# PRACTICE PROBLEMS: SOLUTIONS

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(1) <u>KINETICS</u> (2) EQUILIBRIUM (3)<u>ACID-BASE</u> (4)<u>THERMODYNAMICS</u> (5) <u>ELECTROCHEMISTRY</u> (6) NUCLEAR CHEMISTRY (7) ORGANIC CHEMISTRY (8) <u>BIOCHEMISTRY</u> (9) TRANSITION METALS

# TABLE () F () N F N F N F S

Consider the reaction between nitrogen monoxide and hydrog

 $2 \text{ NO (g)} + 2 \text{ H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{ H}_2\text{O}(\text{g})$ 

Given the following initial rates data collected at 300 K, dete rate law for the reaction.

- answer -

Begin by constructing the generic rate law: Rate  $= k[NO]^{a}[H_{2}]^{b}$ Understand that we will need to solve for the orders *a* and *b* using the isolation method.

Compare experiments 3 and 4 for order a:

$$\frac{\text{Rate}_{4}}{\text{Rate}_{3}} = \frac{k[\text{NO}]_{4}^{a}[\text{H}_{2}]_{4}^{b}}{k[\text{NO}]_{3}^{a}[\text{H}_{2}]_{3}^{b}} \qquad k[\text{H}_{2}]^{b} \text{ cance}$$

$$\frac{\text{Rate}_{4}}{\text{Rate}_{3}} = \left(\frac{[\text{NO}]_{4}}{[\text{NO}]_{3}}\right)^{a}$$

$$\frac{1.2 \times 10^{-4} \text{ M/min}}{3.0 \times 10^{-5} \text{ M/min}} = \left(\frac{0.0020 \text{ M}}{0.0010 \text{ M}}\right)^{a}$$

$$4 = 2^{a}$$

$$a = 2$$

This means that our rate law is:

Rate =  $k[NO]^{2}[H_{2}]^{1}$ 

gen gases:	Expt.	[NO] <sub>0</sub> (M)	[H <sub>2</sub> ] <sub>0</sub> (M)	Initial Rate (M/
	1	0.0060	0.0010	$1.8 \times 10^{-4}$
• . •	2	0.0060	0.0020	$3.6 \times 10^{-4}$
ermine the	3	0.0010	0.0060	$3.0 \times 10^{-5}$
	4	0.0020	0.0060	$1.2 \times 10^{-4}$

*Compare experiments 2 and 1 for order b:* 

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$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[\text{NO}]_2^a[\text{H}_2]_2^b}{k[\text{NO}]_1^a[\text{H}_2]_1^b} \qquad k[\text{NO}]^a \text{ canc}$$
$$\frac{\text{Rate}_2}{\text{Rate}_1} = \left(\frac{[\text{H}_2]_2}{[\text{H}_2]_1}\right)^b$$
$$\frac{3.6 \times 10^{-4} \text{ M/min}}{1.8 \times 10^{-4} \text{ M/min}} = \left(\frac{0.0020 \text{ M}}{0.0010 \text{ M}}\right)^b$$
$$2 = 2^b$$
$$b = 1$$





Consider the reaction between nitrogen monoxide and hydrog

 $2 \text{ NO (g)} + 2 \text{ H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2 \text{ H}_2\text{O}(\text{g})$ 

Given the following initial rates data collected at 300 K, dete rate constant *k* (value and units) for the reaction.

- answer -

From the previous slide, our rate law is: Rate  $= k[NO]^2[H_2]^1$ 

Now that we have our rate law we can solve for the rate constant, *k*, by plugging in the values from any experiment. I'll use experiment 1:

Rate<sub>1</sub> = 
$$k$$
[NO]<sub>1</sub><sup>2</sup>  
1.8 × 10<sup>-4</sup>  $\frac{M}{min} = k(0.00)$   
 $k = 5.0 \times 1$ 

Expt.	[NO] <sub>0</sub> (M)	[H <sub>2</sub> ] <sub>0</sub> (M)	Initial Rate (M/
1	0.0060	0.0010	$1.8 \times 10^{-4}$
2	0.0060	0.0020	$3.6 \times 10^{-4}$
3	0.0010	0.0060	$3.0 \times 10^{-5}$
4	0.0020	0.0060	$1.2 \times 10^{-4}$
	1 2	1       0.0060         2       0.0060         3       0.0010	1         0.0060         0.0010           2         0.0060         0.0020           3         0.0010         0.0060

 ${}^{2}_{1}[H_{2}]^{1}_{1}$ 

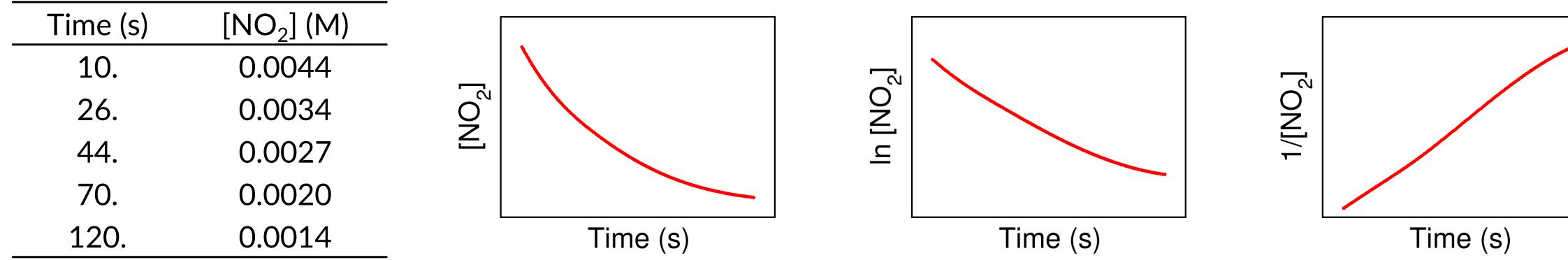
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(60 \text{ M})^2 (0.0010 \text{ M})
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 $0^{3} M^{-2} \cdot min^{-1}$ 



The following concentration-time data are plotted below for the decomposition of nitrogen dioxide gas at 298 K.  $2 \operatorname{NO}_2(g) \rightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$ 

What is the order of the reaction with respect to  $[NO_2]$ ?



#### - answer -

Recall that the concentration-time plot that gives a straight line (y = mx + b) gives us the order of the reaction.

- If  $[NO_2]$  vs. time is a linear plot, then the reaction is zero-order with respect to  $[NO_2]$ .
- If  $\ln [NO_2]$  vs. time is a linear plot, then the reaction is first-order with respect to  $[NO_2]$ . ullet
- If  $1/[NO_2]$  vs. time is a linear plot, then the reaction is second-order with respect to  $[NO_2]$ .



Consider the decomposition of  $NO_2$  (g) from Problem 1.3:

 $2 \operatorname{NO}_2(g) \rightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$ 

Which of the following proposed mechanism(s) is (are) not vali Justify your choice briefly.

- answer -

From the previous slides, our rate law is: Rate =  $k[NO_2]$ 

To find a valid mechanism, we need the elementary rate law for the slowest elementary step to match the overall rate law.

Mechanism (i) Elementary rate laws Step 1:  $NO_2 \rightarrow NO + O$ (slow) rate<sub>1</sub> =  $k_1$ [NO<sub>2</sub>] Step 2:  $N_2O + O \rightarrow N_2 + O_2$  (fast)

Mechanism (ii) Elementary rate laws Step 1:  $NO_2 + NO_2 \rightleftharpoons N_2O_4$  (fast)  $K_c = \frac{[N_2O_4]}{[NO_2]^2} \Longrightarrow [N_2O_4] = K_c[NO_2]^2$ Step 2:  $N_2O_4 \rightarrow NO + NO_3$  (slow) rate<sub>2</sub> =  $k_2[N_2O_4]$  $= k_2 K_{\rm c} [\rm NO_2]^2$  $= k' [NO_2]^2$ Step 3:  $NO_3 \rightarrow NO + O_2$ (fast)

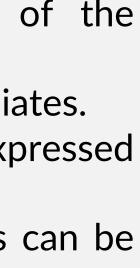
	(i)	$NO_2 \rightarrow NO + O$ $NO_2 + O \rightarrow NO + O_2$	(slow) (fast)
<u>lid</u> ?	(ii)	$NO_2 + NO_2 \rightleftharpoons N_2O_4$ $N_2O_4 \rightarrow NO + NO_3$ $NO_3 \rightarrow NO + O_2$	(fast) (slow) (fast)
$[NO_2]^2$	(iii)	$NO_2 + NO_2 \rightarrow NO + NO_3$ $NO_3 \rightarrow NO + O_2$	(slow) (fast)

Mechanism (iii)	Elementary rate laws
Step 1: $NO_2 + NO_2 \rightarrow NO + NO_3$	(slow) rate <sub>1</sub> = $k_1 [NO_2]^2$
Step 2: $NO_3 \rightarrow NO + O_2$	(fast)

Mechanism (i) is not valid since it is first-order in  $[NO_2]$ .

Some notes about rate laws:

- We can write elementary rate laws based on the stoichiometry of the elementary steps.
- The rate laws can only be depend on reactants, not products or intermediates. If an intermediate is present in the elementary rate law, it must be re-expressed in terms of reactants somehow – see Mechanism (ii).
- If a prior step is in equilibrium, the reactant or product concentrations can be expressed in terms of the  $K_c$  expression – see Mechanism (ii).



Consider the decomposition of  $NO_2$  (g) from Problem 1.3 and 1.4: The initial concentration of  $[NO_2]_0 = 5.56 \times 10^{-3}$  M. After 500 s have elapsed, the concentration of  $NO_2$  is  $4.14 \times 10^{-4}$  M. Calculate the rate constant *k* (value and units) for the reaction. - answer -

Rate =  $k[NO_2]^2$ From the previous slides, our rate law is:

We can use the second-order integrated rate law to determine the value of the rate constant k:

$$\frac{1}{[NO_2]_t} = kt + \frac{1}{[NO_2]_0}$$
$$\frac{1}{4.14 \times 10^{-4} \text{ M}} = k(500 \text{ s}) + \frac{1}{5.56 \times k}$$
$$k = 4.47 \text{ M}^{-1} \cdot \text{s}^{-1}$$

 $2 \operatorname{NO}_2(g) \rightarrow 2 \operatorname{NO}(g) + \operatorname{O}_2(g)$ 

10<sup>-3</sup> M

### EQUILIBRIUM: PROBLEM 2.1

 $2 H_2 S(g) =$ Consider the following gaseous equilibrium: the value of  $K_c$ ?

- answer -

Step 1: Write down the expression for the equilibrium constant,  $K_p$ .

Step 2: Prepare an ICE chart (Initial, Change, and Equilibrium)

Step 3: Recognize that  $x = P_{S_2} = 0.020$  atm

Step 4: Solve for the equilibrium partial pressures.

Step 5: Use the Equilibrium (E) values to evaluate  $K_p$ .

Step 6: Solve for  $K_c$ .

Note that  $\Delta n = \Sigma n_{prod} - \Sigma n_{react} = 3 - 2 = 1$ 

$$K_{\rm p} = \frac{\left(P_{\rm H_2}\right)^2 P_{\rm S_2}}{\left(P_{\rm H_2S}\right)^2}$$
$$= \frac{(0.040)^2 (0.020)}{(9.9_6)^2}$$
$$K_{\rm p} = 3.2_3 \times 10^{-7}$$

$$\Rightarrow 2 H_2 (g) + S_2 (g)$$

A 10.0 L vessel contains 10.0 atm of  $H_2S$  gas at 800 K initially. If the partial pressure of  $S_2$  gas is 0.020 atm at equilibrium, what is

	$2 H_2 S$	<u>+</u>	$2 H_2$	+	S
<u> </u>	10.0 atm	<b>`</b>	0 atm	•	0 atm
С	- 2x		+ 2x		+ x
E	10.0 – 2x		2x		X

 $P_{S_2} = 0.020$  atm  $P_{\rm H_2} = 2(0.020 \, {\rm atm}) = 0.040 \, {\rm atm}$  $P_{\rm H_2S} = (10.0 - 2 \times 0.020)$  atm = 9.9<sub>6</sub> atm

$$K_{\rm p} = K_{\rm c} (RT)^{\Delta \rm n}$$
  
3.2<sub>3</sub> × 10<sup>-7</sup> =  $K_{\rm c} (0.08206 \times 800)^{3-2}$   
 $K_{\rm c} = 4.9 \times 10^{-9}$ 



#### EQUILIBRIUM: PROBLEM 2.2

Which of the following changes would increase the concentration of  $[H_2]$  in the following chemical equilibrium?

 $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2$ 

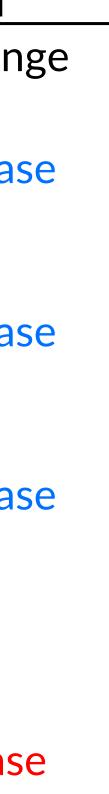
- answer -

Write down the expressions for the equilibrium constant

	Change	Response of system	[H <sub>2</sub> ]
(a)	Adding more C (s).	Since pure solids/liquids do not affect equilibria, there will be no shift.	No chan
(b)	Adding more CO (g).	Adding products will make $Q > K$ , and the system will shift to the left to achieve equilibrium.	Decreas
(c)	Removing H <sub>2</sub> O (g).	Removing reactants will make $Q > K$ , and the system will shift to the left to achieve equilibrium.	Decreas
(d)	8	Increasing the total pressure of the system increases the partial pressures of the gases. As such, the system will shift to the side with a lesser number of moles of gas (left) in order to decrease the partial pressures and total pressure of the system.	Decreas
(e)	Increasing the temperature.	Since the reaction is endothermic ( $\Delta H > 0$ ), we can treat heat as a reactant. heat + C (s) + H <sub>2</sub> O (g) $\Rightarrow$ CO (g) + H <sub>2</sub> (g) Increasing temperature/heat would shift the reaction to the right (Q < K).	Increase

(g) 
$$; \Delta H = +131 \text{ kJ}$$

nts: 
$$K_{\rm c} = \frac{[{\rm CO}][{\rm H}_2]}{[{\rm H}_2{\rm O}]}$$
  $K_{\rm p} = \frac{P_{\rm CO}P_{{\rm H}_2}}{P_{{\rm H}_2{\rm O}}}$ 



### ACID-BASE: PROBLEM 3.1

What is the pH of a 125 mL solution of 0.10 M  $C_6H_5COOH$ ? - answer -

Benzoic acid (C<sub>6</sub>H<sub>5</sub>COOH) is a weak acid with a  $K_a = 6.25 \times 10^{-5}$  at 298 K. Step 1: Note that  $C_6H_5COOH$  is a weak acid because  $K_a$  is small, so we have to consider the weak acid dissociation equilibrium. Step 2: Write out the balanced equilibrium for the weak acid dissociation and the  $K_{a}$  expression. Step 3: Construct an ICE chart. Fill in the initial values, then the stoichiometric changes (x), and then equilibrium concentrations. Step 4: We can use the equilibrium (E) concentration values to plug into our expression for  $K_a$ . Step 5: Finally solve for x. What does x represent? Step 6: Calculate the pH.

		C <sub>6</sub> H₅COOH ≓	H+	+ C <sub>6</sub> H <sub>5</sub> CO
-	Ι	0.10 M	0	0
	С	- X	+ x	+ X
	Е	0.10 – x	X	X
-				

Because the value of  $K_a$  is very small, we know that the system undergo very little change (x value) toward the right in o achieve equilibrium. In other words, we can take "x" to I small/negligible and invoke the approximation that:  $0.10 - x \approx 0.10$ 

$$K_{a} = \frac{[H^{+}][C_{6}H_{5}COO^{-}]}{[C_{6}H_{5}COOH]} = 6.25 \times 10^{-5}$$

$$6.25 \times 10^{-5} = \frac{(x)(x)}{0.10 - x}$$

$$6.25 \times 10^{-5} \approx \frac{x^{2}}{0.10}$$

$$x = 2.5 \times 10^{-3} M = [H^{+}]$$

$$pH = -\log(2.5 \times 10^{-3}) = 2.60$$

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#### ACID-BASE: PROBLEM 3.2

Hydrazoic acid (N<sub>3</sub>H) is a weak acid with a  $K_a = 1.9 \times 10^{-5}$  at 298 K. To 100. mL of 0.25 M N<sub>3</sub>H we add 0.50 g of NaOH. What is the pH of the resulting solution? You may assume no change in volume or temperature. - answer -

Step 1: Determine the number of moles of  $N_3H$  and  $OH^-$ :  $n_{N_3H} = 0.100 \text{ L} \times \frac{0.25 \text{ mol } N_3H}{1 \text{ L}} = 0.025 \text{ mol } N_3H \quad n_{OH}$ 

Step 2: Consider the reaction (not equilibrium) between  $N_3H$  a Step 3: Note we are not at the equivalence point, so we can use the Henderson-Hasselbach equation to find the pH.

		N <sub>3</sub> H	+ OH-	$\rightarrow$ N <sub>3</sub> <sup>-</sup>
	Ι	0.025 mol	0.012 <sub>5</sub> mol	0 mol
	С	- 0.012 <sub>5</sub>	- 0.012 <sub>5</sub>	+ 0.0125
	"E"	0.0125	0	0.0125
Convert to M by dividing by V <sub>tot</sub> = 0.100 L		► 0.12 <sub>5</sub> M	0 M	0.12 <sub>5</sub> M

Because NaOH is a strong base it dissociates completely: NaOH (s)  $\rightarrow$  Na<sup>+</sup> (aq) + OH<sup>-</sup> (aq)

$$- = 0.50 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{39.998 \text{ g}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.012_5 \text{ mol OH}^-$$
  
and OH<sup>-</sup>.

+ H<sub>2</sub>O  
n/a 
$$\longrightarrow$$
 OH<sup>-</sup> is the limiting reactant.  
n/a  
n/a  
 $pH = pK_a + log \frac{[N_3^-]}{[N_3H]}$   
 $= -log(1.9 \times 10^{-5}) + log \frac{[0.12_5]}{[0.12_5]}$   
 $= 4.72_1 - 0$   
pH = 4.72

#### ACID-BASE: PROBLEM 3.3

A buffer with pH = 4.87 is made from 10.0 mL of 0.75 M acetic acid (CH<sub>3</sub>COOH) and 5.0 mL of 2.0 M sodium acetate (NaCH<sub>3</sub>COO). Acetic acid is a weak acid with a  $K_a = 1.8 \times 10^{-5}$  at 298 K. Calculate the pH of the solution if 0.00010 mol of NaOH are added to the buffer. You may assume no change in volume or temperature. - answer -

First, ask yourself what NaOH will react with in the buffer equilibrium: the acid or its conjugate-base? Since NaOH is a base, it should react with the acid (not equilibrium) via:  $CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$ We can construct an IC"E" chart in moles to help us out here.

	CH <sub>3</sub> COOH +	OH-	$\rightarrow$	CH <sub>3</sub> COO <sup>-</sup>	+	$H_2O$	<b>Why "ICE" in quotations?</b> Remember that ICE charts are for equilibrium processes. At the instant of mixing HC
Ι	0.0075 mol	0.00010 mol		0.010 mol		n/a	the buffer, we get a non-equilibrium and unidirectional reaction between the conjugate and H <sup>+</sup> to form acid. The "ICE" chart is still <i>useful</i> because it simplifies the stoichion
С	- 0.00010	- 0.00010		+ 0.00010		n/a	calculations we would normally have to do for non-equilibrium chemical reactions: (1
"E"	0.0074	0		0.0101		n/a	the limiting reactant, (2) determine how much excess reactant is left, and (3) determine much product is formed.

Now, just apply the Henderson-Hasselbach equation to estimate

ate the pH:  

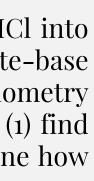
$$pH = pK_{a} + \log\left(\frac{[CH_{3}COO^{-}]}{[CH_{3}COOH]}\right)$$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{\frac{0.010_{1} \text{ mol}}{0.0150 \text{ L}}}{\frac{0.0074 \text{ mol}}{0.0150 \text{ L}}}\right)$$

$$= 4.74_{5} + 0.13_{5}$$

$$pH = 4.88$$





#### THERMODYNAMICS: PROBLEM 4.1

Consider the following reaction:

 $CaSO_4 \cdot 2H_2O(s) \rightarrow CaSO_4(s) + 2H_2O(g)$ Given the following thermodynamic data at 25 °C, calculate the standard Gibbs free energy change ( $\Delta G_{rxn}^{o}$ ) at 25 ° C.

#### - answer -

There are two ways to find the value of  $\Delta G_{rxn}^{o}$ :

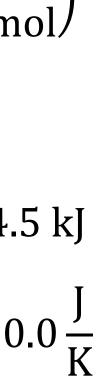
(1) 
$$\Delta G_{\text{rxn}}^{o} = \sum n_{\text{prod}} \Delta G_{\text{f,prod}}^{o} - \sum n_{\text{react}} \Delta G_{\text{f,react}}^{o}$$
$$= \left[ (1 \text{ mol } \text{CaSO}_4) \times \left( -1322.0 \frac{\text{kJ}}{\text{mol}} \right) + (2 \text{ mol } \text{H}_2\text{O}) \times \left( -228.6 \frac{\text{kJ}}{\text{mol}} \right) \right] - (1 \text{ mol } \text{CaSO}_4 \cdot 2\text{H}_2\text{O}) \times \left( -1797.4 \frac{\text{kJ}}{\text{mol}} \right)$$
$$\Delta G_{\text{rxn}}^{o} = 18.2 \text{ kJ}$$

$$(2) \quad \Delta H_{\rm rxn}^{\rm o} = \left[ (1 \, \text{mol} \, \text{CaSO}_4) \times \left( -1434.5 \frac{\text{kJ}}{\text{mol}} \right) + (2 \, \text{mol} \, \text{H}_2\text{O}) \times \left( -241.8 \frac{\text{kJ}}{\text{mol}} \right) \right] - (1 \, \text{mol} \, \text{CaSO}_4 \cdot 2\text{H}_2\text{O}) \times \left( -2022.6 \frac{\text{kJ}}{\text{mol}} \right) = 104$$

$$\Delta S_{\rm rxn}^{\rm o} = \left[ (1 \, \text{mol} \, \text{CaSO}_4) \times \left( 106.5 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) + (2 \, \text{mol} \, \text{H}_2\text{O}) \times \left( 188.8 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \right] - (1 \, \text{mol} \, \text{CaSO}_4 \cdot 2\text{H}_2\text{O}) \times \left( 194.1 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) = 290$$

$$\Delta G_{\rm rxn}^{\rm o} = \Delta H_{\rm rxn}^{\rm o} - T\Delta S_{\rm rxn}^{\rm o} = 104.5 \, \text{kJ} - (298.15 \, \text{K}) \left( 0.2900 \frac{\text{kJ}}{\text{K}} \right) = 18.0 \, \text{kJ}$$

	CaSO <sub>4</sub> ·2H <sub>2</sub> O (s)	CaSO <sub>4</sub> (s)	H <sub>2</sub> O (g)
$\Delta G_{\rm f}^{\rm o} \left(\frac{\rm kJ}{\rm mol}\right)$	-1797.4	-1322.0	-228.6
$\Delta H_{\rm f}^{\rm o} \left(\frac{\rm kJ}{\rm mol}\right)$	-2022.6	-1434.5	-241.8
$S^{\circ}\left(\frac{J}{\mathrm{mol}\cdot\mathrm{K}}\right)$	194.1	106.5	188.8



#### THERMODYNAMICS: PROBLEM 4.2

Consider the following decomposition reaction:

 $2 \text{ HgO}(s) \rightarrow 2 \text{ Hg}(l) + O_2(g)$ 

Given the following thermodynamic data at 25 °C, determine if the decomposition reaction is spontaneous at 800 K.

- answer -

There are two ways to solve this problem. For both, you will need to first find the following two properties:

$$\Delta H_{rxn}^{o} = \left[ (2 \mod Hg) \times \left( 0 \frac{kJ}{mol} \right) + (1 \mod O_2) \times \left( 0 \frac{kJ}{mol} \right) \right] - (2 \mod HgO) \times \left( -58.5 \frac{kJ}{mol} \right) = 181.66 \text{ kJ}$$

$$\Delta S_{rxn}^{o} = \left[ (2 \mod Hg) \times \left( 75.0 \frac{J}{mol \cdot K} \right) + (1 \mod O_2) \times \left( 205.0 \frac{J}{mol \cdot K} \right) \right] - (2 \mod HgO) \times \left( 70.29 \frac{J}{mol \cdot K} \right) = 216.42 \frac{J}{K}$$
od 1: Calculate  $\Delta G_{rxn}^{o}$  at 800 K  

$$O_{rxn}^{o} = \Delta H_{rxn}^{o} - T\Delta S_{rxn}^{o} = 181.66 \text{ kJ} - (800 \text{ K}) \left( 0.21642 \frac{kJ}{K} \right) = 8.68 \text{ kJ}$$
od 2: Calculate the T at which the reaction would be spontaneous  

$$0 = \Delta H_{rxn}^{o} - T\Delta S_{rxn}^{o}$$

$$T = \frac{\Delta H_{rxn}^{o}}{\Delta S_{rxn}^{o}} = \frac{181.66 \text{ kJ}}{0.21642 \frac{kJ}{K}} = 839 \text{ K}$$

Me

$$\Delta H_{rxn}^{o} = \left[ (2 \mod Hg) \times \left(0 \frac{kJ}{mol}\right) + (1 \mod O_2) \times \left(0 \frac{kJ}{mol}\right) \right] - (2 \mod HgO) \times \left(-58.5 \frac{kJ}{mol}\right) = 181.66 \text{ kJ}$$

$$\Delta S_{rxn}^{o} = \left[ (2 \mod Hg) \times \left(75.0 \frac{J}{mol \cdot K}\right) + (1 \mod O_2) \times \left(205.0 \frac{J}{mol \cdot K}\right) \right] - (2 \mod HgO) \times \left(70.29 \frac{J}{mol \cdot K}\right) = 216.42 \frac{J}{K}$$
ethod 1: Calculate  $\Delta G_{rxn}^{o}$  at 800 K
$$\Delta G_{rxn}^{o} = \Delta H_{rxn}^{o} - T\Delta S_{rxn}^{o} = 181.66 \text{ kJ} - (800 \text{ K}) \left(0.21642 \frac{kJ}{K}\right) = 8.68 \text{ kJ}$$
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Me

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$$T = \frac{\Delta H_{\rm rxn}^{\rm o}}{\Delta S_{\rm rxn}^{\rm o}} = \frac{181.66 \text{ kJ}}{0.21642 \frac{\text{kJ}}{\text{K}}} = 839 \text{ K}$$

	HgO (s)	Hg (I)	O <sub>2</sub> (g)
$\Delta G_{\rm f}^{\rm o} \left(\frac{\rm kJ}{\rm mol}\right)$	-58.5	0	0
$\Delta H_{\rm f}^{\rm o} \left(\frac{\rm kJ}{\rm mol}\right)$	-90.83	0	0
$S^{\circ}\left(\frac{J}{\mathrm{mol}\cdot\mathrm{K}}\right)$	70.29	75.9	205.0

# **ELECTROCHEMISTRY: PROBLEM**

Using the following table of standard reduction potentials, the following redox reactions represent spontaneous reaction place in a voltaic/Galvanic cell?

- answer -

Each of the redox reactions uses the same reducing agent (anode): Mn (s)  $\rightarrow$  Mn<sup>2+</sup> (aq) + 2 e<sup>-</sup> with  $E^{\circ} = -1.185$  V. A spontaneous (voltaic cell) reaction will have:  $E_{cell}^{o} = E_{cathode}^{o}$ 

Redox Reaction		Spontaneous?
(a) Mn (s) + Sn <sup>2+</sup> (aq) $\rightarrow$ Mn <sup>2+</sup> (aq) + Sn (s)	$E_{\text{cell}}^{\text{o}} = -0.136 \text{ V} - (-1.185 \text{ V}) = +1.049 \text{ V}$	Yes
(b) Mn (s) + Ni <sup>2+</sup> (aq) $\rightarrow$ Mn <sup>2+</sup> (aq) + Ni (s)	$E_{\text{cell}}^{\text{o}} = -0.257 \text{ V} - (-1.185 \text{ V}) = +0.928 \text{ V}$	Yes
(c) Mn (s) + 2 Na <sup>+</sup> (aq) $\rightarrow$ Mn <sup>2+</sup> (aq) + 2 Na (s)	$E_{\text{cell}}^{\text{o}} = -2.710 \text{ V} - (-1.185 \text{ V}) = -1.525 \text{ V}$	No
(d) $3 \text{ Mn}(s) + 2 \text{ Al}^{3+}(aq) \rightarrow 3 \text{ Mn}^{2+}(aq) + 2 \text{ Al}(s)$	$E_{\text{cell}}^{\text{o}} = -1.662 \text{ V} - (-1.185 \text{ V}) = -0.477 \text{ V}$	No
(e) Mn (s) + 2 Ag <sup>+</sup> (aq) $\rightarrow$ 3 Mn <sup>2+</sup> (aq) + 2 Ag (s)	$E_{\text{cell}}^{\text{o}} = +0.800 \text{ V} - (-1.185 \text{ V}) = +1.985 \text{ V}$	Yes

1 5.1		
which of	Half-reaction	E° (V)
ons taking	$Ag^+(aq) + e^- \rightarrow Ag(s)$	+0.800
<pre>1 5.1 which of ons taking</pre>	Sn <sup>2+</sup> (aq) + 2 e <sup>-</sup> → Sn (s)	-0.136
	Ni <sup>2+</sup> (aq) + 2 e <sup>−</sup> → Ni (s)	-0.257
	$Mn^{2+}$ (aq) + 2 e <sup>-</sup> $\rightarrow$ Mn (s)	-1.185
	$AI^{3+}$ (aq) + 3 e <sup>-</sup> $\rightarrow$ AI (s)	-1.662
	$Na^+$ (aq) + $e^- \rightarrow Na$ (s)	-2.710

$$-E_{anode}^{o} > 0 \text{ or } E_{cathode}^{o} > E_{anode}^{o}$$
.

# ELECTROCHEMISTRY: PROBLEM 5.2

A voltaic/Galvanic cell is made from a compartment with 1.20 1.10 M Fe(NO<sub>3</sub>)<sub>2</sub>, a compartment with 0.95 M Cr(NO<sub>3</sub>)<sub>2</sub> and both at 25 °C, connected by a wire, salt bridge, and two platinu Calculate the initial potential of this cell.

- answer -

First, consider the two aqueous metal cations that exist in each compartment: Second, write the net ionic equation for the spontaneous redox reaction that would take place between these ions:

Cathode (Reduction):	Fe <sup>3+</sup> (aq) +	e⁻	$\rightarrow$
Anode (Oxidation):		Cr <sup>2+</sup> (aq)	$\rightarrow$
Cell	Fe <sup>3+</sup> (aq) +	Cr <sup>2+</sup> (aq)	

Now, we can apply the Nernst equation find the nonstandard initial cell potential, keeping in mind the form of Q.  $[2^{+}][Cr^{3+}]$  $^{3+}][Cr^{2+}]$ 

$$E_{\text{cell}} = E_{\text{cell}}^{\text{o}} - \frac{RT}{nF} \ln \frac{[\text{Fe}]^2}{[\text{Fe}]^2}$$

$$= +1.180 \text{ V} - \frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(298._{15} \text{ K})}{(1 \text{ mol } e^{-})\left(96485 \frac{\text{C}}{\text{mol } e^{-}}\right)} \ln \frac{[1.10][1.00]}{[1.20][0.95]}$$

 $E_{\rm cell} = 1.181 \, {\rm V}$ 

$O M Fe(NO_3)_3$ and	Half-reaction	E° (V)
1.00 M Cr(NO <sub>3</sub> ) <sub>3</sub> ,	$Fe^{3+}$ (aq) + $e^- \rightarrow Fe^{2+}$ (aq)	+0.770
um electrodes.	$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	-0.410
	$Fe^{2+}$ (aq) + 2 $e^- \rightarrow Fe$ (s)	-0.447
	$Cr^{3+}$ (aq) + 3 e <sup>-</sup> $\rightarrow$ Cr (s)	-0.740

 $Fe^{3+}$  (aq),  $Fe^{2+}$  (aq) and  $Cr^{2+}$  (aq),  $Cr^{3+}$  (aq)

Fe<sup>2+</sup> (aq)
$$E_{cell}^{o} = E_{cathode}^{o} - E_{anode}^{o}$$
Cr<sup>3+</sup> (aq)+e<sup>-</sup>= +0.770 V - (-0.410 V)Fe<sup>2+</sup> (aq)+Cr<sup>3+</sup> (aq) $E_{cell}^{o} = +1.180 V$ 



# ELECTROCHEMISTRY: PROBLEM 5.3

Sodium metal (Na) can be obtained by electrolyzing molten NaC sodium metal can be produced when molten NaCl is electrolyzed with 5.13 A of current?

- answer -

The reaction we are interested in is the cathodic reaction: Na<sup>+</sup> (aq) +  $e^- \rightarrow$  Na (s).

$$m_{\rm Na} = 10.3 \, {\rm hr} \times \frac{60 \, {\rm min}}{1 \, {\rm hr}} \times \frac{60 \, {\rm s}}{1 \, {\rm min}} \times \frac{5.13 \, {\rm G}}{1 \, {\rm s}}$$

Cl. What mass of	Half-reaction	<i>E</i> ° (V)
ed for 10.3 hours	$Cl_2(g) + 2 e^- \rightarrow 2 Cl^-(aq)$ Na <sup>+</sup> (aq) + e <sup>-</sup> $\rightarrow$ Na (s)	+1.358 -2.710

We can determine the amount of Na using the stoichiometry of the equation above where  $n = 1, F = 96485 \frac{C}{mol e^{-}}$ , and  $1 \text{ A} = 1 \frac{C}{s}$ .

 $\frac{C}{S} \times \frac{1 \text{ mol } e^{-}}{96485 \text{ C}} \times \frac{1 \text{ mol } \text{Na}}{1 \text{ mol } e^{-}} \times \frac{22.99 \text{ g}}{1 \text{ mol } \text{Na}} = 45.3 \text{ g } \text{Na } (\text{s})$ 



#### NUCLEAR CHEMISTRY: PROBLEM 6.1

#### For each of the following nuclides, predict the types of radioactive decay and reactants/products of such decays.

	Nuclide	Neutron/Proton Ratio	Decay Type	Nuclear Equation
(a)	<sup>37</sup> Ca	$^{37}_{20}$ Ca $\rightarrow \frac{17 \text{ n}}{20 \text{ p}}$	electron capture -or- position emission	$ \begin{array}{c} {}^{37}_{20}\text{Ca} \ + \ - \overset{0}{_{-1}}\beta \ \rightarrow \ \overset{37}{_{19}}\text{K} \\ & - or - \\ {}^{37}_{20}\text{Ca} \ \rightarrow \ \overset{37}{_{19}}\text{K} \ + \ \overset{0}{_{+1}}\beta \end{array} $
(b)	<sup>34</sup> P	$^{34}_{15}P \rightarrow \frac{19 n}{15 p}$	beta decay	$^{34}_{15}P \rightarrow ^{34}_{16}S + ^{0}_{-1}\beta$
(c)	<sup>212</sup> Fr	$^{212}_{87}\mathrm{Fr} \rightarrow \frac{125 \mathrm{n}}{87 \mathrm{p}}$	alpha decay Z > 83	$^{212}_{87}\mathrm{Fr} \rightarrow ^{208}_{85}\mathrm{At} + ^{4}_{2}\alpha$
(d)	<sup>129</sup> Sb	$^{129}_{51}Sb \rightarrow \frac{78 \text{ n}}{51 \text{ p}}$	beta decay	$^{129}_{51}Sb \rightarrow ^{129}_{52}Te + ^{0}_{-1}\beta$

#### NUCLEAR CHEMISTRY: PROBLEM 6.2

A <sup>8</sup>B nuclide decays into a <sup>8</sup>Be nuclide through positron emission. Calculate the energy produced from this type of radioactive decay based on the following masses: <sup>8</sup>B (8.02460 amu), <sup>8</sup>Be (8.00530 amu), and  $^{0}_{+1}\beta$  (0.00055 amu). 1 amu = 1.6605 × 10<sup>-27</sup> kg c = 3.00 × 10<sup>8</sup> m/s 1 J = 1 kg  $\cdot \frac{m^2}{s^2}$ Recall: - answer -

The reaction we are interested is:  ${}_{5}^{8}B \rightarrow {}_{4}^{8}Be + {}_{+1}^{0}\beta$ 

We can determine the energy released by first finding the mass defect ( $\Delta m$ ):

$$\Delta m = \sum m_{\text{products}} + \sum m_{\text{reactans}}$$
$$= [8.00530 \text{ amu} + 0.00055 \text{ am}]$$
$$\Delta m = -0.01875 \text{ amu}$$

Finally, we can use Einstein's equation to convert the mass defect into an energy value:

$$\Delta E = (\Delta m)c^{2}$$

$$= \left(-0.01875 \text{ amu} \times \frac{1.6605 \times 10^{-27} \text{ kg}}{1 \text{ amu}}\right) \left(3.00 \times 10^{8} \frac{\text{m}}{\text{s}}\right)^{2}$$

$$\Delta E = -2.80 \times 10^{-12} \text{ J}$$

[nu] - 8.02460 amu



# NUCLEAR CHEMISTRY: PROBLEM 6.3

A piece of paper from an ancient scroll undergoes <sup>14</sup>C-decay with a rate of 9.07 decays/min. A fresh piece of paper also undergoes <sup>14</sup>C-decay but with a rate of 13.6 decays/min. If the half-life for <sup>14</sup>C-decay is 5730 years, how old is the scroll? - answer -

The assumption in carbon dating is that the amount of radioactive  $^{14}C(N)$  decreases over time. As such, the older an object is, the lower the <sup>14</sup>C-decay rate because radioactive decay follows first-order kinetics: Rate = kN

So, if we compare the  $^{14}$ C-decay rates between the ancient and fresh paper, we can get a ratio of the  $^{14}$ C content:

$$\operatorname{Rate}_{t} = kN_{t} = 9.07 \frac{\operatorname{decays}}{\min}$$

$$\operatorname{Rate}_{t} = \frac{kN_{t}}{\operatorname{Rate}_{0}} \to \frac{\operatorname{Rate}_{t}}{\operatorname{Rate}_{0}} = \frac{N_{t}}{N_{0}} = \frac{9.07}{13.6} = 0.666_{9}$$

We can now use this ratio in the integrated rate law to find the age of the ancient scroll:

 $t = 3349 \, \text{yr}$ 

$$Rate_0 = kN_0 = 13.6 \frac{decays}{min}$$

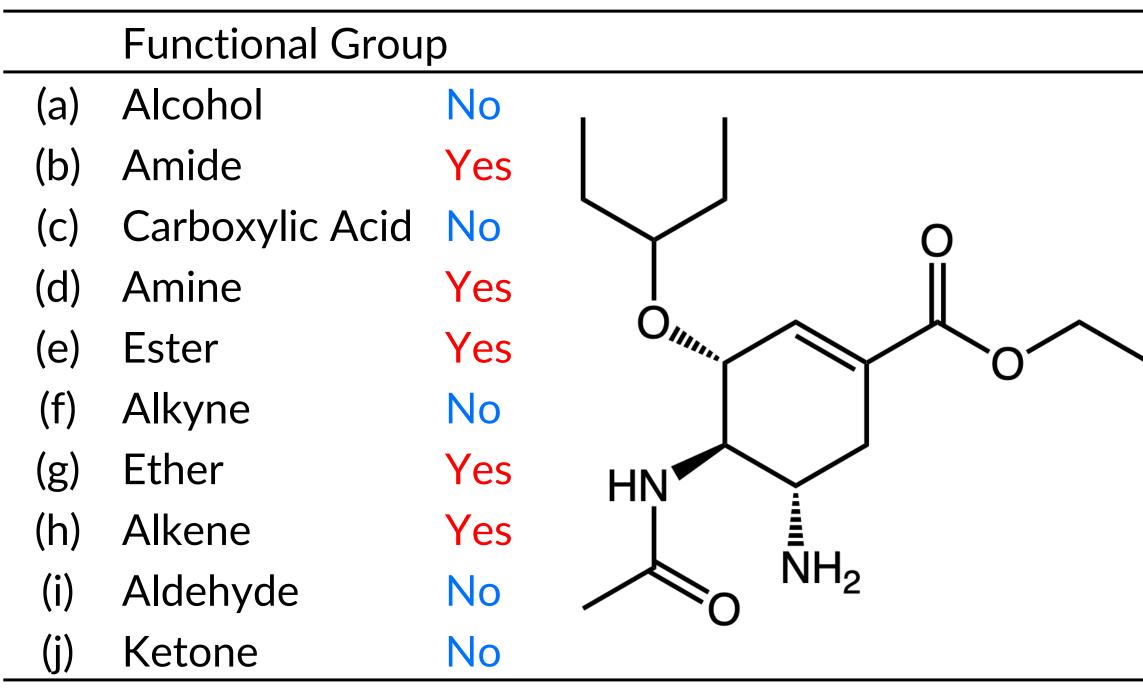
$$\frac{t_1}{\frac{2}{n}} \ln \frac{N_t}{N_0}$$

$$\frac{5370 \text{ yr}}{\ln 2} \ln 0.666_9$$

$$\frac{19 \text{ yrs old}}{100}$$



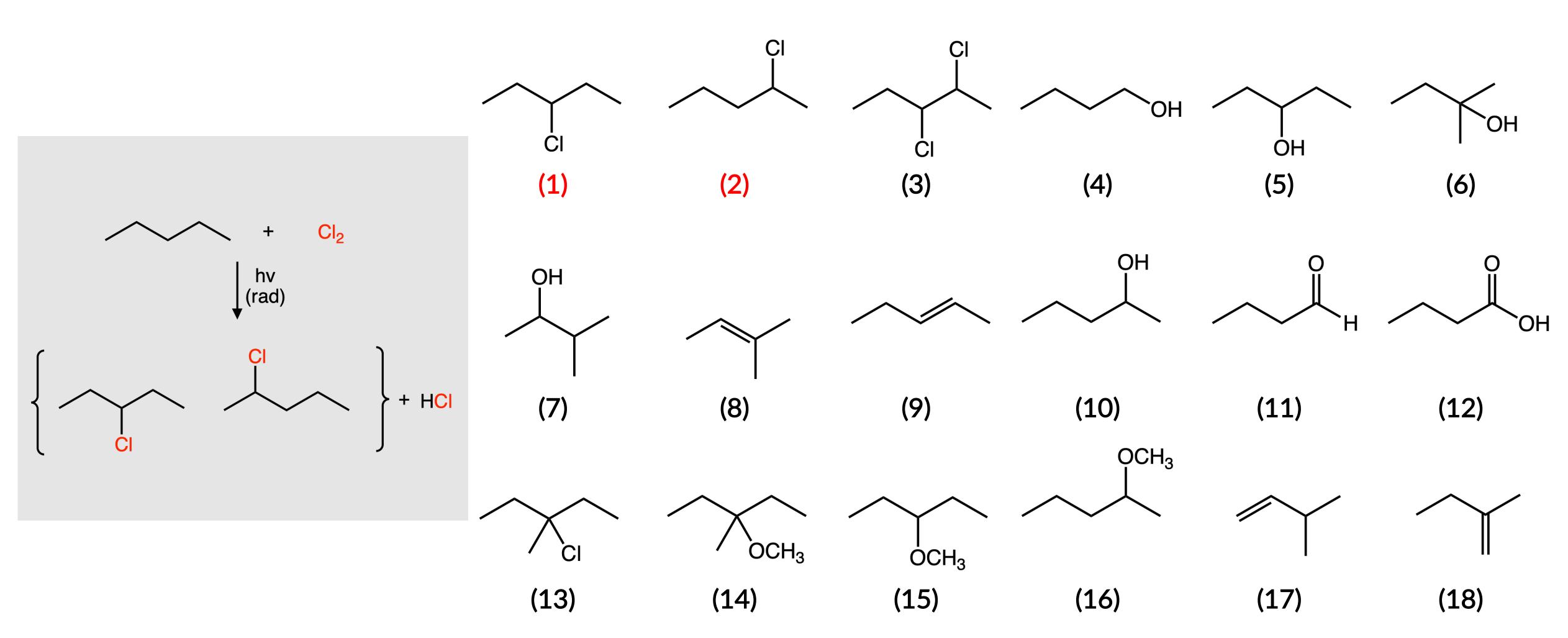
#### For the two compounds shown below, identify if the following functional groups are present.



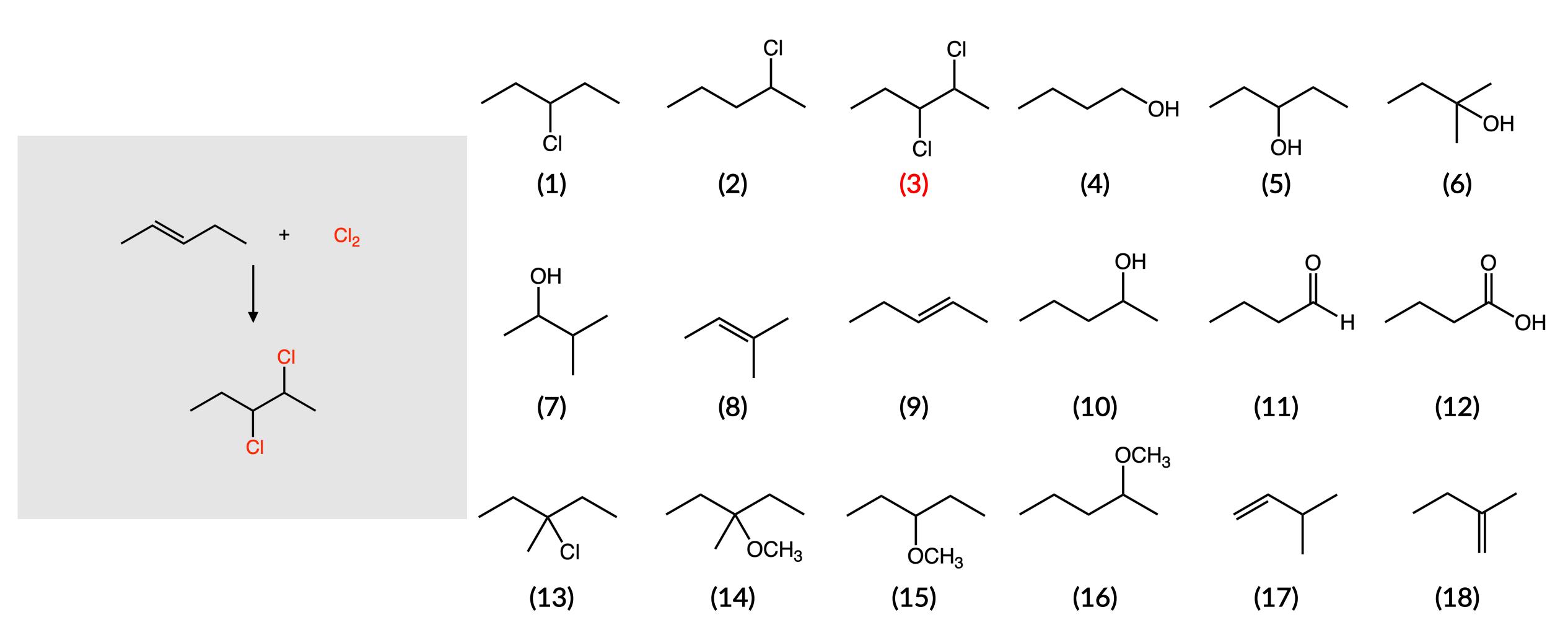
	Functional Grou	р			
(a)	Alcohol	Yes	F	10	
(b)	Amide	No		$\gamma$	
(c)	Carboxylic Acid	No		L ,	
(d)	Amine	No	O II		
(e)	Ester	Yes			
(f)	Alkyne	No	$\gamma$		
(g)	Ether	No			
(h)	Alkene	Yes		$\forall  \checkmark$	
(i)	Aldehyde	No			
(j)	Ketone	No	IIIIIIII		



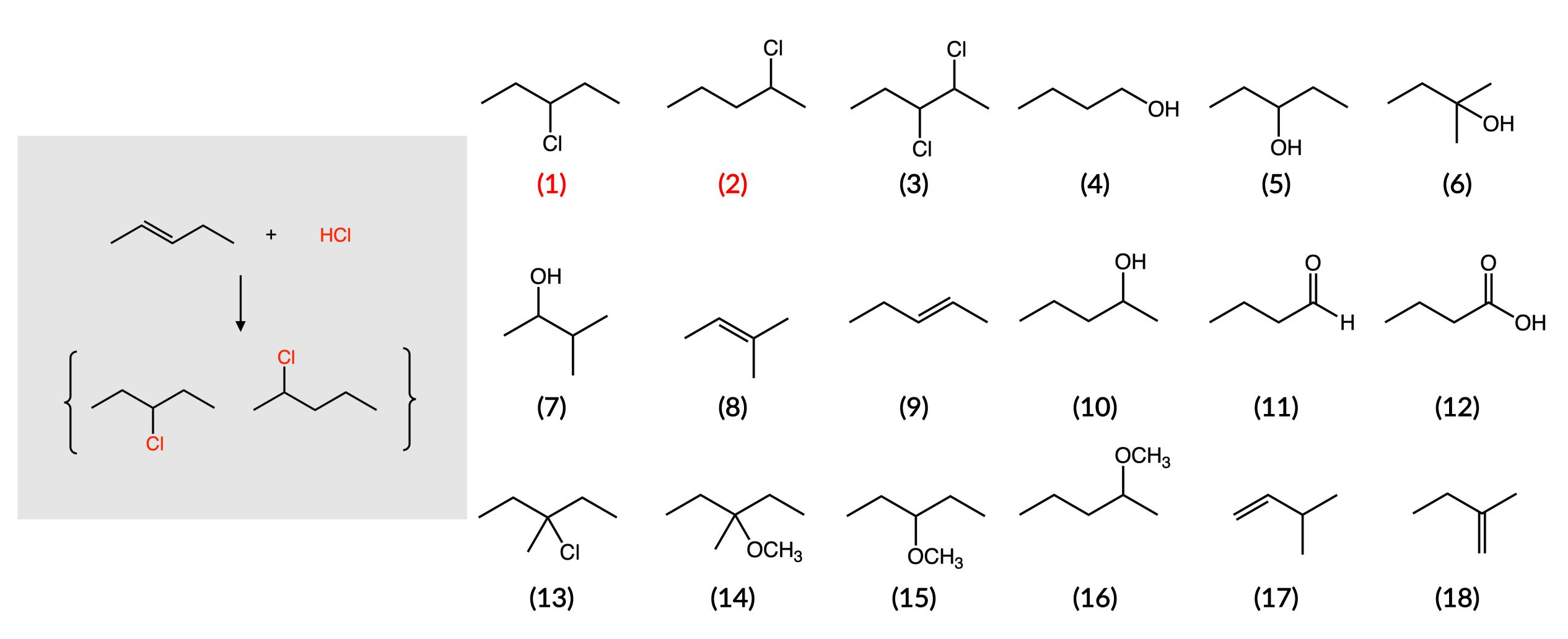
Choose the possible product(s) for the reaction between pentane and Cl<sub>2</sub> using UV radiation.



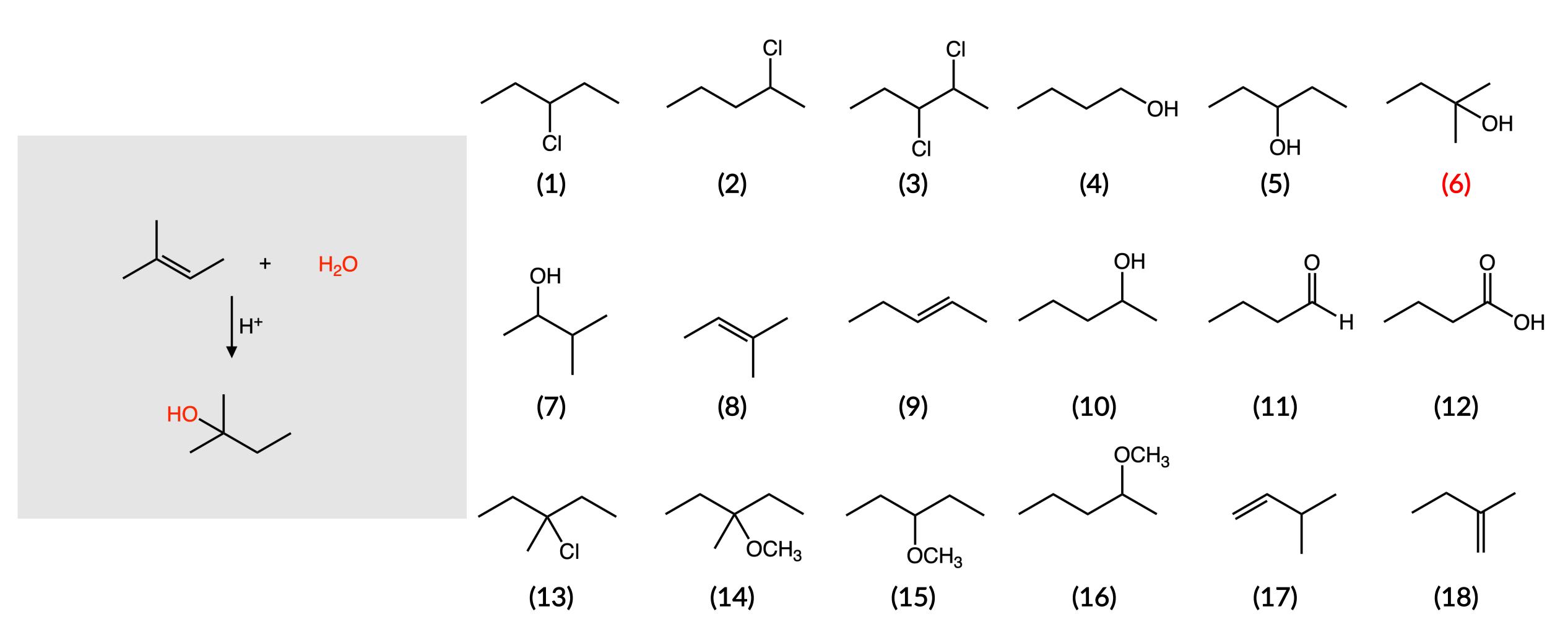
Choose the possible product(s) for the addition reaction between 2-pentene and  $Cl_2$ .



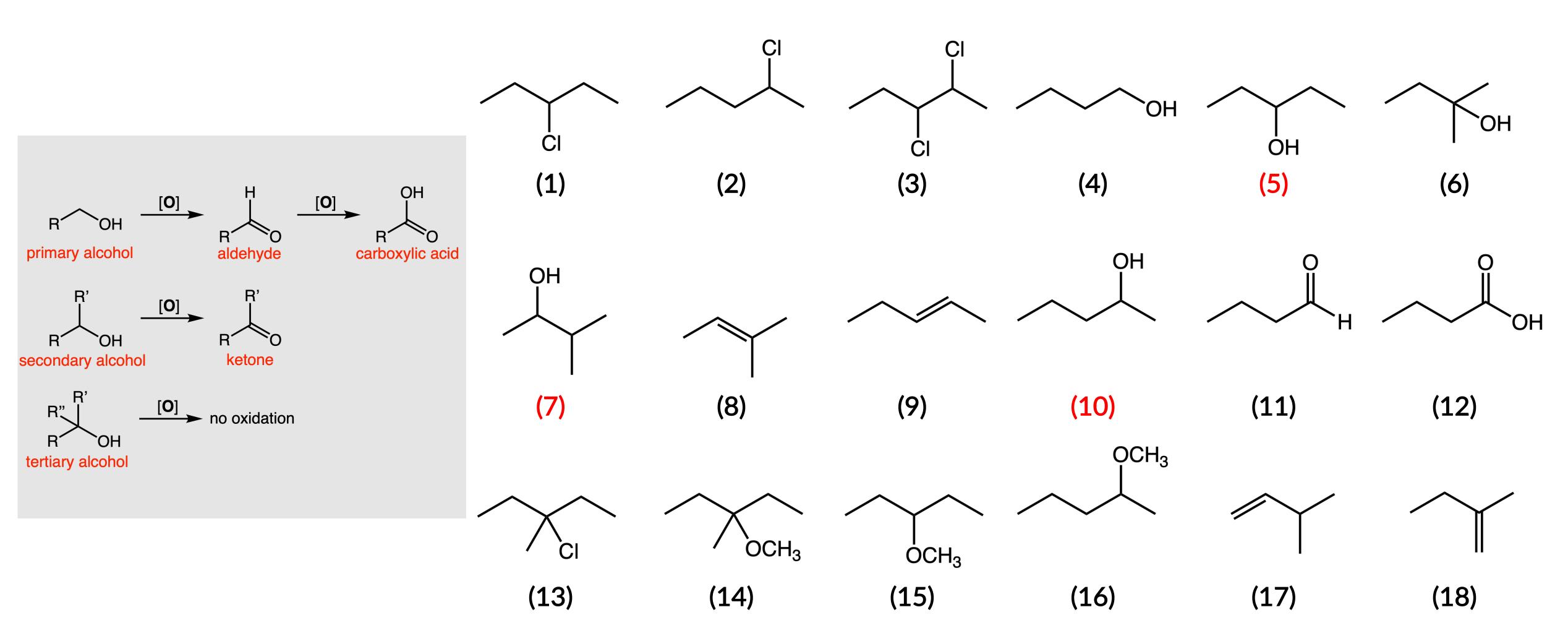
Choose the possible product(s) for the addition reaction between 2-pentene and HCI.



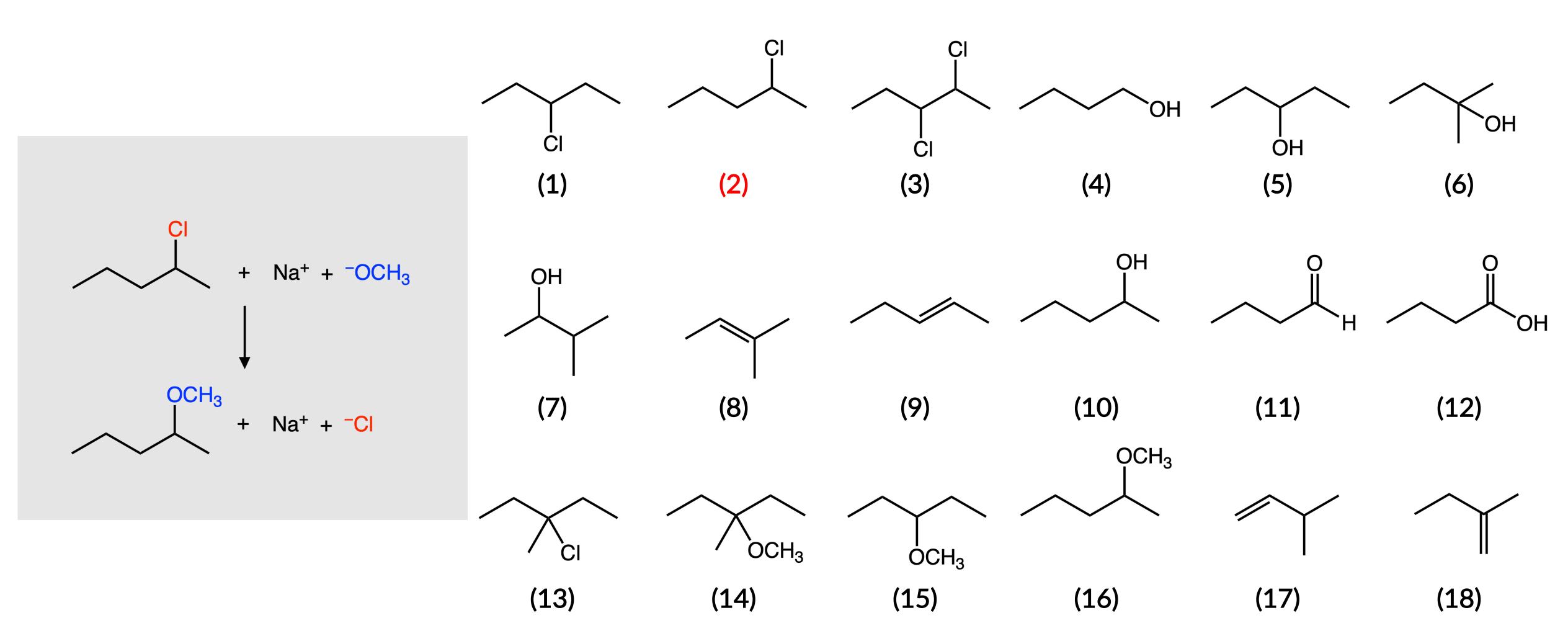
Choose the possible product(s) for the addition reaction between 2-methyl-2-butene, water, and an acid catalyst.



Which of the following compounds could be oxidized to produce a ketone?



Which of the following compound could be mixed with NaOCH<sub>3</sub> to make compound 16?



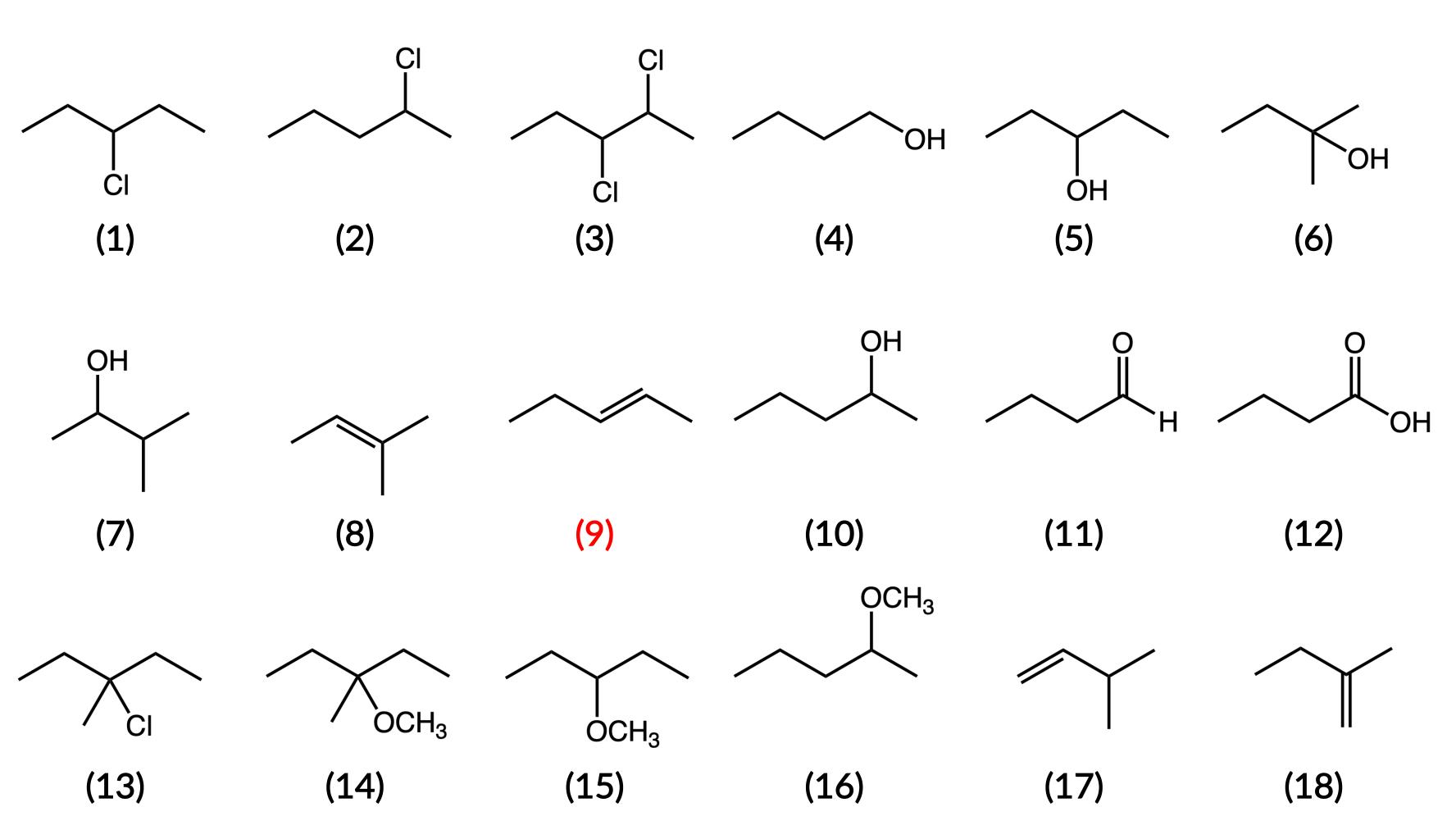
### <u>ORGANIC CHEMISTRY</u>: PROBLEM 7.8

Which of the following compounds could exhibit geometric isomerism? - answer -

In order for an compound to exhibit geometric isomerism (cis/trans or E/Z), you need to look for a structure with an alkene group (8, 9, 17, 18). From the alkenes, you need to look at the groups sticking off of each carbon of the alkene (see redline). If the groups on each side of the double bond are different from each other (9), the compound can exhibit geometric isomerism.



This carbon attached to -H and  $-CH_2CH_3$ 

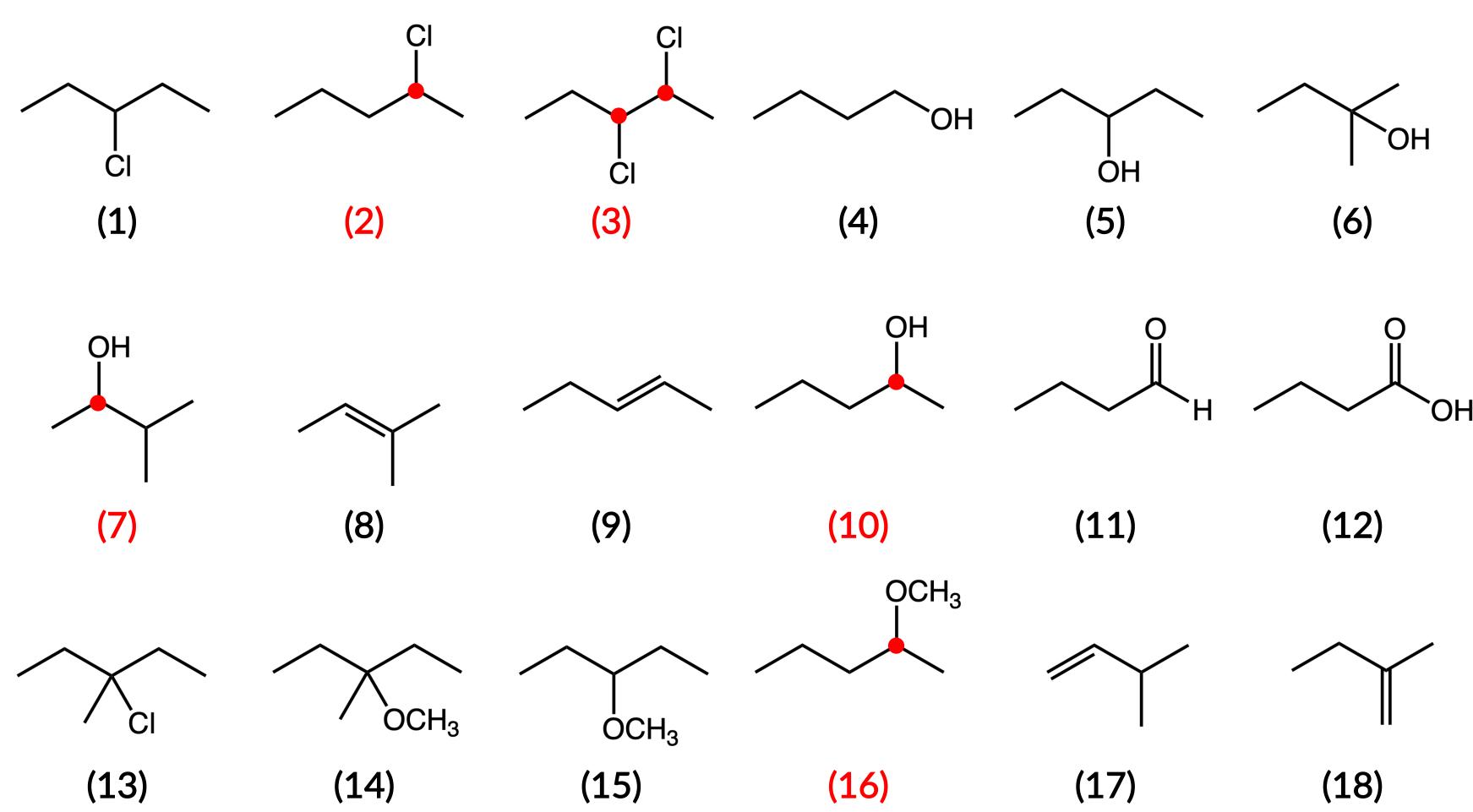


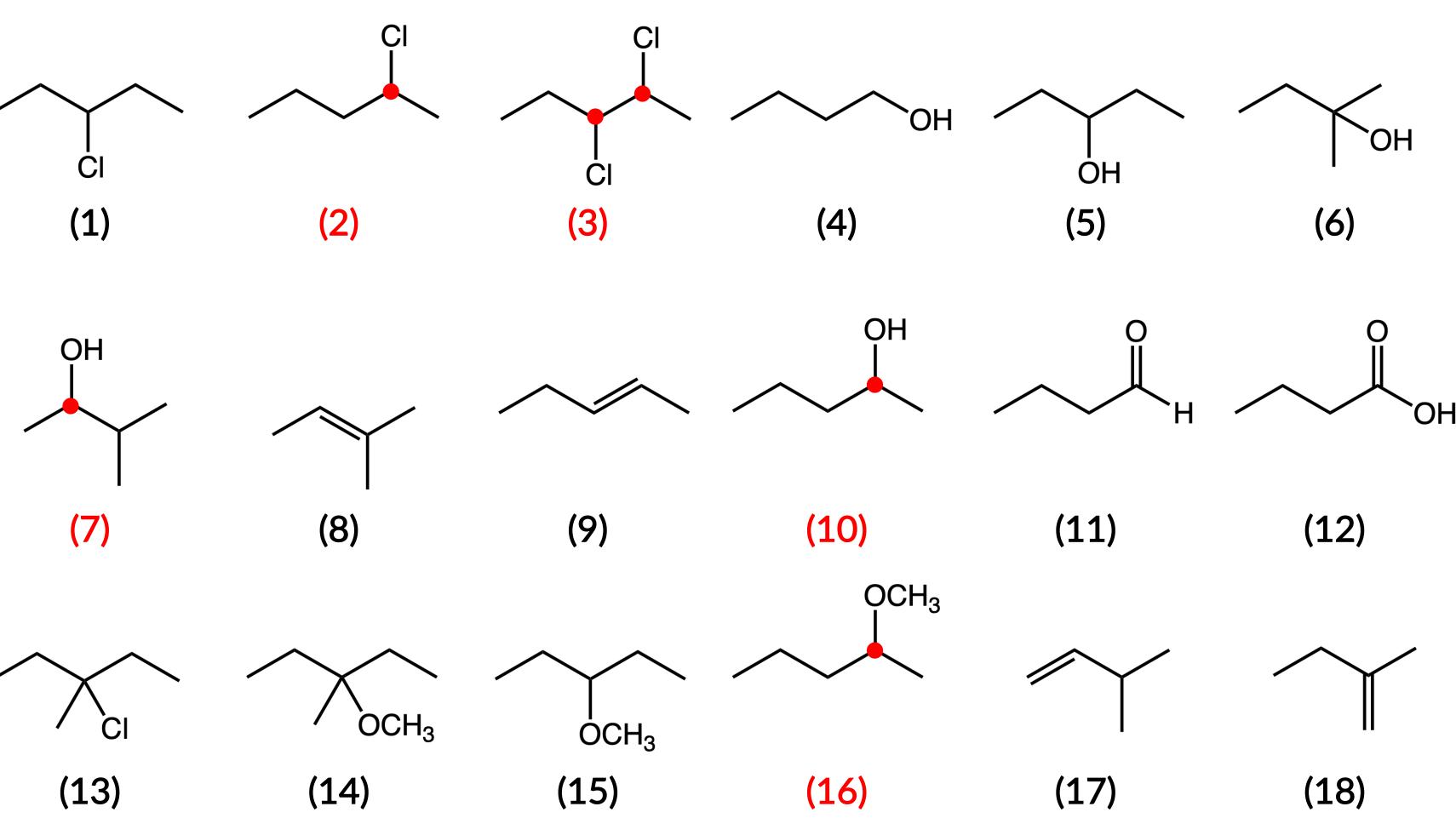
Which of the following compounds contains a chiral carbon center?

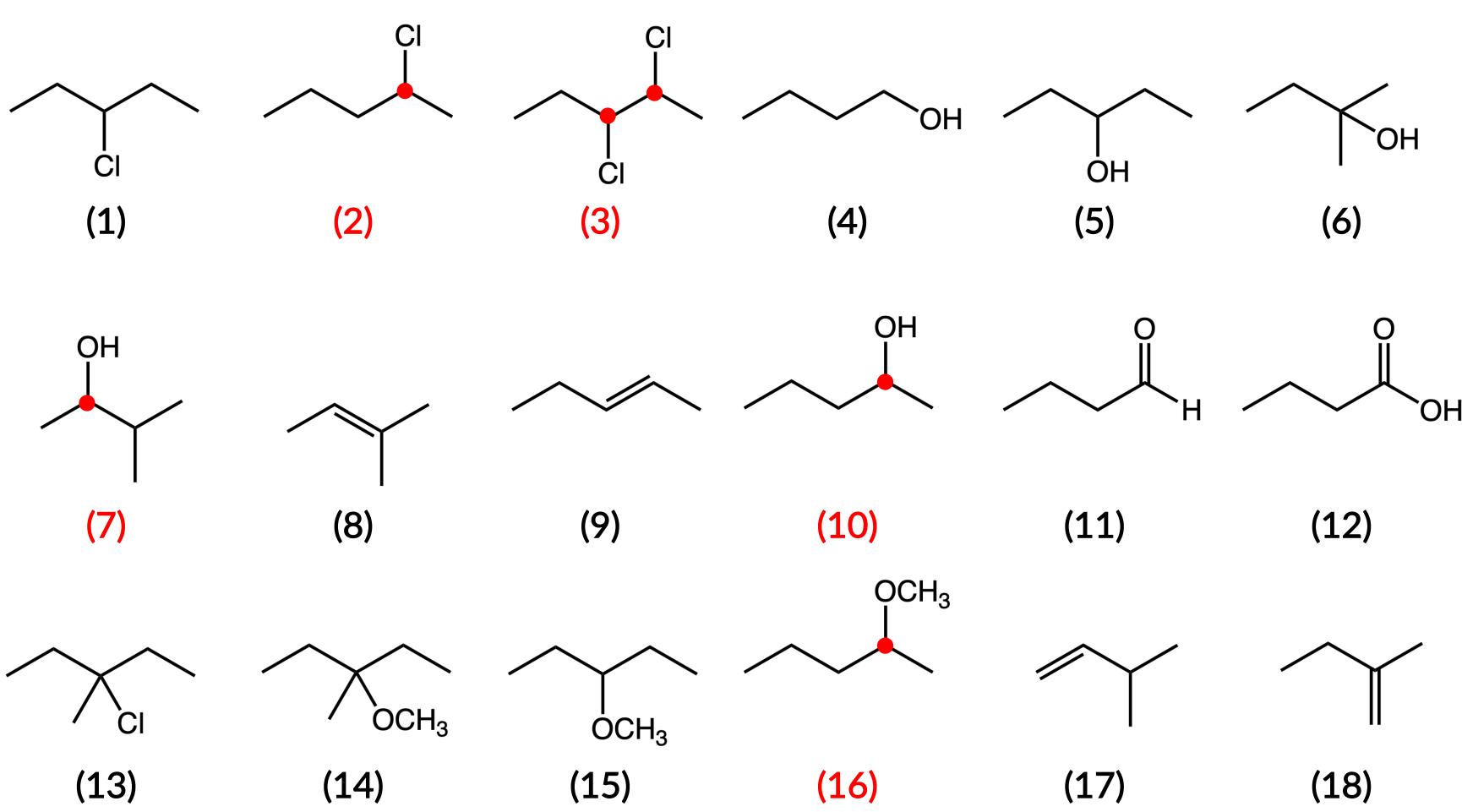
- answer -

A chiral carbon center is an  $sp^3$ hybridized carbon attached to 4 different groups.

Chiral centers have been identified with red dots.

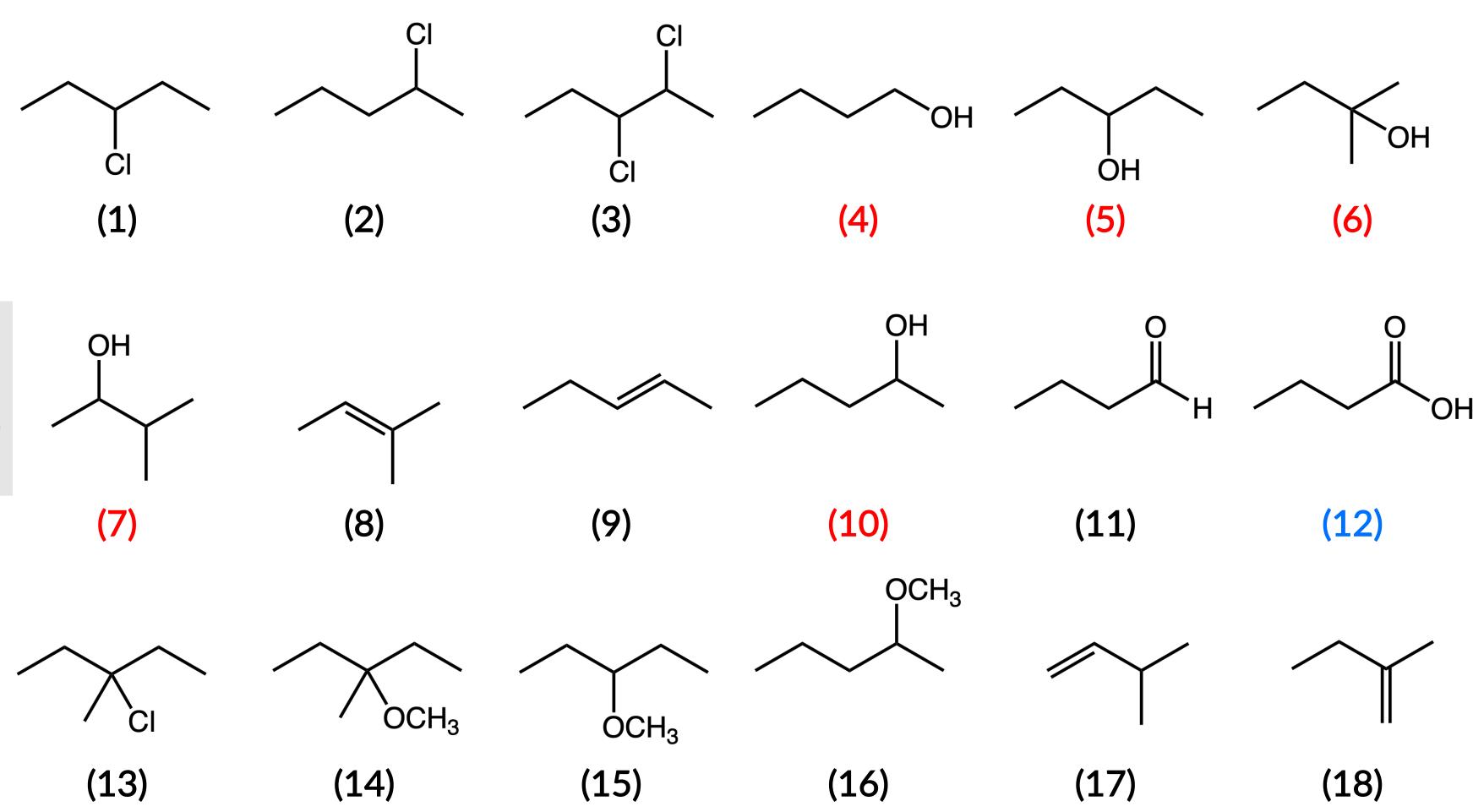


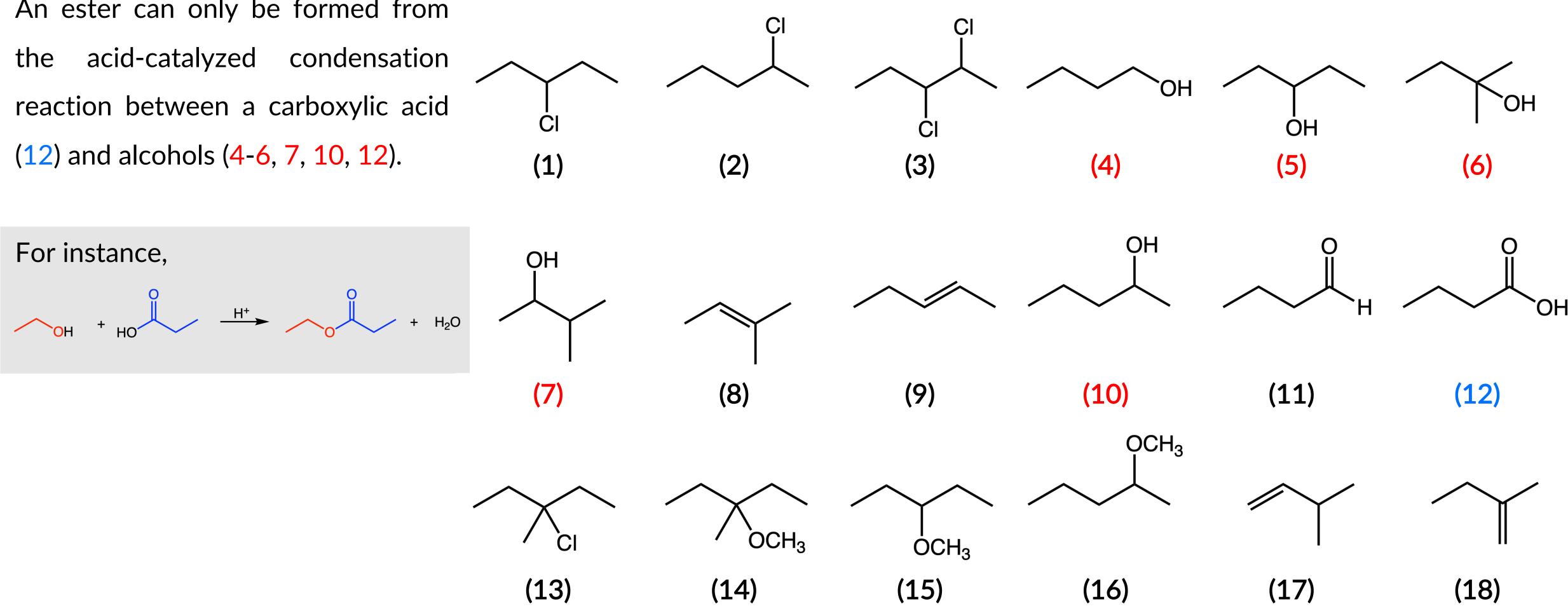




Choose any two compounds that can be mixed together with an acid catalyst to produce an ester via condensation. - answer -

An ester can only be formed from acid-catalyzed condensation

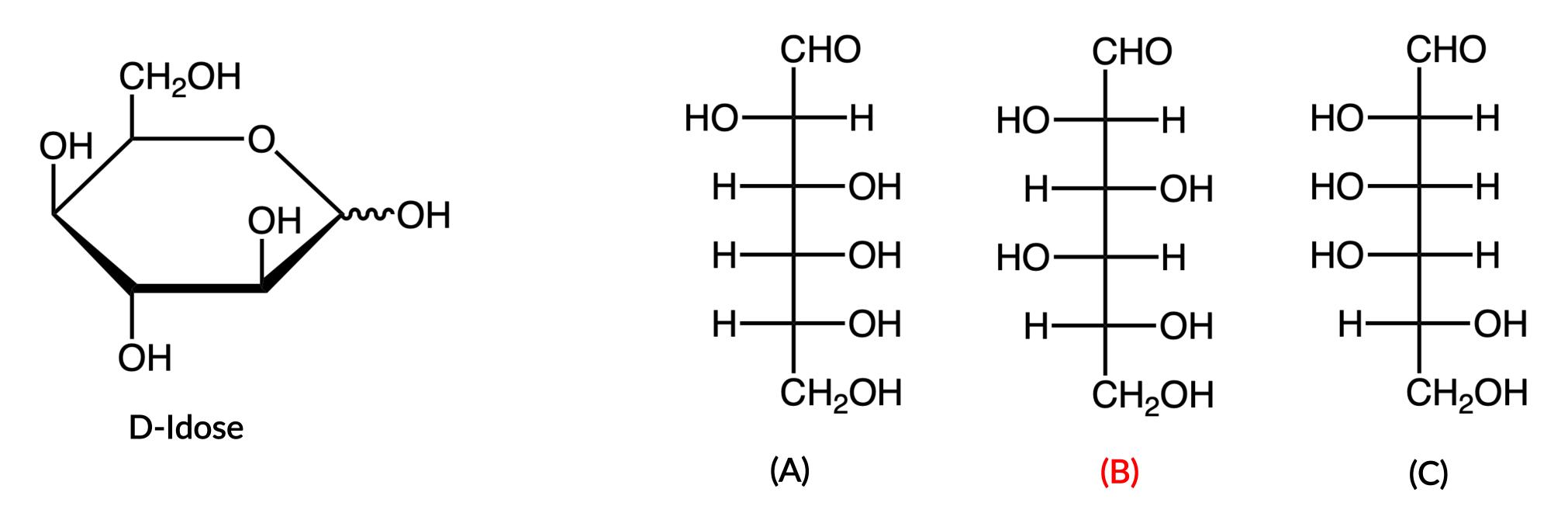




# **BIOCHEMISTRY: PROBLEM 8.1**

The Haworth projection for the D-Idose pyranose is shown below. Which is the correct Fischer projection for D-Idose?

- answer -



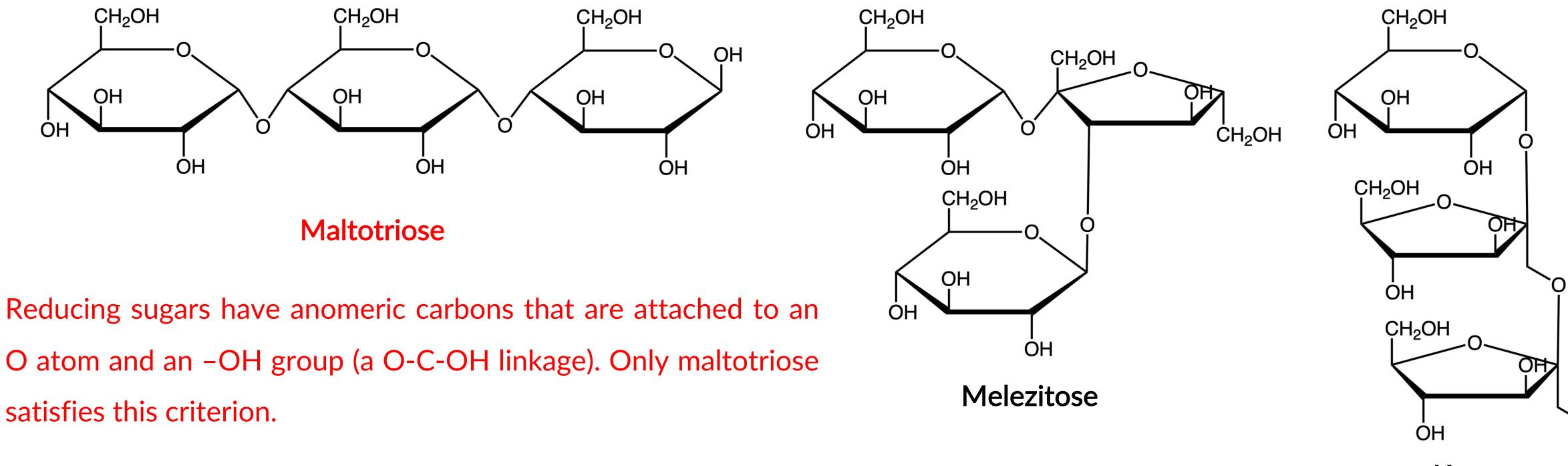
Recall:

- We number sugars from the top-to-bottom in the Fischer projection.  $\bullet$
- The anomeric carbon is the last (bottom-most) chiral center in the Fischer projection. ullet
- The anomeric carbon bonds to the C=O at the top of the sugar in the Fischer projection. ullet
- For the orientation of the –OH groups:

-OH groups that are on the right side of a Fischer projection stick down in the Haworth projection. -OH groups that are on the left side of a Fischer projection stick up in the Haworth projection.

### **BIOCHEMISTRY: PROBLEM 8.2**

The trisaccharaides maltotriose, melezitose, and kestose are shown below. Which is a reducing sugar? - answer -



satisfies this criterion.

Melezitose and kestose have O-C-CH<sub>2</sub>OH linkages.

Kestose

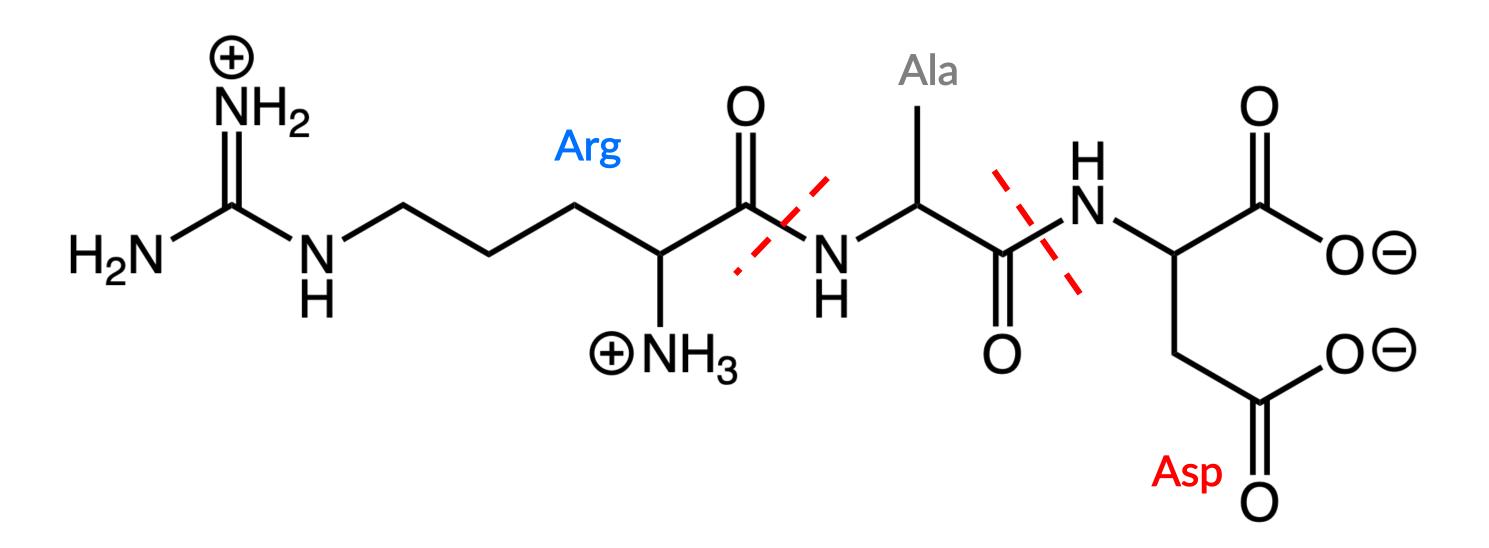


#### **BIOCHEMISTRY:** PROBLEM 8.3

The tripeptide shown below is comprised of three amino acids. Which amino acid would travel the farthest toward the positive

electrode during electrophoresis with a pH = 6 buffer.

- answer -



Alanine (pl = 6.0) will not travel to either electrode because it is neutral at pH = 7 solution.

Aspartic acid (pl = 2.8) will travel the farthest toward the positive electrode because it is negatively charged in pH = 7 solution.

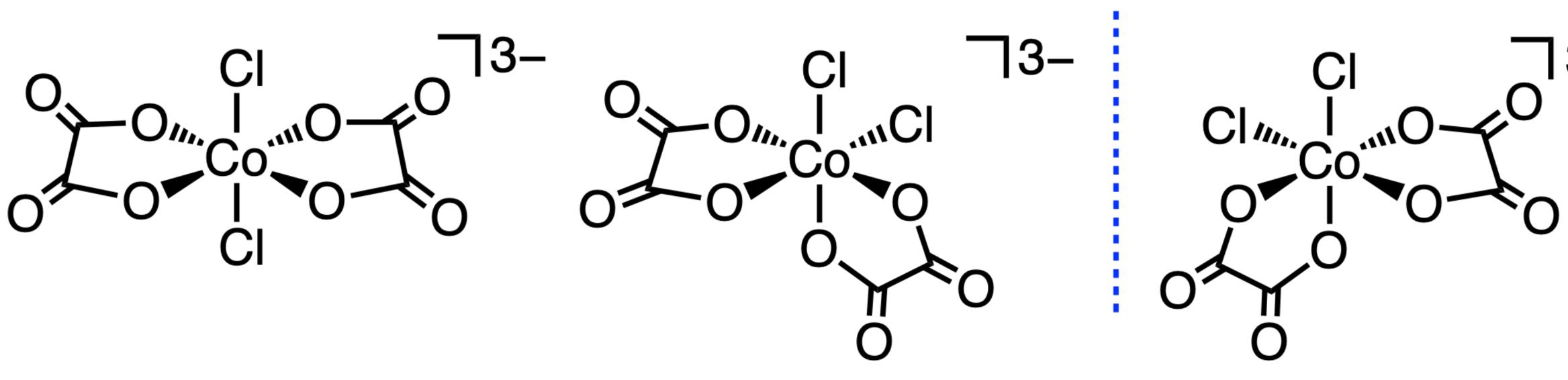
Arginine (pl = 10.8) will travel the farthest toward the negative electrode because it is positively charged in pH = 7 solution.



### TRANSITION METALS: PROBLEM 9.1

#### Dichlorobisoxalatocobaltate(III) can exist as three optical isomer. One is drawn below. Draw the other two stereoisomers.

- answer -



These two are enantiomers (non-superimposable mirror images).



# TRANSITION METALS: PROBLEM 9.2

You have three colored solutions: (1) violet, (2) yellow, and (3) green. Match each of the colored solutions (1–3) to the corresponding complex ions: (a)  $[Cr(NH_3)_6]^{3+}$ , (b)  $[Cr(H_2O)_6]^{3+}$ , and (c)  $[Cr(H_2O)_4CI_2]^+$ . Spectrochemical series:  $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > CI^- > Br^- > I^-$ 

#### - answer -

Recall that the complementary color of the observed color of a complex is an indirect estimate of the energy splitting ( $\Delta_0$ ). As light passes through the solution, photons of a specific wavelength equal to the value of  $\Delta_0$  are absorbed by the complex, while all other wavelengths of light are transmitted through the solution for our eyes to observe.

Therefore, we need to consider the complimentary colors for each solution:

Solution	<b>Observed Color</b>	Absorbed Color ( $\sim \Delta_o$ )	Complex	Reasoning
 (1)	Violet (λ <sub>obs</sub> ~410 nm)	Yellow (λ <sub>abs</sub> ~570 nm)	[Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup>	$H_2O$ is a low-field ligand, so $\Delta_o$ is relatively small and $\lambda_{abs}$ is large.
(2)	Yellow (λ <sub>obs</sub> ~570 nm)	Blue (λ <sub>abs</sub> ~450 nm)	[Cr(NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	NH <sub>3</sub> is a high-field ligand, so $\Delta_o$ is relatively large and $\lambda_{abs}$ is small.
(3)	Green (λ <sub>obs</sub> ~520 nm)	Red (λ <sub>abs</sub> ~650 nm)	[Cr(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ]+	$\rm H_2O$ and $\rm CI^-$ are low-field ligands, so $\Delta_o$ relatively small and $\lambda_{abs}$ is large. $\rm CI^-$ is a stronger low-field ligand than $\rm H_2O$ , so $\Delta$ is even smaller than [Cr(H <sub>2</sub> O) <sub>6</sub> ] <sup>3+</sup> .

IS

# TRANSITION METALS: PROBLEM 9.3

For each pair of complex ions, determine: (a) the number of 3d electrons and oxidation state, (b) if each is high- or low-spin, (c) if each is paramagnetic or diamagnetic, and (d) the magnetic moment ( $\mu_{eff}$ ). Spectrochemical series:  $CN^- > NO_2^- > CN^- > en > NH_3 > H_2O > F^- > CI^- > Br^- > I^-$ 

#### - answer -

First, determine the number of d electrons for each set of complex ions. Then, use the spectrochemical series to determine whether the complex is high- or low-spin and fill the crystal field diagram appropriately. Lastly,

 $\mu_{\rm eff} = \sqrt{n(n+2)}$ ; n = # unpaired  $e^-$ 

Complex ions	No. 3d electrons?	Spin?	
(i) $[Fe(H_2O)_6]Cl_3$	Fe <sup>3+</sup> : [Ar] 3d <sup>5</sup>	High-spin	
$Na_3[Fe(CN)_6]$		Low-spin	
(ii) $[Co(NH_3)_6]Cl_3$	Co <sup>3+</sup> : [Ar] 3d <sup>6</sup>	Low-spin	
$K_3[CoF_6]$		High-spin	

