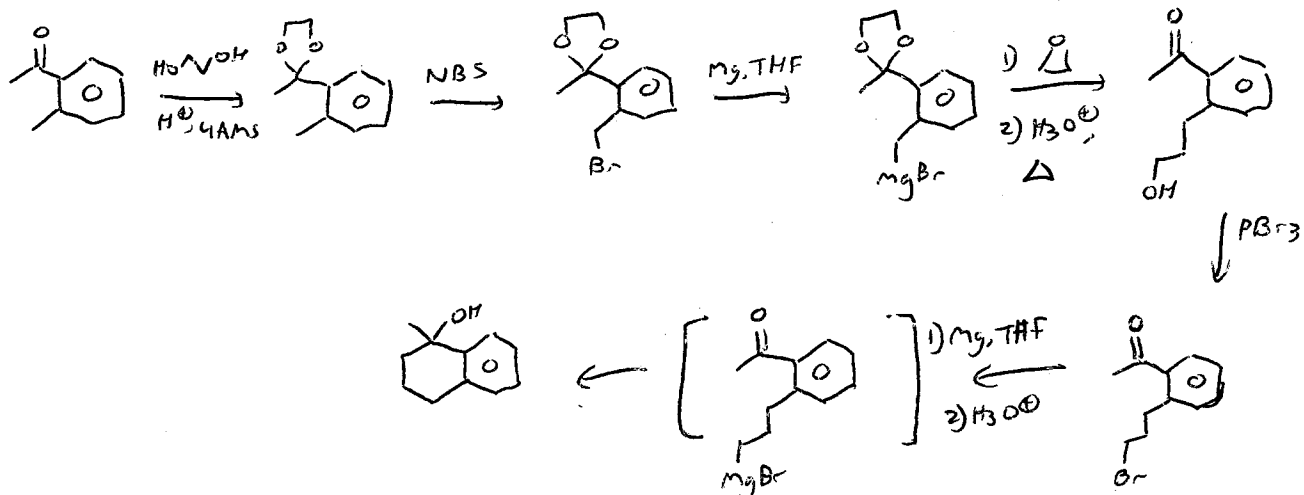
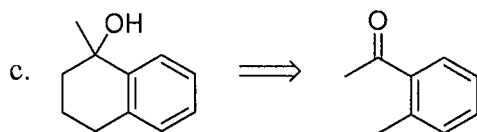
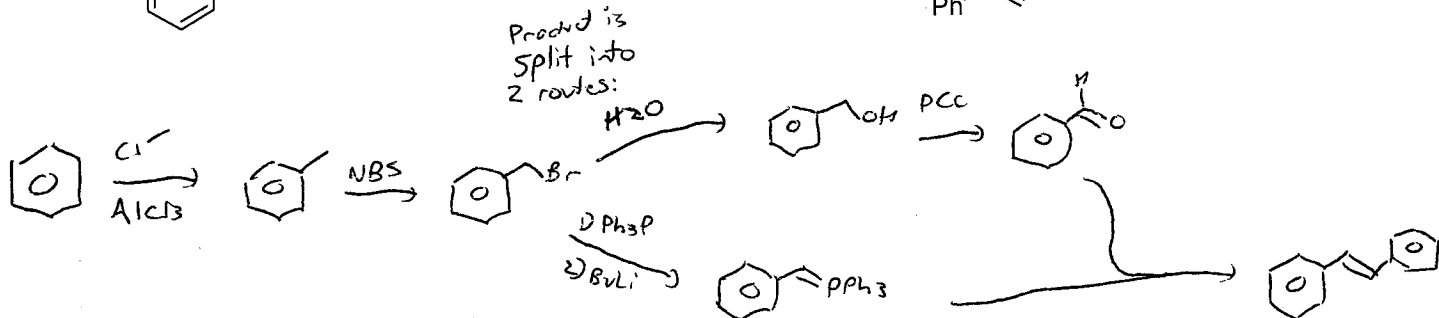
4) Find a way to synthesize the desired product from the given starting material plus any other reagents containing at most six carbon atoms. (30 pts; 10 pts each)



Make right side:

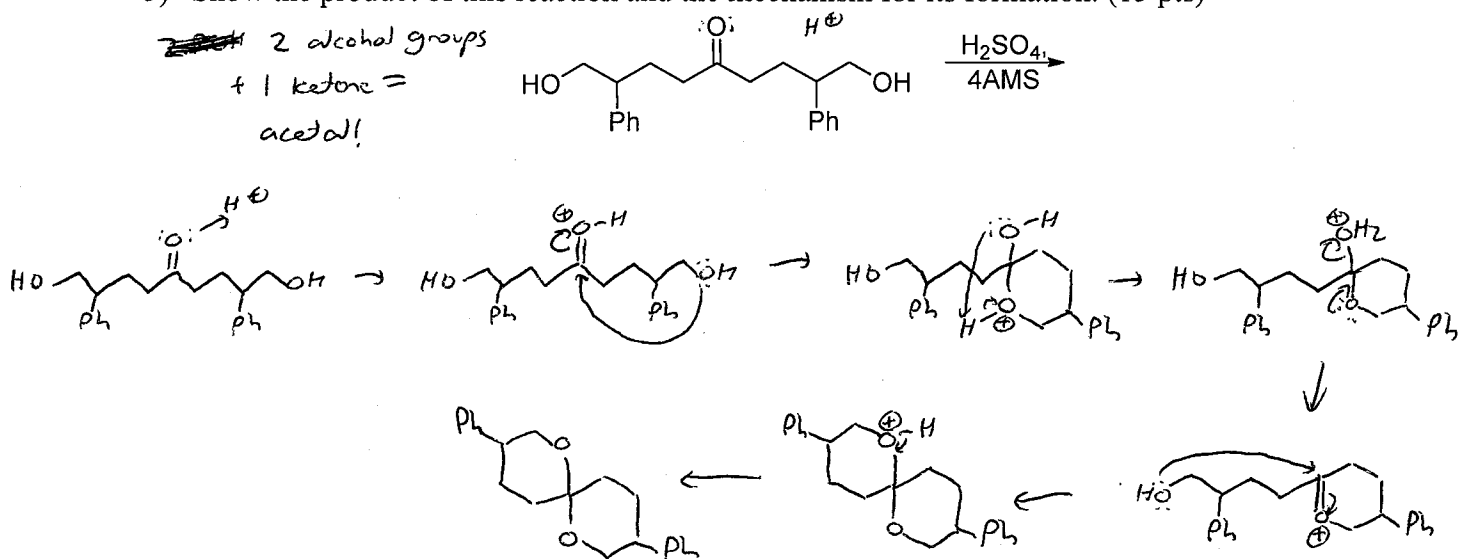


This should be the **only** regioisomer formed - no 

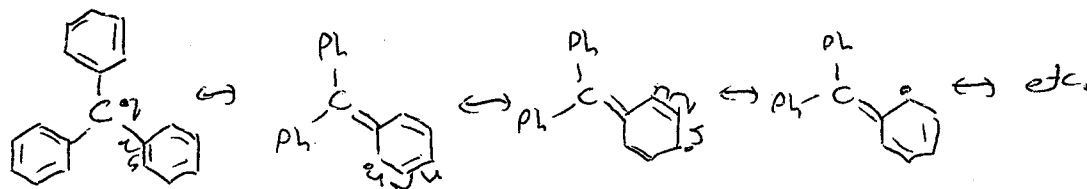


5) Show the product of this reaction and the mechanism for its formation. (15 pts)

~~2~~ 2 alcohol groups  
+ 1 ketone =  
acetal!



6) Moses Gomberg was the first chemist to synthesize the trityl radical,  $\text{Ph}_3\text{C}\cdot$ , which is extraordinarily stable for a radical. Explain its stability in 20 words or less. (5 pts)



This radical is triply benzylic, so there are (3 locations per ring) + (1 location on central C) = 10 possible locations for radicals & it's very heavily resonance-stabilized.

7) Extra credit! Rank these compounds by how much they favor forming the gem-diol (1 = largest amount of gem-diol at equilibrium). (10 pts e.c.)

