ANWEISUNGEN

- Write your name on each page and number these.
- You have three hours to solve the problems. Wait for the **START** signal before you begin.
- Use a new page for each problem.
- Write all necessary calculations legibly.
- Put your pages into the provided envelope at the end of the exam. Do not stick down the envelope.
- Finish your work immediately when the **STOP** signal is given.
- Leave your seat only when allowed to do so.
- Only answers written on the answer sheets can be considered.
- This test has 17 pages.

Viel Erfolg!

Bonne chance!

Buona fortuna!

Good luck!

CONSTANTS AND FORMULAE

Avogadro constant	$N_A = 6.022 \cdot 10^{23}\ \text{mol}^{-1}$	Ideal gas equation	$pV = nRT$
Gas constant	$R = 8.314\ \text{J mol}^{-1}\ \text{K}^{-1}$	Gibbs energy	$G = H - TS$
Faraday constant	$F = 96485\ \text{C mol}^{-1}$	$\Delta_r G^0 = -RT \cdot \ln(K) = -nFE^0_{\text{Zelle}}$	
Planck constant	$h = 6.626 \cdot 10^{-34}\ \text{J s}$	Nernst equation	$E = E^0 + \frac{R \cdot T}{z \cdot F} \cdot \ln\left(\frac{c_{\text{ox}}}{c_{\text{red}}}\right)$
Speed of light	$c = 2.998 \cdot 10^{8}\ \text{m s}^{-1}$	Energy of a photon	$E = \frac{h \cdot c}{\lambda}$
Temperature	$0\ ^\circ\text{C} = 273.15\ \text{K}$	Lambert-Beer law	$A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot c \cdot L$

For the calculation of equilibrium constants all concentrations refer to the standard concentration $1\ \text{mol dm}^{-3} = 1\ \text{mol l}^{-1}$. If not stated otherwise in a task, consider all gases ideal throughout this test.

Periodic table with relative atomic masses

1 H 1.008																	2 He 4.003
3 Li 6.94	4 Be 9.01											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.64	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.96	43 Tc –	44 Ru 101.07	45 Rh 102.91	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	57–71	72 Hf 178.49	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po –	85 At –	86 Rn –
87 Fr –	88 Ra –	89–103	104 Rf –	105 Db –	106 Sg –	107 Bh –	108 Hs –	109 Mt –	110 Ds –	111 Rg –	112 Cn –						

57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 140.24	61 Pm –	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.05	71 Lu 174.97
89 Ac –	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np –	94 Pu –	95 Am –	96 Cm –	97 Bk –	98 Cf –	99 Es –	100 Fm –	101 Md –	102 No –	103 Lr –

TASK 1 - MULTIPLE QUESTIONS — 9.5 POINTS

a) How many Flourine atoms are present in 1 mol Kryolith ($Na_3[AlF_6]$)?

b) One liter of a 0.1 mol l^{-1} NaBr solution is mixed with one liter of a 0.1 mol l^{-1} NaI solution. In which concentrations are the individual ions present in the mixture?

c) Give the stoichiometric coefficients of the following combustion reaction of ammonia:

$$NH_3 + O_2 \rightarrow N_2 + H_2O$$

d) Indicate in the following pairs of substances which substance has the lower pK_a value within every pair:

HCl / HF $\quad$ HNO_3 / CH_3COOH (acetic acid) $\quad$ H_2S / H_2O $\quad$ NH_3 / H_2O

e) Calculate the volume of 1.00 mol water vapor at standard pressure (1 bar) and 100 °C.

f) Draw the threedimensional structure of the following molecules:

CO_2, H_2O, CH_4, SF_4, SF_6

g) Give the reaction equation for the reaction of water with potassium.

TASK 2 - ACIDS AND BASES — 8 POINTS

Calculate the pH values of the following aqueous solutions:

a) 0.1 mol HCl in 1 l water.

b) 10 mmol HI in 100 ml water.

c) 1 mmol KOH in 100 ml water.

d) 1 g acetic acid (CH_3COOH, $pK_s = 4.75$) in 100 ml water.

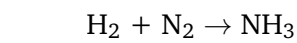
e) 1 g pyridine (C_5H_5N, $pK_b = 8.7$) in 100 ml water.

f) 1 g acetic acid (CH_3COOH, $pK_s = 4.75$) und 1 g sodium acetate (CH_3COONa) in 100 ml water.

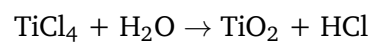
TASK 3 - STOICHIOMETRY **5 POINTS**

Find the stoichiometric coefficients of the following reactions.

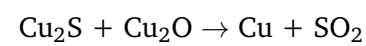
a)



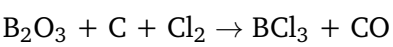
b)



c)

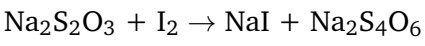


d)

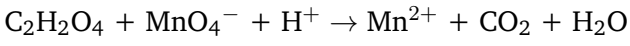


Write for each of the following redox reaction the balanced semi reactions as well as the balanced overall reaction.

e)



f)



TASK 4 - TITRATION 7 POINTS

We have $1\,\text{l}$ solution of NaCl and Na_2SO_4 in an unknown ratio of the two substances. We want to determine this with two titrations. Bear in mind that $BaSO_4$ and AgCl are virtually insoluble in water. In the first them we take a sample from the starting solution of $10\,\text{ml}$ and dilute it with water up to $100\,\text{ml}$. This sample is then titration with a $0.1\,\text{mol}\,\text{l}^{-1}$ $BaCl_2$ titration until there is no more precipitation. The measured titration volume is $7.8\,\text{ml}$.

a) Write the titration equation for the titration with $BaCl_2$.

b) Calculate the concentration of Na_2SO_4 in the diluted titrated sample solution.

c) Calculate the amount of Na_2SO_4 in the original solution.

After the first titration, the precipitation is separated by filtration. The filtrate is filled up to $120\,\text{ml}$ with water and then titrated with a $0.2\,\text{mol}\,\text{l}^{-1}$ $AgNO_3$ solution until there is no more precipitation. The measured titration volume is $13.2\,\text{ml}$.

a) Write the titration equation for the titration with $AgNO_3$.

b) Calculate the concentration of NaCl in the diluted titrated sample solution.

c) Calculate the amount of NaCl in the original solution.

TASK 5 - SOLUBILITY PRODUCT **4 POINTS**

a) Calculate with the solubility constants $K_{L,\,Ag_2S} = 5.5{\cdot}10^{-51}\text{mol}^3\text{l}^{-3}$ and $K_{L,\,CuS} = 8{\cdot}10^{-37}\text{mol}^2\text{l}^{-2}$ whether Ag_2S or CuS is more soluble.

b) Which concentration of $Ni(OH)_2$ is dissolved in one liter of soda lye with pH $= 12.34$? The solubility constant of $Ni(OH)_2$ is $K_{L,\,Ni(OH)_2} = 1.6 \cdot 10^{-16}\ \text{mol}^3\ \text{l}^{-3}$.

TASK 6 - REDOX CHEMISTRY 5.5 POINTS

Take the following standard cell

$$\text{Sn} \mid \text{Sn}^{2+} \mid\mid \text{Pb}^{2+} \mid \text{Pb}$$

with the standard reduction potentials $E^\circ_{\text{Sn}} = -0.136\,\text{V}$ and $E^\circ_{\text{Pb}} = -0.126\,\text{V}$.

a) Write down both occuring half reactions as well as the overall reaction.

b) Calculate the E° of the cell.

c) When the cell is in use, the concentration of Sn^{2+} rises while the concentration of Pb^{2+} decreases. At the start, the concentrations of both ions are $1\,\text{mol}\,\text{l}^{-1}$ and in the same amount present. What are the ion concentrations when the electrochemical equilibrium is reached?

TASK 7 - CHEMICAL EQUILIBRIUM **5 POINTS**

Gaseous SO_3 dissociates according to

$$2\ SO_3(g) \rightleftharpoons 2\ SO_2(g) + O_2(g)$$

We add 0.060 mol SO_3 in a 1 l vessel and heat it up to 1000 K. At this temperature, 36.7% of the SO_3 is dissociated.

a) Calculate the equilibrium concentrations of the three involved substances.

b) Calculate K_c for this reaction at 1000 K.

c) In which direction does the equilibrium shift when the volume of the vessel is decreased at constant temperature (with short reasoning)?

d) Calculate K_p for this reaction at 1000 K.

TASK 8 - IDEAL GAS: REFRIDGERATOR **6 POINTS**

After opening and closing a refridgerator it cannot be opened for a short time. We can explain this phenomena using thermodynamics. In this task we look at a refridgerator of length $0.5\,\text{m}$, width $0.4\,\text{m}$ and height $1\,\text{m}$. Tip: In this whole task we assume that air behaves like an ideal gas.

a) Assume that the refridgerator is open long enough that the air inside is at room pressure ($1\,\text{bar}$) and room temperature ($22\,^\circ\text{C}$). Calculate the number of moles n of air in the opened refridgerator.

b) Air consists approximately of 80 volume-% N_2 and 20 volume-% O_2. Using this ratio, calculate the mass of N_2 and O_2 in the open refridgerator.

c) Then the refridgerator is closed and the enclosed air cooled to $5\,^\circ\text{C}$. Assume that the refridgerator is a closed system: There is no air exchange between the outside and the inside of the refridgerator. Calculate the pressure inside the refridgerator.

d) Using the pressure difference between the room air and the cooled refridgerator air, calculate the force which acts on the refridgerator door ($0.5\,\text{m}^2$).

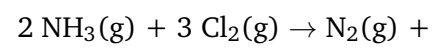
In order to be able open the refridgerator door again they have membranes permeable to air, so that more air gets inside the refridgerator until the pressure is equalized.

TASK 9 - ENTHALPY OF FORMATION, HESS'S LAW **7 POINTS**

a) The enthalpy of formation is the enthalpy that is needed to create a molecule or substance from its pure elements. Per definition, one mole of a pure element like *e.g.* $N_2(g)$, $O_2(g)$, $Cl_2(g)$ or Fe(s) has a standard enthalpy of formation of $\Delta_B H^0 = 0$ kJ mol^{-1}. The superscript 0 indices standard pressure. In this whole task we assume a temperature of 25 °C.
The standard reaction enthalpy $\Delta_R H$ of a reaction can be calculated as the sum of the standard enthalpies of formation of the reactants multiplied with their stoichiometric coefficients (in this formulation, the stoichiometric coefficients of the educts are negative). With the (all positive) stoichiometric coefficients ν from the reaction equation we have

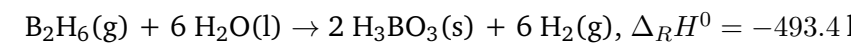
$$\Delta_R H^0 = \sum \nu \cdot \Delta_B H^0(\text{products}) - \sum \nu \cdot \Delta_B H^0(\text{educts})$$

i) Calculate the standard reaction enthalpy of the reaction



$$2\ NH_3(g) + 3\ Cl_2(g) \rightarrow N_2(g) + 6\ HCl(g)$$

ii) Calculate the standard enthalpy of formation of the of diborane (B_2H_6) with



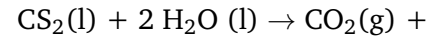
$$B_2H_6(g) + 6\ H_2O(l) \rightarrow 2\ H_3BO_3(s) + 6\ H_2(g),\ \Delta_R H^0 = -493.4\ \text{kJ mol}^{-1}$$

Use the data from the following table:

Molecule	$\Delta_B H^0$
$NH_3(g)$	-46.2 kJ mol^{-1}
$HCl(g)$	-92.3 kJ mol^{-1}
$H_2O(l)$	-285.9 kJ mol^{-1}
$H_3BO_3(s)$	-1088.7 kJ mol^{-1}

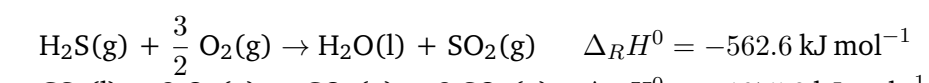
b) Hess's law states that state variables like *e.g.* the enthalpy change ΔH of a reaction is constant, independent on whether the reaction occurs in one or several steps.

i) Calculate $\Delta_R H^0$ for the following reaction

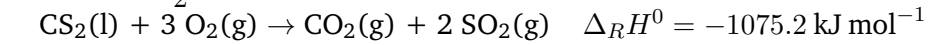


$$CS_2(l) + 2\ H_2O\ (l) \rightarrow CO_2(g) + 2\ H_2S(g)$$

using

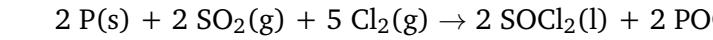


$$H_2S(g) + \frac{3}{2}\ O_2(g) \rightarrow H_2O(l) + SO_2(g) \qquad \Delta_R H^0 = -562.6\ \text{kJ mol}^{-1}$$



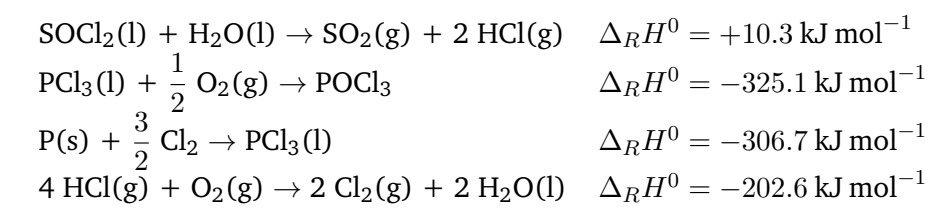
$$CS_2(l) + 3\ O_2(g) \rightarrow CO_2(g) + 2\ SO_2(g) \qquad \Delta_R H^0 = -1075.2\ \text{kJ mol}^{-1}$$

ii) Calculate $\Delta_R H^0$ for the following reaction



$$2\ P(s) + 2\ SO_2(g) + 5\ Cl_2(g) \rightarrow 2\ SOCl_2(l) + 2\ POCl_3(l)$$

using



$$SOCl_2(l) + H_2O(l) \rightarrow SO_2(g) + 2\ HCl(g) \qquad \Delta_R H^0 = +10.3\ \text{kJ mol}^{-1}$$

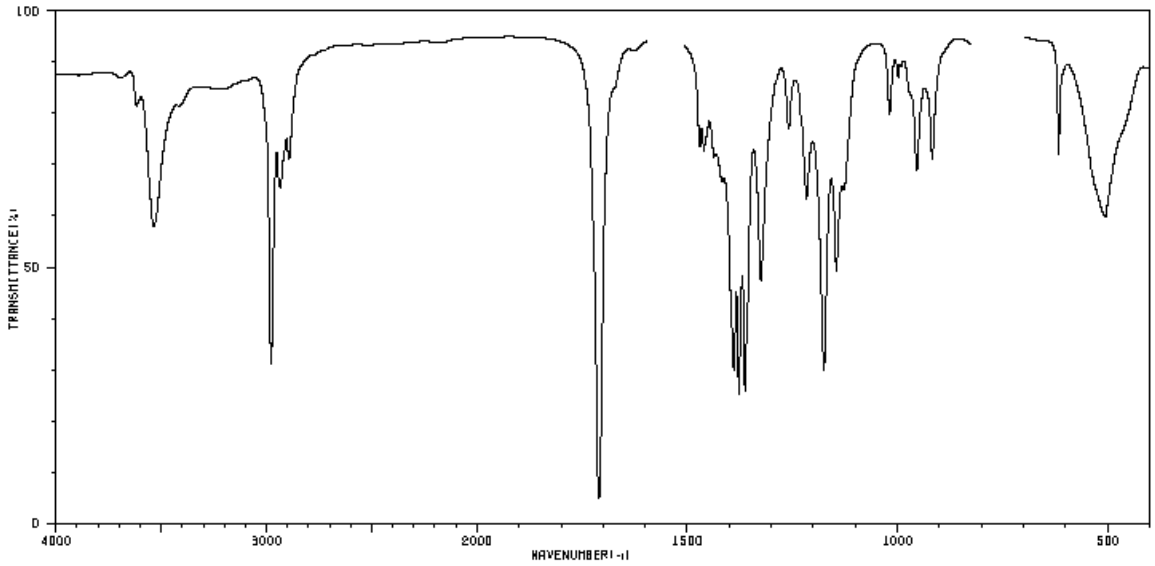
$$PCl_3(l) + \frac{1}{2}\ O_2(g) \rightarrow POCl_3 \qquad \Delta_R H^0 = -325.1\ \text{kJ mol}^{-1}$$

$$P(s) + \frac{3}{2}\ Cl_2 \rightarrow PCl_3(l) \qquad \Delta_R H^0 = -306.7\ \text{kJ mol}^{-1}$$

$$4\ HCl(g) + O_2(g) \rightarrow 2\ Cl_2(g) + 2\ H_2O(l) \qquad \Delta_R H^0 = -202.6\ \text{kJ mol}^{-1}$$

TASK 10 - INFRARED SPECTROSCOPY 5 POINTS

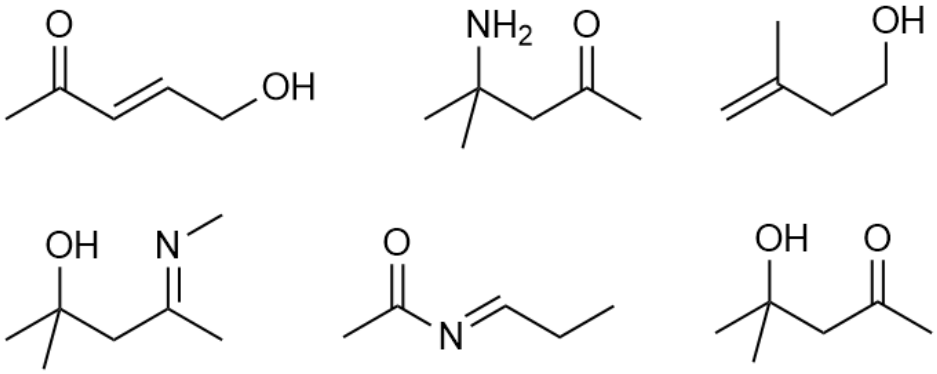
Infrared spectroscopy (IR-spectroscopy) is an old but still commonly used technique to identify and prove functional groups in molecules. The infrared radiation is absorbed by a functional group when the frequency of the infrared radiation is equal to the vibrational frequency of the functional group. This means that if a certain functional group is present, you see a peak in the measured spectrum.
The vibrational frequencies are usually within certain regions of the frequency spectrum and got tabulated. The usual unit is the wavenumber cm^{-1}, the inverse of the wavelength.



a) For all the functional groups in the table below, state whether they are present in the molecule whose IR spectrum is given above.

Funktionelle Gruppe	Wellenzahl in cm^{-1}
O-H	$3650 - 3500$
N-H	$3500 - 3300$
C-H	$3100 - 2850$
C=O	$1800 - 1650$
C=N	$1650 - 1550$
C=C	$1680 - 1630$

b) Which of the molecules shown below fits the IR spectrum given above (with explanation)?



TASK 11 - NOMENCLATURE AND ISOMERIE OF ORGANIC MOLECULES — 12 POINTS

a) Draw the constitutional formulae of the following molecules:

i) 2-Methylbutane

ii) Pent-2-ine

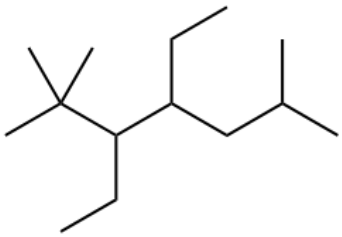
iii) 1-Chloro-3-ethylcyclohexane

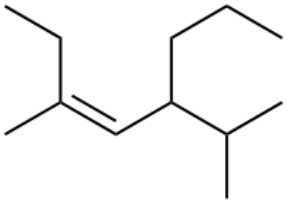
iv) 3-Methylbutan-2-one

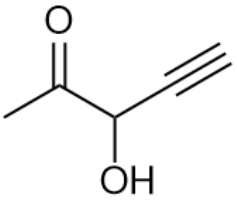
v) (*E*)-5-Hydroxy-2-methylpent-2-enal

vi) *m*-(1-Methylethyl)nitrobenzene

b) Give the names of the following molecules:

i) 

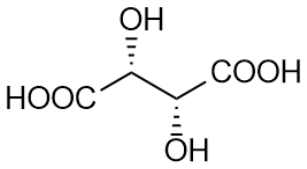
ii) 

iii) 

c) Draw 8 different isomers of C_4OH_8. Designate clearly which molecules shall be corrected. You can hand in more than 8 isomers, but additionally designated from isomers will lead to point deductions.

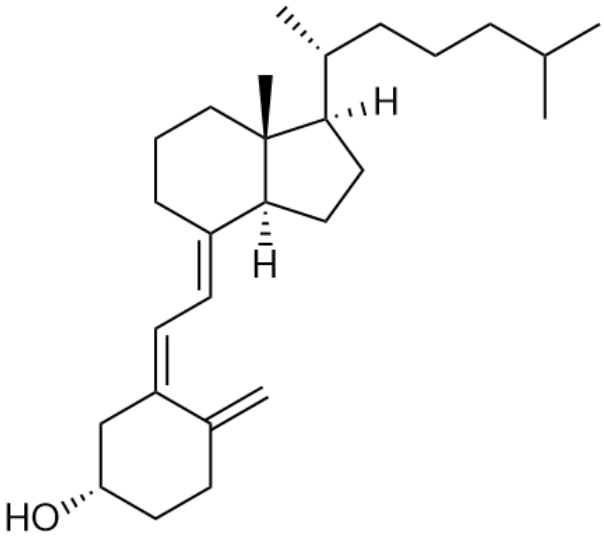
TASK 12 - STEREOCHEMISTRY **5 POINTS**

a) The following molecule is a stereoisomer of tartaric acid.



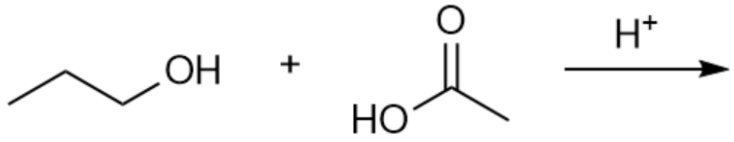
Name the stereocenters with *R/S* and draw the enantiomer.

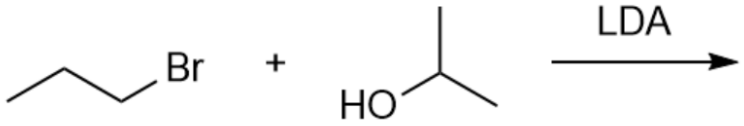
b) Given below is Cholecalciferol (Vitamin D). Find all stereocenters and name them using the *E/Z* or *R/S* notation.

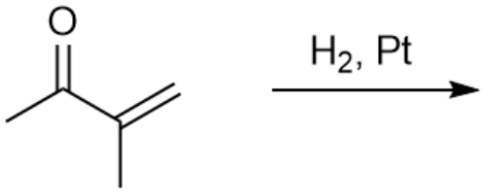


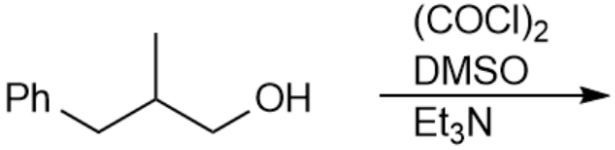
TASK 13 - ORGANIC CHEMITRY **7 POINTS**

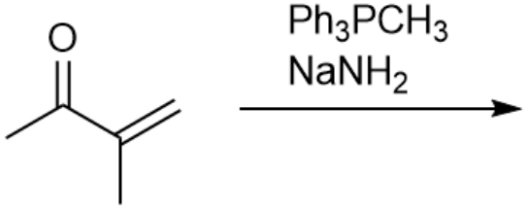
Draw the constitutional formulae of the following reactions (LDA is a strong base):

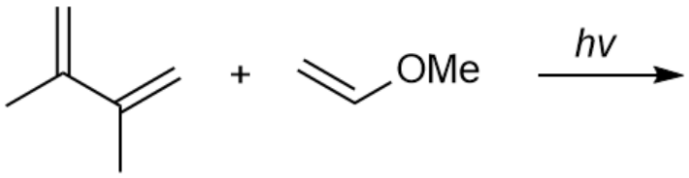
a) 

b) 

c) 

d) 

e) 

f) 

g)