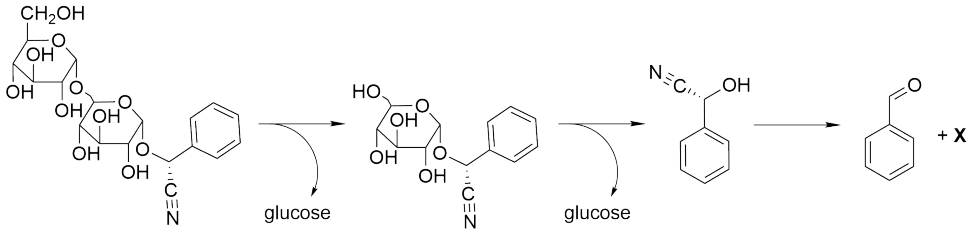
5th Chemistry Race: Questions and Solutions



10th February 2024

Question A.1 (Daniel Čičovský)

Amygdalin is an organic molecule found in the seeds of many stone fruits (almonds, apricots, plums, ...). Its likely purpose is to discourage fruit-eating animals from consuming the seeds in the drupes, the metabolism of this substance is indicated in the following diagram. Write a formula of a simple molecule **X** that is produced in the last reaction and is toxic to the vast majority of eukaryotic organisms.



Solution:

X = HCN

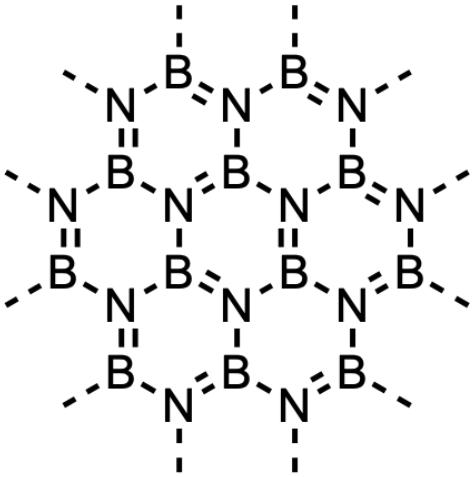
The identity of the missing product can be deduced from the last reaction.

Question A.2 (Sam Holmes)

Boron nitride is valence isoelectronic to carbon, meaning it has the same number of valence electrons and therefore has some similar properties. Give the *empirical formula* of so-called 'hexagonal' boron nitride, which has a similar molecular structure to graphite.

Solution:

Boron has one electron fewer than carbon, and nitrogen one electron more – so $(BN)_n$ has the same number of electrons as C_n. Hexagonal boron nitride has the same structure as graphite, with alternating boron and nitrogen atoms.


B
N
B
N
B
N

Solution:

We can easily work out which element should be more positively charged and which one more negatively charged by comparing the electronegativities of chlorine and iodine. The more electronegative chlorine is negatively charged, and iodine should thus have a positive charge. We know that the lowest possible oxidation state of chlorine is −I, and by simply summing up the charges of all six chlorine atoms and dividing by the number of iodine atoms, we can arrive at the solution that iodine should be in a +III oxidation state, which we know is relatively stable for halogens.

Question A.4 (Petr Linhart)

Recently, there has been a lot of discussion about which energy sources the UK should invest in. Can you recognise the main reaction serving as an energy source in each type of power plants mentioned below? Match the equation with the corresponding power plant.

1. Nuclear fusion (lately successfully performed with a positive energetic balance for the first time)
2. Coal power plant
3. Nuclear power plant (fission)
4. Natural gas power plant

(a) $\mathrm{C + O_2 \longrightarrow CO_2}$
(b) $\mathrm{CH_4 + 2\,O_2 \longrightarrow 2\,H_2O + CO_2}$
(c) $\mathrm{{}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n}$
(d) $\mathrm{{}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{92}_{36}Kr + {}^{141}_{56}Ba + 3\,{}^{1}_{0}n}$

Solution:

Nuclear fusion is a process which creates energy by combining atomic nuclei. This process is only exergonic at lighter elements (the delimiter is at the nuclide $^{56}_{26}\mathrm{Fe}$). The biggest energy gain occurs when hydrogen atoms are fused and form helium. Such processes are also the main source of energy in nuclei of stars such as our Sun (1c):

$$\mathrm{{}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n}$$

Turbines of generators of electric energy in coal power plants are powered by steam which is generated by heating water upon coal burning (2a):

$$\mathrm{C + O_2 \longrightarrow CO_2}$$

In the nuclear power plant, electricity is generated by steam turning turbines as well, however, the process of heating is based on a nuclear fission reaction (3d):

$$^{235}_{92}\mathrm{U} + {}^{1}_{0}\mathrm{n} \longrightarrow {}^{92}_{36}\mathrm{Kr} + {}^{141}_{56}\mathrm{Ba} + {}_{3}\,{}^{1}_{0}\mathrm{n}$$

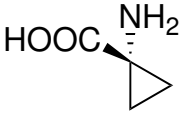
Gas power plant works similarly to the coal power plant, only instead of coal, methane is burnt (4b):

$$\mathrm{CH_4} + 2\,\mathrm{O_2} \longrightarrow 2\,\mathrm{H_2O} + \mathrm{CO_2}$$

Question A.5 (Daniel Čičovský)

Ethene is one of the simplest plant hormones, with a role in regulating the ripening of fruit. Its precursor is 1-aminocyclopropane-1-carboxylic acid (see picture), which is oxidised in plant cells to form ethylene, hydrogen cyanide, water, and carbon dioxide. Biochemist Vlado discovered that this reaction takes place in bananas, and that he could try to exploit the bananas to solve his problem with increasing fuel prices.

A kilogram of bananas produces on average 2.6 microliters of ethylene per hour at a temperature of 15 °C. How many kilograms of bananas does Vlado need to buy to get one kilogram of ethylene per week? Ignore the respiration of bananas and other disturbing phenomena.



Solution:

1 kilogram of ethylene is approximately 35.71 moles, which corresponds to 800 litres of gas. From ideal gas equation of state $pV = nRT$ we compute the molar quantity of the gas released by the bananas (for $p = 100\,000\,\mathrm{Pa}$):

$$n = \frac{pV}{RT} = \frac{100000 \times 2.6 \times 10^{-9}}{8.314 \times (273 + 15)} = 1.09 \times 10^{-7}\,\mathrm{mol\,h^{-1}}$$

Molar mass of the $M_{\mathrm{ethylene}} \doteq 28\,\mathrm{g\,mol^{-1}}$, and so the mass of released ethylene is

$$m = M \times n = 28 \times 1.09 \times 10^{-7}\mathrm{g} \doteq 3.04 \times 10^{-9}\,\mathrm{kg\,h^{-1}},$$

which recalculated for a week makes $m = 3.04 \times 10^{-9} \times 168 = 5.1 \times 10^{-7}\,\mathrm{kg}$ of gas per kilogram of bananas. If Vlado wants to get a kilogram of ethylene per a week, he need to buy $\frac{1}{5.1 \times 10^{-7}} \doteq 1\,960\,000\,\mathrm{kg}$ of bananas.

Question A.6 (Sam Holmes)

Chloramines are amine derivatives in which one or more of the N−H bonds has been replaced by an N−Cl bond. They are responsible for the distinctive smell of swimming pools, where they can form by the reaction of bleach, NaOCl (added as a disinfectant) with amines (from human sweat and other excretions). Trichloramine is dangerous because it is a strong irritant, and in high concentrations it can explosively decompose. Write down the balanced chemical equation for the explosive decomposition of trichloramine.

Solution:

$$2\,\mathrm{NCl_3} \longrightarrow \mathrm{N_2} + 3\,\mathrm{Cl_2}$$

Question B.1 (Marie Grunová)

Enzyme activity can be expressed using two different units. Either the so-called international unit IU is used, where $1\,\mathrm{IU} = 1\,\mu\mathrm{mol/min}$, or the so-called katal, shortened as kat, where $1\,\mathrm{katal} = 1\,\mathrm{mol\,s^{-1}}$. Determine the conversion factor from IU to katal.

Solution:

$$1\,\mathrm{IU} = 1\,\mu\mathrm{mol/min} = 10 \times 10^{-7}\,\mathrm{mol/min} = \frac{10^{-6}}{60}\,\mathrm{mol\,s^{-1}} \doteq 1.667 \times 10^{-8}\,\mathrm{katal}$$

Question B.2 (Adam Tywoniak)

"Monkeys Eat Peanut Butter" is a mnemonic meant to help you remember the names of the four simplest hydrocarbons **m**ethane, **e**thane, **p**ropane, **b**utane.

Grossane is our affectionate name for a saturated straight-chain alkane containing 144 carbon atoms. How many hydrogen atoms does a grossane molecule contain?

Solution:

Alkanes have the general formula $\mathrm{C}_n\mathrm{H}_{2n+2}$. Therefore, grosanne has $(144 \times 2) + 2 = 290$ hydrogen atoms.

Question B.3 (Sam Holmes)

Technical drawings are often called blueprints owing to their distinctive colour. An early method for creating these intricately detailed diagrams involved the reaction of iron(II) with potassium ferricyanide to form insoluble ferrous ferricyanide, $Fe_7(CN)_{18}$, otherwise known as Prussian blue. Ferrous ferricyanide contains iron in +II and +III oxidation states only. Work out the ratio of Fe(II) to Fe(III) in Prussian blue. Give your answer as the smallest whole number ratio in the form $n_{\mathrm{Fe(II)}} : n_{\mathrm{Fe(III)}}$.

Solution:

A trial and error is probably sensible here, but formally a system of equations can also be constructed thus:

$$A + B = 7$$

$$2A + 3B = 18$$

Eliminating B:

$$2A + 3(7 - A) = 18$$

Rearranging:

$$-A = 18 - 21 = -3 \implies A = 3, B = 4 \text{ (by substituting A back in)}$$

Question B.4 (Jiří Ledvinka)

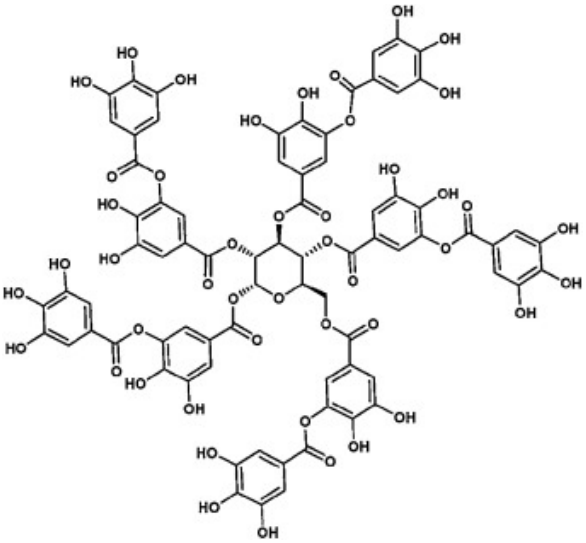
Sulfur hexafluoride is infamous because of its ability to deepen the voice - this is due to its relatively high density. Unfortunately, its sale has been restricted in recent years due to its adverse effect on the ozone layer. Let's imagine that we would like to use tellurium hexafluoride instead, and let's neglect for the moment the relatively significant difference in their reactivity (tellurium hexafluoride is highly toxic). Let us further assume that tellurium hexafluoride behaves as an ideal gas. What is its density at 25°C and a pressure of 101 325 Pa?

Solution:

$$pV = nRT$$
$$\frac{n}{V} = \frac{p}{RT} = 40.88\,\mathrm{mol\,m^{-3}}$$
$$\rho = M_r \times \frac{n}{V} = 9875\,\mathrm{g\,m^{-3}} = 9.875 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$$

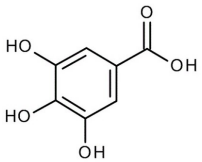
Question B.5 (Daniel Čičovský)

Oak gall ink is a type of ink that was commonly used in Europe from the 12th century until the 19th century. Its production involves the formation of iron(II) complexes from ferrous sulfate and tannins, which can be obtained from oak apples. Oak apple is a neoplasm on oak leaves that develops in response to parasites such as the oak gall midge (*Cynips quercusfolii*). These neoplasms contain large amounts of tannins that are intended to make the life of the parasite uncomfortable. An important group of tannins are the esters of gallic acid and saccharides. A typical example is tannic acid (see appendix). The heating of this acid causes hydrolysis of the ester bonds and the release of gallic acid, which is used to make oak gall ink. Draw the structural formula of gallic acid. Hint: all of the ester bonds in tannic acid are hydrolysed upon heating.



Solution:

Tannic acid is formed by the esterification of gallic acid dimers with glucose.



Question B.6 (Jiří Ledvinka)

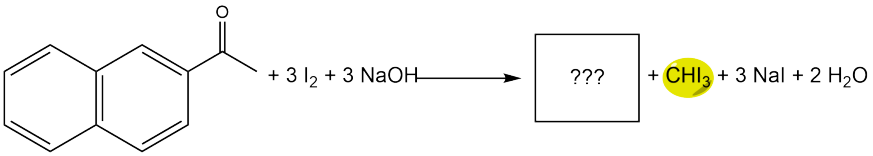
The first discovered organometallic compounds are thought to be dicacodyl $((CH_3)_2As)_2$ and dicacodyl oxide $((CH_3)_2As)_2O$, which were obtained as brown oily liquids that smelled rather foul and fumed in the air. These substances were prepared by a rather unusual reaction of potassium acetate (ethanoate) with arsenic trioxide. Write down the balanced chemical equation for the formation of dicacodyl oxide from arsenic trioxide and potassium acetate (only potassium carbonate and carbon dioxide are formed as by-products).

Solution:

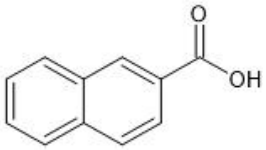
$$4\ CH_3COOK + As_2O_3 \rightarrow ((CH_3)_2As)_2O + 2\ K_2CO_3 + 2\ CO_2$$

Question C.1 (Peter Rukovansky)

The iodoform reaction is used to oxidise methyl ketones. It can also be used as a test for methyl ketones because iodoform (CHI_3) is formed as a yellow solid with a distinct odour, which is insoluble in water. A balanced chemical equation for this reaction is given below, but one of the products is missing. Draw the structure of the missing organic product.



Solution:



The question can be solved by employing knowledge of the reaction (and its product), figuring out the mechanism or simply by counting atoms. We are left with the 2-naphtyle group (R), one carbon, two oxygen and one hydrogen atoms (R, C, O, O, H). This together gives naphtalene-2-carboxylic acid as drawn above. The statement that it is an oxidation that occurs (ketone to acid) should also help to solve this question.

Question C.2 (Jiří Ledvinka)

Almost every portable electronic device today gets its power from lithium-ion batteries. Manufacturing of these batteries requires mining for feedstock materials, including lithium metal. A huge deposit of lithium ore is located under the Czech mountain Cínovec, which has an estimated mass of 134 million tons and an average lithium content of 0.28% (by weight). How many megatons of lithium carbonate, a feedstock for battery production, could be produced from this reserve?

Solution:

The lithium located under Cínovec amounts to $134 \times 10^6 \times 0.0028 = 375.2$ kilotons. Lithium carbonate has the following content, i.e. the mass fraction of lithium:

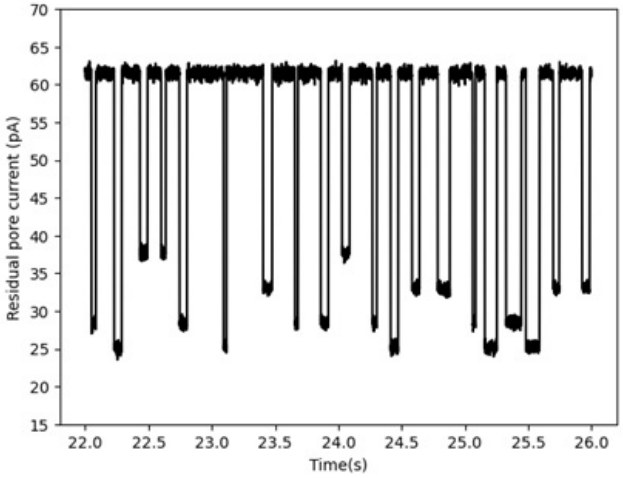
$$w(\mathrm{Li}) = \frac{2 \cdot A(\mathrm{Li})}{(2 \cdot A(\mathrm{Li}) + A(\mathrm{C}) + 3 \cdot A(\mathrm{O}))} = \frac{2 \times 6.941}{2 \times 6.941 + 12.011 + 3 \times 15.999} = 0.188$$

Therefore the theoretical mass of lithium carbonate that can be produced from the ore is $m/w(\mathrm{Li}) = \frac{375.2}{0.188}$ kilotons $= 1.996$ megatons.

Question C.3 (Sam Holmes)

The flow of ions through channels is a fundamental process in biology, and one which we can exploit in chemistry. We can measure the current associated with the flow of ions through a small perforation in a membrane (a 'nanopore') under an applied electric potential, and this can be used to detect how other molecules (such as DNA) interact with the pore.

When DNA bases block the pore, they restrict the flow of ions through it – the stronger the binding of the DNA base, the greater the restriction and the lower the measured current. You are given that DNA bases bind inside the pore with strength G > T > A > C.. Consider the following (idealised) trace resulting from a nanopore sequencing of an oligonucleotide. Work out how many cytosine bases and how many adenine bases are present in this fragment of DNA. See the idealized record of nanopore sequencing of an oligonucleotide below.



Solution:

3× cytosine, 5× adenine

Cytosine binds the least strongly, we simply have to look for the binding events with the highest residual current (around 40 pA). There are three such events in the trace shown. Using a similar method, we can determine that there are 5 adenine bases in the fragment.

This question has been sponsored by Oxford Nanopore Technologies plc.

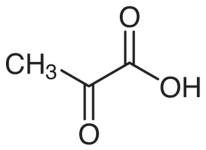
Question C.4 (Jiří Ledvinka)

Glycols (derived from Greek, meaning 'sweet') are 1,2-diols. The simplest molecule of this class, ethylene glycol (ethane-1,2-diol), is toxic because it is metabolised in the body to oxalic acid (HOOCCOOH). However, propylene glycol (propane-1,2-diol) is not toxic, because it is metabolised into a molecule which is also produced naturally in the body. Write down the structure of this molecule.

Hint: During the metabolism of propylene glycol, no C−C bonds are broken.

Solution:

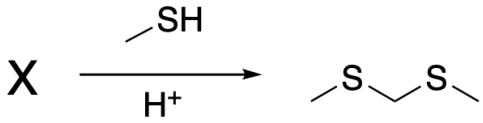
Pyruvic acid (pyruvate)



Taking inspiration from the metabolism of ethylene glycol, we should predict that both alcohol groups can be oxidised – rather than a dialdehyde, we instead oxidise further to a far less electrophilic oxoacid – pyruvic acid, which appears in several metabolic pathways including the citric acid (Krebs) cycle.

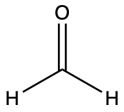
Question C.5 (Supatpong Juntarawatt)

2,4-Dithiapentane (or bis(methylthio)methane) is an additive for truffle flavouring in various products like truffle oil. It can be synthesised from acid-catalysed condensation (eliminating water) between 2 equivalents of methanethiol (which, ironically, is the main component in bad breath and foot odour) and compound X ($M_r = 30$). Draw a skeletal structure of X.



Solution:

From the structure of the thiol, X must contain a carbon atom. Further, since it condenses water under acid catalysis, it will have an oxygen atom too. To reach the molecular mass two more hydrogens are needed, yielding a molecular formula of CH_2O. This is instantly reconizable as formaldehyde:



formaldehyde

Question C.6 (Ondra Daněk)

You probably already know that bananas are a really good source of potassium. But just how much potassium does a banana contain?

100 bananas with a total mass of 10 kg were sliced, dehydrated, and burned. The ash was leached in water, the insoluble impurities were filtered out and the solution was concentrated by evaporation. A saturated solution of ammonium perchlorate was added and the resulting white precipitate was filtered off and dried. The mass of the precipitate was 74.576 g.

Calculate how much potassium (in mg) an average banana contains.

Hint: K^+ and ClO_4^- form one of the few examples of a pair hard Lewis acid – hard Lewis base which renders the resulting compound practically insoluble in water.

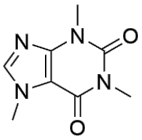
Solution:

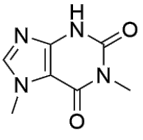
$$\begin{aligned} n(\mathrm{KClO_4}) &= \frac{74.576\,\mathrm{g}}{138.6\,\mathrm{g\,mol^{-1}}} = 0.538\,\mathrm{mol} \\ n(\mathrm{K}) &= n(\mathrm{KClO_4}) = 0.538\,\mathrm{mol} \\ m(\mathrm{K}) &= 0.538\,\mathrm{mol} \times 39.1\,\mathrm{g\,mol^{-1}} = 21.0\,\mathrm{g} \end{aligned}$$

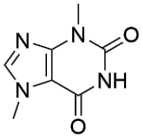
So in whole solution, there is 21.0 g of potassium. Divide that by 100 to get 0.21 g = 210 mg of potassium per banana.

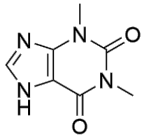
Question D.1 (Tadeáš Grabic)

Tired chemist Tadeáš had to get up for his mathematics lecture one Monday. The weekend before the lecture he slept for a total of about 5 hours, so he made himself a strong cup of coffee in the morning. The caffeine contained in the coffee is metabolised in the liver. 84% of the caffeine is metabolised to paraxanthine, 12% to theobromine and the rest is converted to theophylline. 100 mℓ of drip coffee contains about 40 mg of caffeine. How many milligrams of each metabolite will be formed if Tadeáš drank 300 mℓ of drip coffee? The structures of caffeine and its metabolites are given in the appendix. Skeletal formula for caffeine and its metabolic products.


Caffeine


Paraxanthine


Theobromine


Theophylline

Solution:

Paraxanthine – 93.5 mg ± 0.2 mg; Theobromine – 13.4 mg ± 0.2 mg; Theophylline – 4.5 mg ± 0.2 mg.

A 300 mℓ cup contains $3 \times 40 = 120$ mg. The molecular formula of caffeine is $C_8H_{10}N_4O_2$, so $M_r = 194\,\mathrm{g\,mol^{-1}}$.
The three products of metabolism are isomers – this simplifies the calculation significantly!

$$M_r(\text{Paraxanthine}) = M_r(\text{Theobromine}) = M_r(\text{Theophylline}) = 180\,\mathrm{g\,mol^{-1}}$$

Use these to find chemical amounts and therefore masses:

$$n(\text{Caffeine}) = \frac{120\,\mathrm{mg}}{194\,\mathrm{g\,mol^{-1}}} = 0.00515\,\mathrm{mol}$$

$$m(\text{Paraxanthine}) = M \times n = 180 \times \frac{120}{194} \times 0.84 = 93.5\,\mathrm{mg}$$

$$m(\text{Theobromine}) = M \times n = 180 \times \frac{120}{194} \times 0.12 = 13.4\,\mathrm{mg}$$

$$m(\text{Theophylline}) = M \times n = 180 \times \frac{120}{194} \times 0.04 = 4.5\,\mathrm{mg}$$

Question D.2 (Sam Holmes)

The electron configuration of elements is not always easy to predict. Using the Madelung rule, you might expect the electron configuration of Pd to be $[Xe]4d^8 5s^2$, i.e. the 5s subshell is filled before the 4d. In fact, the ground state electronic configuration of Pd is $[Xe]4d^{10} 5s^0$, i.e. the 4d subshell has been filled first.

Excluding palladium (and any other similar rule-breakers), how many elements would you predict to have no unpaired electrons in the ground state electron configuration of their separated atoms?

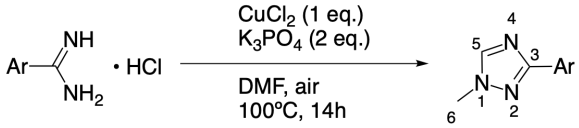
Solution:

19

The elements are those in groups 2, 12 and 18, plus Yb and No in the f-block. You can automatically eliminate all elements with an odd number of electrons, but then remember that the p^4 configuration actually contains 2 unpaired electrons (according to the Hund's rule of maximum multiplicity) to avoid electron-electron repulsion, so the number of elements with no unpaired electrons is rather small.

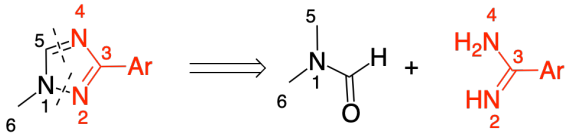
Question D.3 (Jiří Ledvinka)

Unsubstituted 1,2,4-triazole is a relatively frequently used bridging ligand. Substituted 1,2,4-triazoles are in turn found in many pharmaceuticals. New synthetic methods are being developed for their wide application. One of them is the reaction of amidine hydrochloride with *N*,*N*-dimethylformamide (DMF). Which product atoms come from *N*,*N*-dimethylformamide? (Write their numbers.)



Solution:

While the exact mechanism for this reaction is not clear, we are still able to make deductions by understanding the carbon skeleton. The reaction conditions (air, Cu^{2+} and acid) are mildly oxidizing, which means the presence of nucleophiles strong enough to attack the DMF and amidine is unlikely. Therefore, atoms 3, 2 and 4 are probably part of the amidine hydrochloride unit. This leaves out 1,5 and 6 as part of the DMF unit. This is pretty reasonable, as DMF contains a $-N(CH_3)_2$ unit. Although one of the methyl groups from DMF is missing in the product, however, understanding the mechanism of its disappearance is not critical for answering this question correctly.



Question D.4 (Štěpán Novák)

Coryzalia, sold in pharmacies as homeopathic medicine, contains a highly toxic substance called "Kalium bichromicum". As chemists, we do not shy away from the medical name and realise that it is potassium dichromate. It is specified that a single tablet contains 3 CH 0.333 mg. This means the preparation started with 0.333 mg of compound and was followed by three dilutions, where each dilution reduces the concentration by a factor of 100. The LD_{50} for oral ingestion of potassium dichromate for a rat is 25 mg/kg of body weight. Let us approximate that the LD_{50} for a human will be similar and the average human weighs 80 kg. Calculate how many tablets an average person would need to eat to get to the LD_{50} dose.

Solution:

First we need to calculate LD_{50} for a 80 kg human:

$$LD_{50} = 80 \times 0.025 = 2.0\,\text{g}$$

Mass of dichromate in one tablet of the homeopatic cure after three rounds of 100-fold dilution is:

$$3.331 \times 10^{-4}\,\text{g} \times 10^{-6} = 3.33 \times 10^{-10}\,\text{g}$$

Dividing LD_{50} by the mass of dichromate in 1 tablet gives us the number of tablets:

$$\frac{2\,\mathrm{g}}{3.33 \times 10^{-10}\,\mathrm{g}} = 6\,006\,006\,006$$

Potassium dichromate is, however, dangerous even in less than acutely lethal doses because of its mutagenic and carcinogenic properties.

Question D.5 (Tadeáš Grabic)

A nice lab demonstration is the so-called "volcano on the table". An orange substance containing 41.27% Cr; 3.17% H; 11.11% N and 44.44% O decomposes thermally after initiation to form a green powder containing chromium, inert gas, and water. Write a balanced equation of the decomposition reaction taking place.

Solution:

$(NH_4)_2Cr_2O_7 \longrightarrow Cr_2O_3 + N_2 + 4\,H_2O$

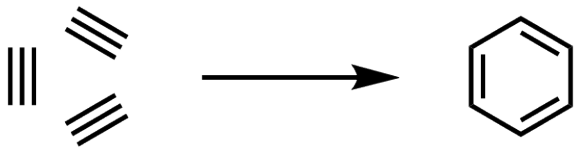
Determine the reactant through a standard molecular formula calculation. For 100g of starting material, there are: 0.794 mol Cr, 3.145 mol H, 0.793 mol N, 2.778 mol O. Divide by the smallest to get the ratio

$$n_{\mathrm{Cr}} : n_{\mathrm{H}} : n_{\mathrm{N}} : n_{\mathrm{O}} = 1 : 4 : 1 : 3.5 \sim 2 : 8 : 2 : 7.$$

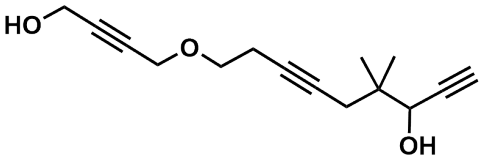
Furthermore, from the orange colour and tendency to decompose, we can guess the compound in question is ammonium dichromate. Once the starting substance has been determined, all that remains is to quantify the redox equation.

Question D.6 (Jiří Ledvinka)

Cyclotrimerization of alkynes is a useful reaction in which three alkynes form a benzene ring. The general reaction is shown below.

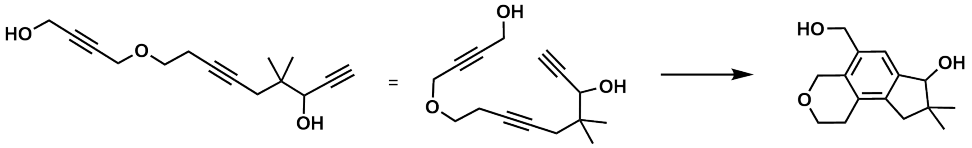


This reaction is very useful for the preparation of densely substituted benzenes. Draw the product that results from the intramolecular cyclotrimerization of the following molecule.



Solution:

If we redraw the molecule with all the triple bonds close together, we can easily draw the product.



Question E.1 (Jakub Štěpánek)

Aluminium is most often produced electrochemically through the well-known Hall–Héroult process, where alumina (Al_2O_3) is electrolysed at high temperature. However, in order to convert the alumina to a melt at reasonable temperatures, it is still necessary to add a so-called cryolite – $Na_3[AlF_6]$ which causes the formation of a eutectic mixture with a lower melting point. The cathode for the reaction is a steel bottom covered with a layer of aluminium, the anode is a carbon electrode. A skilled chemist would think that the reaction produces oxygen in addition to aluminium, but thermodynamics has other plans. Instead, carbon monoxide is produced at the anode, since the graphite electrode is also a reactant during the process.

Your task now, however, will not be to deal with carbon monoxide, but with a by-product that is very problematic because of its inert properties – carbon fluoride. This is produced from cryolite when oxide anions are absent at the anode. As a heavy gas, carbon fluoride can coat the anodes and therefore prevent the electrochemical reaction continuing further. Using the bond dissociation energy (BDE) theory, determine the amount of energy required to form one mole of CF_4.

$\mathrm{BDE(Al{-}F)} = 664\,\mathrm{kJ\,mol^{-1}}$
$\mathrm{BDE(C{-}F)} = 485\,\mathrm{kJ\,mol^{-1}}$
$E_{\mathrm{atomisation}}(\mathrm{graphite}) = 717\,\mathrm{kJ\,mol^{-1}}$
$E_{\mathrm{atomisation}}(\mathrm{Al}) = 186\,\mathrm{kJ\,mol^{-1}}$

Solution:

The key is realising that cryolite is a mixture of aluminium fluoride and sodium fluoride $3\,\mathrm{NaF}\cdot\mathrm{AlF_3}$ and realising that only $\mathrm{AlF_3}$ reacts. Next, it is necessary to write the balanced equation of the parasitic reaction:

$$4\,\mathrm{AlF_3} + 3\,\mathrm{C} \rightarrow 3\,\mathrm{CF_4} + 4\,\mathrm{Al}$$

Then it is necessary to realise that the BDE denotes the amount of energy required to split a bond to two isolated atoms in the gas phase.

Now, we need to calculate the energy required to break all the bonds in all the reactants to form atoms. Then, we need to calculate the energy released when each of the atoms reforms into a bond in the product (this is the same magnitude as the BDE but is negative). The overall energy change is then obtained by adding the values obtained from dissociating the reactants (positive) and the forming bonds in the products (negative value). Bearing in mind the stoichiometry of the reaction, this will give us the energy required to form 3 moles of carbon fluoride, so dividing this value by 3 will give us the energy for one mole.

This way, we obtain

$$\begin{aligned} E &= \frac{1}{3}\,E_{\mathrm{reaction}} \\ &= \frac{1}{3} \times [(4 \times 3 \times \mathrm{BDE(Al{-}F)} + 3\,E_{\mathrm{atomisation}}(\mathrm{graphite})) \\ &\qquad - (3 \times 4 \times \mathrm{BDE(C{-}F)} + 4\,E_{\mathrm{atomisation}}(\mathrm{Al}))] \\ &= \frac{1}{3} \times [(12 \times 664 + 3 \times 717) - (12 \times 485 + 4 \times 186)] = 1185\,\mathrm{kJ}. \end{aligned}$$

Question E.2 (Jakub Sochor)

Uranium-232 is an artificially prepared isotope of uranium. Experimental measurements of a 1 gram sample of this radionuclide revealed an activity $A = 8.26 \times 10^{11}$ Bq (activity is defined as a number of radioactive decays per second). Radioactive decay is described by the following equation:

$$N(t) = N_0 \, \mathrm{e}^{-\lambda \, t},$$

where $N(t)$ is the count of particles at the time t, N_0 is the initial amount of particles in the sample, and λ is the decay constant.

Using the equation above, calculate the half-life of U-232 as an integer number of years.

Hint: Radioactive decay follows first-order kinetics. Activity is defined as the number of decays per unit of time, i.e., the 'speed' of decay. Mathematically, this corresponds to the so-called negatively taken time derivative of the number of particles $N(t)$ which has the meaning of 'instantaneous speed' of the decay. The following example can help you connect the decay law and the activity: consider a function $f = A \, \mathrm{e}^{y \, z}$. Then its derivative concerning the variable y is

$$\frac{\mathrm{d}f}{\mathrm{d}y} = A \, z \, \mathrm{e}^{y \, z}.$$

Solution:

We know that $N(t) = N_0 \, \mathrm{e}^{-\lambda \, t}$. According to the question text, activity is defined as

$$A = \frac{\Delta N}{\Delta t},$$

which in terms of derivatives gives

$$A = -\frac{\mathrm{d}N}{\mathrm{d}t}.$$

After examining the hint, we can work out the derivative:

$$A(t) = -\frac{\mathrm{d}N}{\mathrm{d}t} = -(-\lambda) \, N_0 \, \mathrm{e}^{-\lambda \, t} = \lambda \, N(t).$$

At the beginning of the experiment, our sample contained

$$N = n \, N_A = \frac{m}{M} \, N_A \doteq \frac{1}{232} \times 6.022 \times 10^{23} \doteq 2.59 \times 10^{21} \text{ particles},$$

hence

$$\lambda = \frac{A}{N} = \frac{8.26 \times 10^{11}}{2.59 \times 10^{21}} \doteq 3.18 \times 10^{-10}\,\mathrm{s}^{-1}.$$

The half-life $\tau_{1/2}$ is the time required for a substance to reduce its count to half of the original value:

$$N(t) = \frac{1}{2}N_0 = N_0\,\mathrm{e}^{-\lambda\,\tau_{1/2}}$$

$$\lambda = \frac{\ln(2)}{\tau_{1/2}}$$

$$\tau_{1/2} = \frac{\ln(2)}{\lambda} = \frac{\ln(2)}{3.18 \times 10^{-10}} \doteq 69\,\mathrm{years}.$$

Question E.3 (Petr Linhart)

The quantity of calcium ions Ca^{2+} in a solution can be determined by the following indirect method. First, the calcium salt solution is allowed to react with the simplest dicarboxylic acid **A**, forming its water-insoluble salt **B**. Salt **B** is then allowed to react with acid **C**, resulting in water-insoluble compound **D**, whose partially hydrated form is used, for example, in healthcare or sculpture. The released acid **A** is determined manganometrically. Write an equation of the manganometric titration in acidic environment including all products (it is not necessary to balance it). Identify substances **A**–**D**.

Salt **B** crystallises in the form of so-called raphides; these are needle-like structures which are used by some organisms as a defence mechanism.

Solution:

Reaction (balancing not required):
$KMnO_4 + (COOH)_2 + H_2SO_4 \longrightarrow MnSO_4 + K_2SO_4 + CO_2 + H_2O$

substance **A** – oxalic acid ($(COOH)_2$)

substance **B** – calcium oxalate ($(COO)_2Ca$)

substance **C** – sulfuric acid (H_2SO_4)

substance **D** – calcium sulfate ($CaSO_4$)

Question E.4 (Jiří Ledvinka)

Phosphonium iodide (PH_4I) is analogous to more known ammonium chloride. It is a stable and convenient source of phosphane (which is released after its reaction with a base) and can be used for incorporating phosphorus into organic molecules. Phosphonium iodide can be prepared by reaction of diphosphine tetraiodide (P_2I_4) with white phosphorus in water, resulting in the formation of phosphoric acid as one of the products. Provide a balanced equation for this reaction.

Hint: It may be beneficial to solve this problem using a system of equations.

Solution:

The general reaction equation is

$$a\,P_2I_4 + b\,P_4 + c\,H_2O \longrightarrow d\,PH_4I + e\,H_3PO_4,$$

where a–e are the yet unknown stochiometric coefficients. The water on the left-hand side is required for the formation of phosphoric acid (it is the only source of hydrogen atoms). We can now write down a system of balanced equations for the individual elements (these equations express that the same number of atoms of given element have to be present on both sides):

- P: $2\,a + 4\,b = d + e$,
- I: $4\,a = d$,
- H: $2\,c = 4\,d + 3\,e$,
- O: $c = 4\,e$.

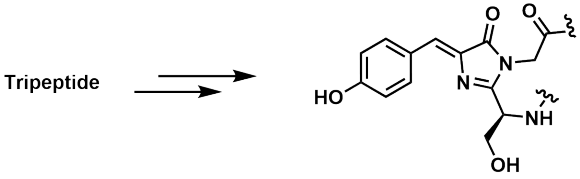
Thus, we obtain 4 equations with five variables which do not have a unique solution (in fact, there are infinitely many solutions of this system). We therefore select $a = 1$, then we get $d = 4$ from the equation for I. We can substitute the coefficient c from the equation for O into the equation for H, obtaining $e = 16/5$. Then $c = 64/5$ from equation for O and $b = 13/10$ can be calculated from equation for P. In order to get integer values for a–e, we just need to multiply all the obtained coefficients by 10.

The solution is

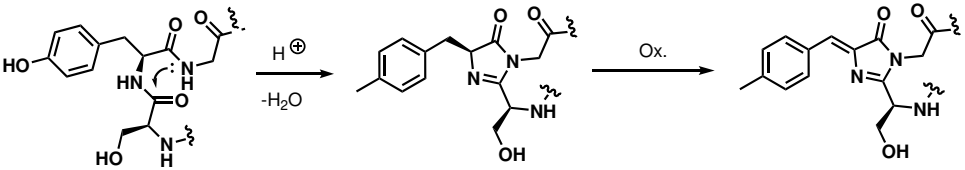
$$10\,P_2I_4 + 13\,P_4 + 128\,H_2O \longrightarrow 40\,PH_4I + 32\,H_3PO_4.$$

Question E.5 (Tatiana Nemirovich)

In a study published in the prestigious journal Nature Chemistry in 2011, scientists inserted genes encoding green fluorescent protein (GFP) synthesis into the genome of domestic cats. This genetic engineering resulted in the cat tissues showing green fluorescence when illuminated with ultraviolet light. However, the main goal of this experiment was not just to achieve a visual effect. The key scientific purpose was to monitor and analyse the resistance of these genetically modified cats to the feline immunodeficiency virus (FIV), a virus analogous to the human immunodeficiency virus (HIV). The green fluorescent protein (GFP) exhibits fluorescence due to a chromophore whose structure is indicated in the figure below. The chromophore is formed by a cascade of biochemical cyclization reactions from a tripeptide. Write down the sequence of amino acids of this tripeptide using three-letter abbreviations.



Solution:



To solve this question, we first have to try to figure out what reactions lead to the formation of the fluorescent part of GFP from the tripeptide. We can see that one carbonyl oxygen is missing, and an amidine motif is present instead. At the same time, one of the nitrogens in the peptide bond between the last two amino acids s bound to the amidine carbon while in the peptide it should have one hydrogen bound to it. One transformation thus must be an intramolecular condensation that forms this amidine. We can also see that there is one extra double bond in the fluorescent fragment next to the phenyl ring which must be formed by oxidation. Reversing these two reactions on paper gives us the structure of the starting peptide and either from memory or with a table of the proteinogenic amino acids, we can write the order of the amino acids from *N*- to the *C*- terminus: Serine - Tyrosine - Glycine, or, in three letter code: Ser–Tyr–Gly.

Question E.6 (Rostislav Huňa)

Transmittance T is the ratio of the intensity of light that has passed through the sample to the intensity of light that has entered the sample. Absorbance A is a quantity which indicates how much light was absorbed by the measured sample. Absorbance can be calculated from transmittance followingly:

$$A = -\log_{10}(T).$$

The relationship between concentration of a species and its absorbance is given by the Beer–Lambert law:

$$A = \epsilon_\lambda \, c \, l,$$

where ϵ_λ is the molar absorption coefficient which depends on the wavelength of the radiation λ, c is the molar concentration and l is the length of the cuvette.

A sample transmittance $T = 0.7$ was measured in a given cuvette for a light of a given wavelength. What transmittance will we get if we measure the same sample at the same wavelength but in a cuvette twice as long?

Solution:

If neither the wavelength nor the sample change, absorbance is directly proportional to the length of the cuvette. The absorbance in the original measurement was $A_0 = -\log_{10}(0.7) \doteq 0.1549$. In a cuvette two times longer, absorbance will also double in magnitude: $A = 2\,A_0 \doteq 0.3098$, from this we get $T = 10^{-A} = 0.49$.

Question F.1 (Štěpán Novák)

How much Cornish clotted cream does a bus need to get from Oxford to Jeremy Clarkson's farm in Chipping Norton? The distance between these two places is 20 miles. Consider that a Wright Gemini 2 double-decker bus has an average consumption of $24.1\,\ell$ of diesel per 100 miles. For simplicity, consider that the diesel is composed purely of hexadecane. The heat of combustion of hexadecane is $\Delta_{\text{comb}}H^{\ominus}(\text{hexadecane}) = 10.7\,\text{MJ}\,\text{mol}^{-1}$, and the density is $\rho(\text{hexadecane}) = 773.7\,\text{kg}\,\text{m}^{-3}$. The energy density of Cornish clotted cream is $1355\,\text{kJ}/100\,\text{g}$. Calculate how much Cornish clotted cream (by weight) would the bus need to travel the given route, assuming that the energy consumption of the engine is the same when burning Cornish clotted cream and diesel, and the consumption is constant throughout the journey.

Solution:

For a 20-mile-long ride, the bus will consume $\frac{20}{100} \times 24.1 = 4.82\,\ell$ of diesel. The weight of this amount of diesel is

$$m(\text{diesel}) = \rho(\text{diesel}) \times V = 773.7 \times \frac{4.82}{1000} = 3.7292\,\text{kg}.$$

According to the question text, we will approximate diesel as pure hexadecane ($C_{16}H_{34}$) which has the molar mass $M = 226.446\,\text{g mol}^{-1}$. Therefore, the corresponding amount of substance gives $n = \frac{m}{M} = \frac{3.7292 \times 1000}{226.446} \doteq 16.469\,\text{mol}$.

Combusting this amount of diesel yields

$$E = \Delta_{\text{comb}} H^{\ominus}(\text{hexadecane}) \times n = 10.7 \times 10^3 \times 16.469 \doteq 176\,213.36\,\text{kJ of energy.}$$

We must now obtain the same amount of energy from Cornish clotted cream, which given its nutritional value yields

$$\frac{176\,213.36}{1355} \times \frac{100}{1000} \doteq 13.00\,\text{kg of Cornish clotted cream.}$$

Question F.2 (Marie Grunová)

On Saturday, April 26, 1986, an accident occurred at the Chernobyl nuclear power plant, the consequences of which we are still dealing with today. Environmental contamination was and is worse on the windward side of the mountains from the nuclear plume, such as in the Šumava region in Czechia. This area is known for wild boars, which are occasionally radioactive because they eat mushrooms with ${}^{137}_{55}\text{Cs}$ (one decay has the energy $E = 1.17\,\text{MeV}$). Calculate the maximum number of 200 g servings of wild boar with rosehip that a person (weighing $m_1 = 70\,\text{kg}$) can consume so that they do not develop symptoms of acute radiation sickness which can be delimited by the absorbed dose $D = 0.7\,\text{Gy}$ (gray)? One gray is a unit of absorbed dose of radiation and in the SI system, it has the unit J/kg. The time required for the passage through the human digestive system is approximately $t = 47\,\text{hours}$. Radioactive wild boar weighs $m_2 = 80\,\text{kg}$ on average. Since the half-life of ${}^{137}_{55}\text{Cs}$ is in the order of decades, we can approximate the activity of wild boar to be constant for the whole duration of its passage through the human digestive system, having the value 16 000 decays per second per 1 kg of wild boar.

Solution:

We will start by calculating the maximum amount of radiative energy that a person can absorb during the whole time of digestion: $E_{\max} = 0.7 \times 70 = 49\,\mathrm{J}$. This limit allows us to calculate the maximum amount of decays that can occur during the time of digestion (we must not forget to convert megaelectronvolts to joules):

$$N_{\mathrm{decays}} = \frac{E_{\max}}{E_{\mathrm{decay}}} = \frac{49}{1.17 \times 10^6 \times 1.6 \times 10^{-19}} \doteq 2.618 \times 10^{15}.$$

We consider activity constant and according to the unit given in the question text, we may calculate it as

$$A = \frac{N_{\mathrm{decays}}}{m_{\mathrm{meat}}\, t} \implies m_{\mathrm{meat}} = \frac{N_{\mathrm{decays}}}{A\, t} = \frac{2.618 \times 10^{15}}{16\,000 \times 47 \times 60 \times 60} \doteq 96\,687.4\,\mathrm{kg}.$$

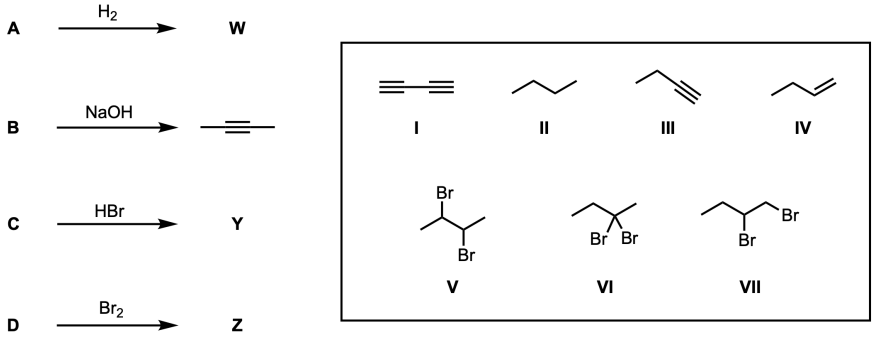
If one portion weights $m_{\mathrm{serving}} = 0.2\,\mathrm{kg}$, we may then overall consume

$$N_{\mathrm{portions}} = \frac{m_{\mathrm{meat}}}{m_{\mathrm{portion}}} = \frac{96\,687.4}{0.2} \doteq 483\,400$$

servings of meat.

Question F.3 (Sam Holmes)

Alkynes (C−C triple bonds) undergo similar reactions to alkenes. Match the molecules I–VII with the letters in the schemes so that all reactions make sense, using each molecule only once.



Solution:

A–I, B–V, C–III, D–IV, W–II, Y–VI, Z–VII

The only place for II is as the product of reduction, so we know that W–II. Y and Z must be two of the brominated molecules V, VI, and VII, and we know that using molecular bromine we should get bromine atoms attached to two carbon atoms next to each other (V or VII) – so this leaves VI–Y. To decide that Z–VII, we can look at B: this is clearly our other brominated molecule which undergoes elimination (twice), and must be B-V since the bromines are attached to the central two carbons. D–IV is now simple to assign. We now just have A–I and C–VI to assign, which is simple because I (C_4H_2) only fits as the substrate for reduction.

Question F.4 (Agustin Lorusso)

Heavy water (D_2O), is water with Deuterium atoms instead of 1-Hydrogen. It has slightly different properties to normal water. One such difference is its dissociation constant:

$$K_w(D_2O) = [D^+][DO^-]$$

$$D_2O \rightleftharpoons DO^- + D^+$$

A normal pH meter – designed to measure H^+ ions – can be used, but because D^+ ions will be measured instead, a systematic correction is needed, which we will call C.

$$\text{measured pH} = \text{pD} + C$$

The measured pH of pure heavy water is 7.03. The measured pH of a $1.000\,\text{mmol}\,\text{dm}^{-3}$ solution of LiOD in heavy water is 11.47.

Calculate the dissociation constant (pK_w) of heavy water.

Solution:

The aim is to set up a system of simultaneous equations.

Equation 1:

Pure heavy water has $[D^+] = [DO^-]$. So $\text{pD} = pK_w/2$. So:

$$7.03 = pK_w/2 + C$$

Equation 2:

LiOD at 1.000 mM makes $[D^+] = K_w/[OD^-]$. So $pD = pK_w + \log[OD^-] = pK_w - 3$. So:

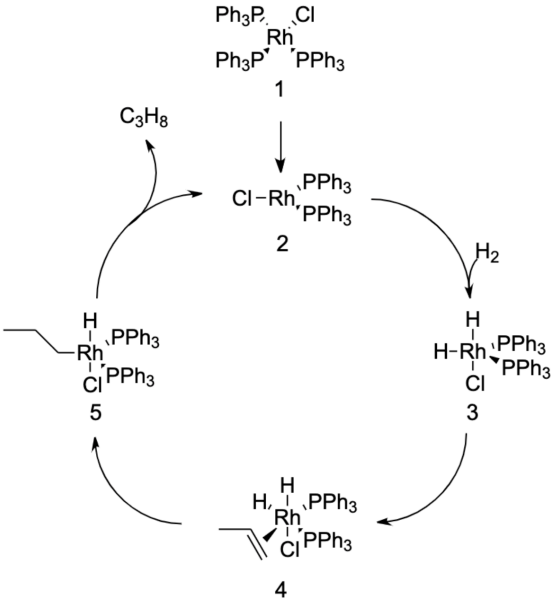
$$11.47 = pK_w - 3 + C$$
$$14.47 = pK_w + C.$$

Solve the system.

Thus $pK_w = 14.88$, $C = -0.41$.

Question F.5 (Kaijia Liu)

In 1965, a new rhodium-based catalyst (Wilkinson's catalyst) was obtained, which enabled us to hydrogenate alkenes under mild conditions. A suggested catalysis mechanism is shown in the diagram provided. Consider the cyclic catalysis process only: when and how does the oxidation number of the rhodium atom change? Give your answer including the respective oxidation numbers. Note that the oxidation state of Rh is not altered by the coordination of an alkene molecule and that all complexes are overall charge neutral.



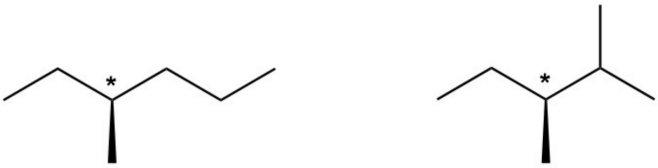
Solution:

The rhodium atom is oxidised from +I to +III in oxidation state when it changes from (2) to (3), and is reduced from +III to +I in oxidation state when it changes from (5) to (2). Both PPh_3 and the propene do not affect the oxidation state of rhodium, as they both donate a pair of electrons to the rhodium atom. However, the covalent bonds formed between Cl and Rh and between H and Rh will cause the oxidation number of the rhodium atom to increase by 1. Since the structure does not have an overall charge, (1) has oxidation state +I, (2) has oxidation state +I, (3) has oxidation state +III, (4) has oxidation state +III, and (5) has oxidation state +III.

Question F.6 (Anh Phung)

Molecules that have non-superimposable mirror images are called *chiral*, derived from the Greek word $\chi\epsilon\iota\rho$ (*kheir*) which means "hand" (you will notice that your hands, screws, or the letter F fulfil this property). In many molecules, chirality arises from one or more carbon atoms with four different groups attached.

The two simplest alkanes (C_nH_{2n+2}) that contain only one chiral centre are shown below.

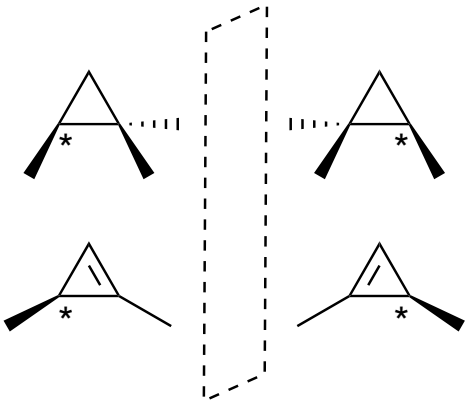


What is the simplest (lowest molecular weight) **hydrocarbon** (with the formula C_nH_{2n}) that contains **exactly one** chiral centre? Draw its skeletal formula and indicate the chiral centre with an asterisk ($*$). Note: do not include isotopes of H and C in your answer.

Solution:

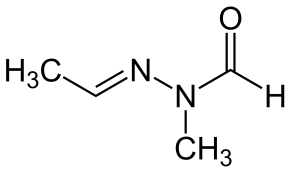
The lowest number of carbon atoms possible in a cycloalkane with one chiral centre is six (C_6H_{12}). The most plausible structure is 1,1 dimethyl-2-methylcyclopropane.

If we permit a double bond, it takes one methyl group fewer to construct a chiral cyclic molecule with exactly one chiral centre. See the diagram below.



Question G.1 (Jakub Sochor)

Gyromitra esculenta is a poisonous mushroom with several recorded cases of fatal poisoning. This mushroom contains 0.14 % (by mass) of a poison called gyromitrin, whose structure is shown below. The mechanism of gyromitrin poisoning lies in its hydrolysis to highly toxic methylhydrazine. Methylhydrazine itself, however, despite its toxicity, finds a really interesting application, namely in rocket propellants as hypergolic (self-igniting) mixture with N_2O_4. Calculate how many kilograms of Gyromitra esculenta we need to collect to hydrolyze gyromitrin to obtain 1 litre of methylhydrazine for our rocket. The density of methylhydrazine is $0.88\,\mathrm{g\,cm^{-3}}$.



Solution:

We want to obtain one litre of methylhydrazine. We recalculate this to the molar amount

$$n_{\text{methylhydrazine}} = \frac{m}{M} = \frac{V \cdot \rho}{M_{\text{methylhydrazine}}}$$

$$V = 1\,\ell = 1000\,\text{cm}^3$$

$$\rho = 0.88\,\text{g}\,\text{cm}^{-3}$$

The molar masses of methylhydrazine and gyromitrin need to be determined from the formulae CN_2H_6 and $C_4N_2OH_8$:

$$M_{\text{methylhydrazine}} = 46\,\text{g}\,\text{mol}^{-1}$$

$$M_{\text{gyromitrin}} = 100\,\text{g}\,\text{mol}^{-1}$$

$$n_{\text{methylhydrazine}} = \frac{1000 \times 0.880}{46} = 19.13\,\text{mol}$$

The stoichiometry of the hydrolysis is 1:1, i.e. one molecule of gyromitrin will give rise to one molecule of methylhydrazine.

$$n_{\text{gyromitrin}} = n_{\text{methylhydrazine}}$$

We get the required mass of gyromitrin from the molar amount and molar mass:

$$m_{\text{gyromitrin}} = n_{\text{gyromitrin}} \cdot M_{\text{gyromitrin}} = 1913\,\text{g}$$

Now we can calculate the mass of the mushroom that we need

$$m_{\text{mushroom}} = \frac{m_{\text{gyromitrin}}}{w_{\text{gyromitrin}}} = \frac{1913\,\text{g}}{0.14\,\%} = 1366\,\text{kg}$$

Question G.2 (Martin Balouch)

Titration is a method in which it is necessary to know the exact concentration of the solution being titrated. In practice, this means that either we have to use the exact weight of the primary standard (a substance that is not hygroscopic and therefore its weight can be directly converted to concentration) or we have to standardise the resulting titration solution.

If we would like to determine the amount of phenol in the reactor, we are offered an elegant bromatometric titration, where $KBrO_3$ is the primary standard, so it is only necessary to weigh and dissolve. Unfortunately, you ended up in Chemistry Race, where elegant solutions are sometimes replaced by stupid and strange ones. The amount of phenol in a sample can also be determined by titration with pure bromine, which is a foul-smelling toxic liquid with a density of $3.1\,\mathrm{g\,cm^{-3}}$. In such a titration, the phenol is brominated three times, and the end of the titration is indicated by the fact that the additional bromine no longer reacts, but remains in the titrated mixture.

Calculate the mass of phenol that was in the titrated sample if we used $3.4\,\mathrm{m\ell}$ of pure bromine in the titration.

Solution:

Reaction equation:

$$\mathrm{C_6H_5OH + 3\,Br_2 \longrightarrow C_6H_2Br_3OH + 3\,HBr}$$

Molar amount of bromine:

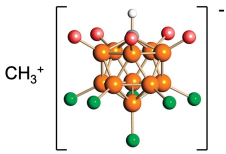
$$n = \frac{V \cdot \rho}{M} = \frac{3.4 \times 3.1}{159.8}$$
$$n = 0.066\,\mathrm{mol}$$

The molar amount of phenol is $\frac{1}{3}$ of that of bromine, that is $0.022\,\mathrm{mol}$.

Molar mass of phenol is $94.11\,\mathrm{g\,mol^{-1}}$, so the resulting mass of phenol is $2.1\,\mathrm{g}$.

Question G.3 (Sam Holmes)

Carborane acids are a family of the strongest known acids to be made: they can readily protonate hydrocarbons. This is because the carborane counterion is exceptionally stable. While carborane acids are an excellent donor of H^+, the molecule $Me(CHB_{11}Me_5Br_6)$, known affectionately as 'mighty methyl', is a ready source of the CH_3^+ cation (drawn below). It reacts readily with n-butane, forming two products, one of which is cationic and can be crystallised as its carborane salt.



Product **A** has tetrahedral symmetry, a boiling point of −161 °C, and a molar mass of $16.04\,\mathrm{g\,mol^{-1}}$.

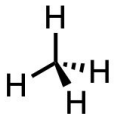
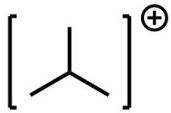
Product **B** has trigonal planar symmetry, and a molar mass of $57.12\,\mathrm{g\,mol^{-1}}$.

Draw the structures of products **A** and **B**, including any charges. You do not need to draw the structure of the carborane counterion.

Solution:

Methane and t-butyl cation. Delocalised positive charge is accepted.

Product A can be easily worked out to be methane via its M_r and shape and the fact that its boiling point can be determined. Product B must be the remainder - it is butane less one proton. We know the molecule must be three-fold symmetric, so drawing the skeleton is not complicated. Then we just have to locate the charge at the central atom, as we know it to be trigonal planar (i.e. three bond pairs, one lone pair). This is the most sensible place for a positive charge: students should know that more substituted carbocations are more stable (due to hyperconjugation from the adjacent C−H sigma bonds).

A  **B** 

Question G.4 (Filip Hůlek)

Popeye had been worried about fuel prices for the past year. So he tried to figure out how he could save money on petrol until he came up with a solution. He decided to fill up at the pumps mainly in the morning, when the temperature is lower, the petrol has a higher density, and he gets more weight for one litre of fuel. Calculate how much Popeye saves when he buys 20 kg of petrol in the morning when it is 2 °C outside, compared to buying the same weight in the afternoon when it is forecast to be 14 °C. At Popeye's favourite petrol station, 1 litre of petrol costs 39.89 CZK. The density of petrol at 2 °C is 755 kg m^{-3}. Assume that the petrol is in thermal equilibrium with the surrounding air. The thermal expansion of gasoline is 1.20×10^{-3} K^{-1}. Thermal expansion indicates the percentage by which a substance increases in volume per degree of temperature.

Solution:

First, the density at 2 °C must be converted to 14 °C using the specified thermal expansion (the volume is proportional to the inverse of the density):

$$\frac{1}{\rho(14\,^\circ\mathrm{C})} = \frac{1}{\rho(2\,^\circ\mathrm{C})} \times (1 + \beta\Delta T),$$

i.e., $\rho(14\,^\circ\mathrm{C}) = 744.3\,\mathrm{kg/m^3}$. From the mass, density, and price per litre, the price at both temperatures is calculated according to the formula:

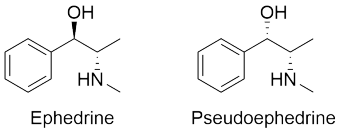
$$\text{price} = \frac{m}{\rho} \times 39.89\,\mathrm{CZK}/\ell$$

At 2 °C, 20 kg of gasoline costs 1057 CZK; at 14 °C, it costs 1072 CZK. So he would save approximately 15 CZK.

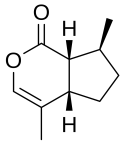
Note: In reality, the difference would be much smaller, since the gasoline is stored underground, where the temperature fluctuations during the day are much smaller.

Question G.5 (Tatiana Nemirovich)

Each chiral centre in a molecule gives rise to two possible epimers (stereoisomers which are related by the inversion of a single chiral centre). You can see two stereoisomers of ephedrine below, which have opposite configurations at one of the chiral centres.

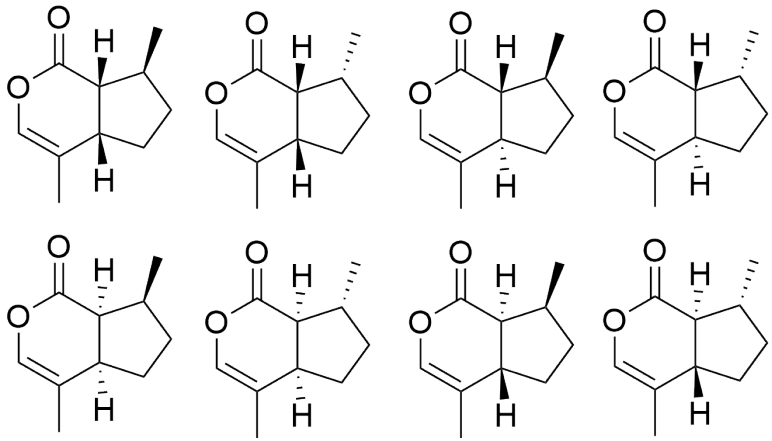


Nepetalactone is an organic substance belonging to the group of lactones found in plants of the genus *Nepeta*, known as catnip. This substance acts like a sex pheromone on cats, which is why many cats respond so intensely to catnip. Write down how many stereoisomers of nepetalactone there are.



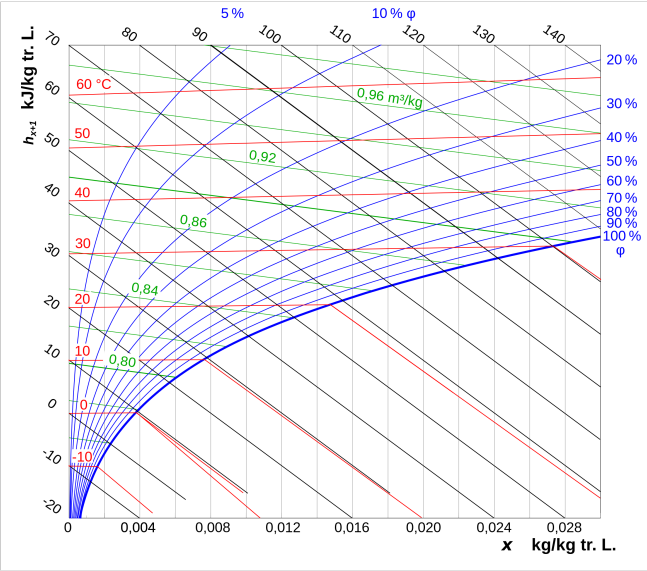
Solution:

Nepetalactone has 3 stereocenters, so the total number of stereoisomers is $2^3 = 8$. Structures of the isomers are shown below:



Question G.6 (Jiří Ledvinka)

Chemist Jiří arrived home on a cold winter day and noticed damp air in his room. He thus started venting the room. The inner temperature was 20 °C and the relative humidity was 79 %. The outside temperature was 0 °C on that day with a relative humidity of 80 %. By venting, all the air in the room was replaced by the fresh air from outside and the temperature then again equilibrated at 20 °C. What was the relative humidity in the room afterwards? Use the attached Mollier h,x-diagram for humid air at a pressure of 1 bar. Black curves show molar fraction of the water in the air, blue curves show the relative humidity of the air, red curves show the temperature.

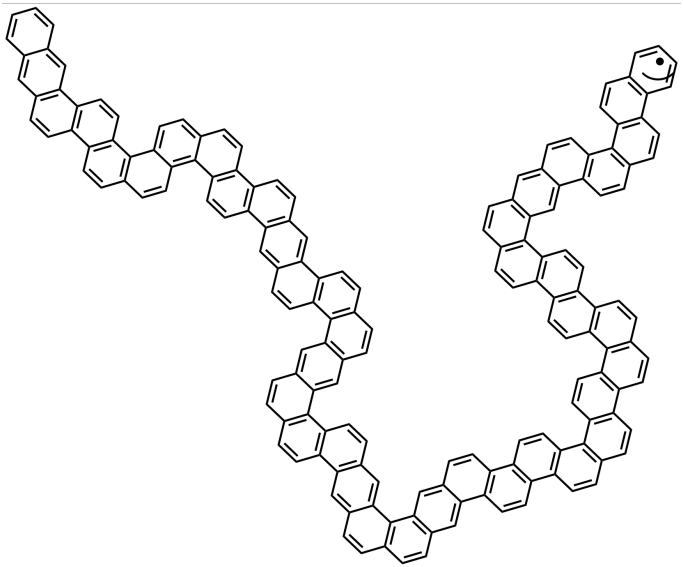


Solution:

First, we find the point in the graph that corresponds to the outside air. This is where the curve of 80 % relative humidity and 0 °C temperature intersects. On the x-axis, we can read that this point corresponds to approximately 3.1 g of water per kg of air. But we just need to move vertically (keeping the same x) until we reach 20 °C (i.e., we heat the outside air to 20 °C). No RH curve passes through this point, but we can imagine that it would be much closer to the 20 % curve than the 30 % curve. Alternatively, we can arrive at a value of 22 % by graphical linear interpolation.

Question H.1 (Sam Holmes)

Chemist Irma is interested in making molecules she calls "benzene snakes". By randomly fusing together benzene rings such that each ring shares exactly two carbon atoms with its neighbour(s), she thinks she might be able to make long chains of high molecular weight. An example of one of Irma's "benzene snakes" is shown.



The mass spectrum of a benzene snake shows a peak at $m/z = 2028$, which is known to be a singly charged ion made up of only ^{12}C and ^{1}H. Work out the molecular formula of the benzene snake responsible for this peak, and give the number of fused benzene rings it contains.

Solution:

The only good approach to this question is a systematic one: form an expression for the RMM from the general molecular formula. The number of carbon atoms is $2 + 4n$, and hydrogen is $4 + 2n$ (where n is the number of rings). So the total mass is

$$12 \times (2 + 4n) + 1 \times (4 + 2n) = 28 + 50n = 2028,$$

giving $n = 40$. So the formula is $C_{162}H_{84}$. (Incidentally, the benzene snake shown has this molecular formula!).

Question H.2 (Anh Phung)

A metallic alloy, consisting of elements **A** and **B**, is used as a coolant in nuclear reactors. A sample of this alloy has a mass of 20.7 g and contains a total of 4.596×10^{23} atoms. The atomic mass of **A** is 1.7× that of **B**, but in this sample, the atoms of **B** contribute a mass 1.7× that contributed by **A**. Identify elements **A** and **B**.

Solution:

This question tests proficiency in converting between masses, relative molar masses, and moles. We extract the following information from the question:

$$\frac{M_r(\mathrm{A})}{M_r(\mathrm{B})} = 1.7 \tag{1}$$

$$\frac{m(\mathrm{B})}{m(\mathrm{A})} = 1.7 \tag{2}$$

$$m(\mathrm{B}) + m(\mathrm{A}) = 20.7 \tag{3}$$

$$N_A \times (n(\mathrm{A}) + n(\mathrm{B})) = 4.596 \times 10^{23} \tag{4}$$

From (1) and (2), we obtain the molar ratio of **B** and **A**:

$$\frac{n(\mathrm{B})}{n(\mathrm{A})} = \frac{M_r(\mathrm{A})}{M_r(\mathrm{B})} \times \frac{m(\mathrm{B})}{m(\mathrm{A})} = 1.7 \times 1.7 = 2.89$$

Combining this information with (4), we obtain $n(\mathrm{A}) = 0.1961\,\mathrm{mol}$ and subsequently $n(\mathrm{B}) = 0.5667\,\mathrm{mol}$. Now, to calculate the masses, we combine (2) and (3) and obtain $m(\mathrm{A}) = 7.6667\,\mathrm{g}$ and $m(\mathrm{B}) = 13.0333\,\mathrm{g}$. Hence,

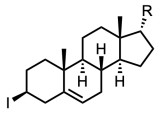
$$M_r(\mathrm{A}) = \frac{m(\mathrm{A})}{n(\mathrm{A})} = \frac{7.6667}{0.1961} = 39.09\,\mathrm{g\,mol^{-1}},$$

which is potassium. Similarly, $M_r(\mathrm{B}) = 22.99\,\mathrm{g\,mol^{-1}}$, which is sodium.

Question H.3 (Sam Holmes)

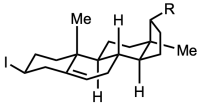
Dorothy Crowfoot Hodgkin was a celebrated chemist at the University of Oxford. She was renowned for advancing the field of X-ray crystallography and solving the 3D structures of complex molecules, such as penicillin, vitamin B12 and steroids, such as cholesteryl iodide for which she was awarded the Nobel Prize in Chemistry in 1964.

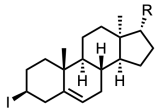
Molecules can be drawn "flat", with the stereochemistry denoted by wedged and hashed bonds, or in 3D, where the shape of the molecule can be seen more clearly. You are provided with the "flat" and "3D" representations of some isomers of cholesteryl iodide: match the flat representation to the 3D representation.



A

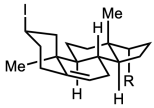
I

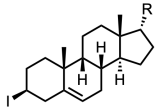




B

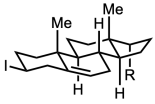
II

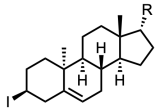




C

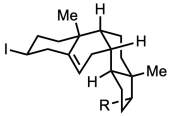
III





D

IV

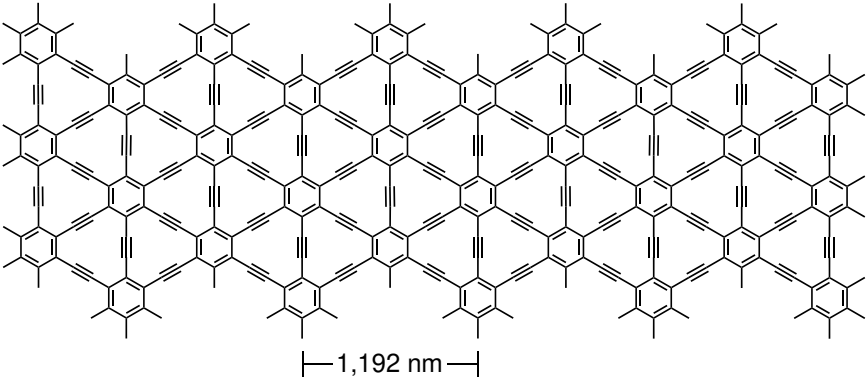


Solution:

One way to spot the matches is to start at the left hand methyl group, decide if it is "up" or "down", and then decide whether the next stereo centre along is on the same side or the opposite side. So for I, the left hand methyl group is up, the proton next to it is down, the proton next to that is up, then down, and the methyl on the right hand side is on the same side as that last proton - so it is down too. That means it must be B. Analogous comparisons can be made with the other pairs of projections.

Question H.4 (Sam Holmes)

Like graphene, graphyne is a 2D allotrope of carbon which can form a covering on a surface. How much carbon (in µg) would be needed to completely cover this A5 page (148 × 210 mm) with a single layer of graphyne?



Solution:

Hexagonal unit cell with a width of 1.192 nm from one side to the opposite side with area corresponding to the area of six equilateral triangles (with side 0.6882 nm and height 0.596 nm):

$$S_{\text{hex}} = 6 \times 0.5 \times 0.6882 \times 0.596 = 1.2305\,\text{nm}^2$$

This unit cell contains: $6 + 6 \times 3$ whole carbon atoms and 4 carbon atoms lie on each edge of the hexagon which count as one half inside the hexagon. So in total, there are 36 carbon atoms in the unit cell.
Area of the page is

$$148 \times 210 = 31\,080\,\text{mm}^2 = 3.108 \times 10^{16}\,\text{nm}^2$$

so the number of unit cells per page is

$$\frac{3.108 \times 10^{16}}{1.2305} = 2.5258 \times 10^{16}$$

The total number of carbon atoms is

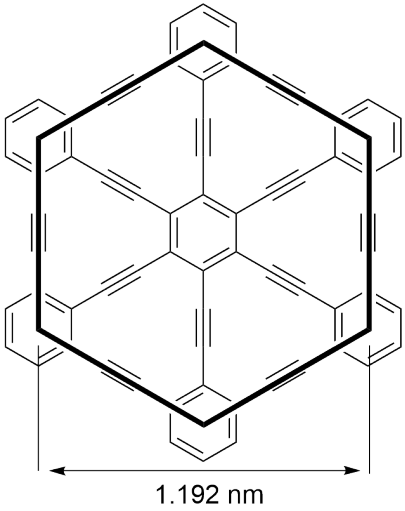
$$N_{\text{C}} = 2.5258 \times 10^{16} \cdot 36 = 9.093 \times 10^{17},$$

which gives the total molar amount

$$n_{\mathrm{C}} = \frac{N}{N_{\mathrm{A}}} = 1.50991 \times 10^{-6}\,\mathrm{mol}$$

and finally the mass:

$$m_{\mathrm{C}} = n_{\mathrm{C}} \cdot M_{\mathrm{r}} = 1.50991 \times 10^{-6} \cdot 12 = 1.812 \times 10^{-5}\,\mathrm{g} = 18.12\,\mu\mathrm{g}$$



Question H.5 (Ondra Daněk)

The rate of alcohol degradation by alcohol dehydrogenase and other alcohol degrading enzymes is concentration-dependent at low ethanol concentrations, but above a certain threshold the enzyme is fully saturated and the rate of ethanol degradation is constant. The Reynolds criterion is a dimensionless criterion by which the nature of fluid flow (laminar or turbulent) can be classified, and is widely used in various chemical engineering calculations. Knowing the flow velocity, characteristic pipe dimension, density and viscosity of a given fluid, the Reynolds criterion can be used as follows:

$$Re = \frac{v \cdot d \cdot \rho}{\eta}$$

where v is the flow velocity in m/sec, d is the characteristic dimension in m (which for circular pipes is equal to their diameter), ρ is the density of the fluid in kg/m^3 and η

is the dynamic viscosity of the fluid in Pa · sec. By performing a dimensional analysis, it can be verified that Re is indeed dimensionless. Patric has came to the conclusion that he enjoys an evening out with friends best when he has a constant alcohol level of 1 part per thousand (which is a concentration high enough to saturate the enzymes and break down the alcohol through zero-order kinetics). Patric replenishes his alcohol level with a constant flow of *Mudweiser* beer, which he introduces directly into his stomach through a 5 mm inner diameter tube because of its not too delicious taste.

The lager has an alcoholic strength of 4 % vol. and, at the temperature of 8 °C to which Patric has cooled it, has a density of 1.1 g/cm^3 and a viscosity of 3 mPa · sec. Patric is a fairly good burner of booze and breaks down ethanol at a rate of 0.2 per mille per hour, and the volume of Patric's blood is 6 litres. However, on average, only 6 % of the alcohol ingested passes into the blood due to dilution throughout the body, of which blood makes up only a small portion.

Calculate the Reynolds criterion for the flow of *Mudweiser* into Patric's stomach. The tube is inserted through the oesophagus, which is 2 cm in diameter. We can approximate Patric with an ideally stirred bioreactor at steady state.

Solution:

First, let's calculate the volumetric flow of beer needed to compensate the metabolic breakdown of alcohol:

$$\dot{V} = \frac{v_{\text{metabolism}} \cdot V_{\text{blood}}}{f \cdot \phi} = \frac{0.0002 \times 6}{0.06 \times 0.04} = 0.5\,\ell\,\text{h}^{-1}$$

where f is the dilution factor and ϕ is the volume fraction of alcohol in beer.

From the volumetric flow we can calculate the linear speed of beer in the tube:

$$v = \frac{\dot{V}}{\pi \cdot r^2} = \frac{500}{\pi \cdot r^2} = 2546.5\,\text{cm}\,\text{h}^{-1} = 0.007074\,\text{m}\,\text{s}^{-1}$$

Now we can input all relevant numbers into the definition of Reynolds criterion:

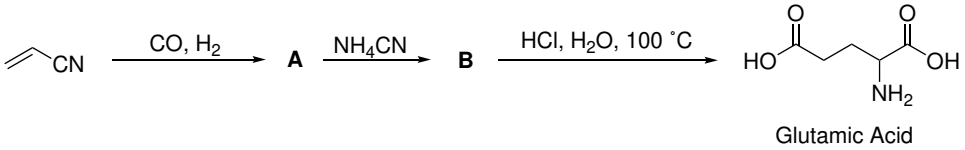
$$Re = \frac{v \cdot d \cdot \rho}{\eta} = \frac{0.007074 \times 0.005 \times 1100}{0,003} = 13$$

Question H.6 (Supatpong Juntarawatt)

In the past, glutamic acid (an amino acid and a precursor to producing monosodium glutamate, MSG) could be obtained via extraction from biological sources. However, chemical synthesis of the amino acid became possible after World War II upon the discovery of the oxo reaction.

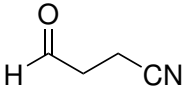
Acrylonitrile is first reacted with carbon monoxide (CO) and hydrogen gas (H_2) to form a key intermediate **A**. Glutamic acid can be obtained by converting intermediate **A** by reaction with ammonium cyanide into compound **B** which can be then hydrolysed into glutamic acid.

Given the synthesis pathway, draw skeletal formulas of **A** and **B**.

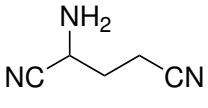


Glutamic Acid

Solution:



A



B

The formation of **A** is the oxo reaction/hydroformylation, whereby a CH_2O unit adds to the double bond. There are two products for this reaction, but only one has the correct carbon skeleton. The second and third steps are characteristic of a Strecker amino acid synthesis, whereby CN^- is the nucleophile and NH_4^+ works as an acid catalyst and to form an imine intermediate. The last step hydrolyses the nitriles into carboxylic acids. Recognizing the Strecker synthesis and working backwards it is possible to deduce the structure of **A** without being familiar with hydroformylation.

Reference: https://doi.org/10.1021/ed081p347

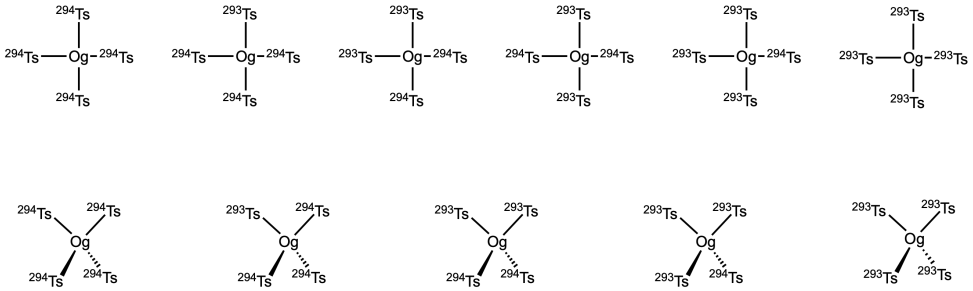
Question K.1 (Anh Phung)

The discoveries of two elements, tennessine ($Z = 117$) and oganesson ($Z = 118$) marked the completion of the 7th period in the periodic table. Two known isotopes of tennessine, $^{293}_{117}$Ts and $^{294}_{117}$Ts, are both unstable; while only one isotope of oganesson, $^{294}_{118}$Og, has been synthesized. Due to their drastically short half-lives, the chemical properties of these elements were not fully understood. However, using computational simulations and considering the relativistic correction, it was predicted that oganesson could react with tennessine to form a relatively stable compound $OgTs_4$, which could adopt either square planar or tetrahedral geometry. This is the heaviest possible penta-atomic molecule.

Suppose that we could successfully synthesize both elements at the same time and let them react according to the relativistic simulations - how many distinct molecular entities could be formed?

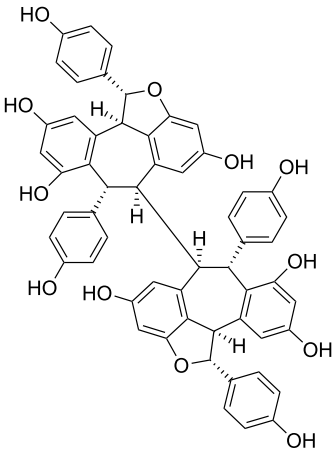
Solution:

A total of 11 structures: 5 tetrahedral and six square planar ones. The trick is to notice that we have the possibility of cis/trans isomerism in the square planar complex, which is not the case for the tetrahedral one.



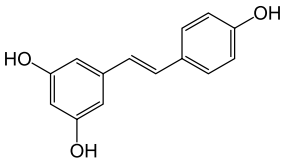
Question K.2 (Jiří Ledvinka)

Hopeaphenol (shown below) is a polyphenol found in wine. Its interesting structure can be formed from four molecules of compound **A**, with each being oxidised by 6 electrons. Provide the structure of compound **A**.



Solution:

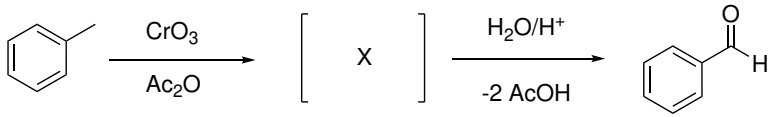
Resveratrol – see below. Cis and trans isomers are acceptable.



At first glance, we see that the bond between two seven-membered cycles connects two identical parts. But we need to cut them in half one more time. In each half we see two 4-hydroxyphenyl substituents and two more benzene nuclei substituted by two oxygens. By further halving, we thus obtain two benzene nuclei, 4-hydroxyphenyl and 3,5-dihydroxyphenyl, connected by two carbons. By calculating the hydrogens, we find that these two nuclei are connected by a double bond.

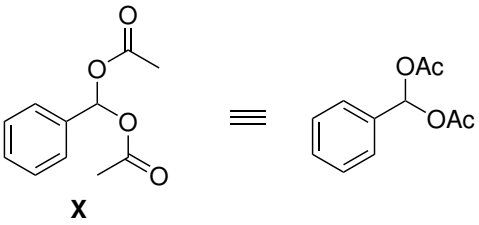
Question K.3 (Štěpán Novák)

One of the older methods of preparing benzaldehydes is the oxidation of the corresponding methylbenzenes (toluenes) using chromium (VI) oxide. By adding acetic anhydride to the reaction mixture, over-oxidation to benzoic acid is avoided because a stable intermediate **X** is formed. Deduce the structure of intermediate **X**, which can be hydrolysed to give the benzaldehyde product.



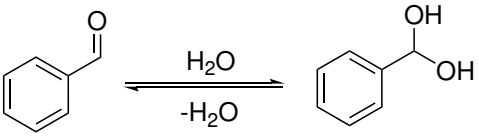
Solution:

The intermediate is phenylmethylene diacetate.



X

The reason for oxidation to acid in the presence of water is the formation of the hydrated form of benzaldehyde, which reacts with chromium oxide like an alcohol would. In the presence of acetic anhydride, the hydrated benzaldehyde is acetylated to form phenylmethylene diacetate, which does not undergo further oxidation.



Question K.4 (Anh Phung)

In the past, automobile airbags' deployment relied mainly on thermal decomposition of sodium azide (NaN_3), which generated sodium metal and lots of nitrogen gas (1). Sodium metal was then further reacted with potassium nitrate to form additional N_2 (2), and the oxides byproducts were converted to inert silicate salts in presence of SiO_2 (3):

$$2\,NaN_3 \longrightarrow 2\,Na + 3\,N_2 \tag{1}$$

$$10\,Na + 2\,KNO_3 \longrightarrow 5\,Na_2O + K_2O + N_2 \tag{2}$$

$$K_2O + Na_2O + 2\,SiO_2 \longrightarrow K_2SiO_3 + Na_2SiO_3 \tag{3}$$

Consider an airbag facing the driver's seat which, when fully inflated, adopts an ellipsoidal shape with semi axes: $a = b = 30.0\,\text{cm}$, $c = 17.5\,\text{cm}$. At the instant of deployment, the temperature of the airbag reaches as high as 200 °C (this heat is quickly dissipated to not burn the driver), with an internal pressure of 1.20 atm. In the inflator chamber, 58.88 g of potassium nitrate is to be mixed with the azide salt. Assuming that N_2 is an ideal gas, and the first two reactions are ideally coupled, calculate the minimum mass of sodium azide (to nearest gram) required to generate enough N_2 to fully inflate the airbag. (Volume of an ellipsoid is $\frac{4}{3}\pi abc$.)

Solution:

Volume of N_2 needed to inflate the ellipsoidal airbag:

$$V = \frac{4}{3}\pi \times 0.30 \times 0.30 \times 0.175 = 0.066\,\text{m}^3 = 66\,\ell$$

Using the ideal gas law:

$$n = \frac{pV}{RT} = \frac{1.2 \times 101325 \times 0.066}{8.3145 \times (200 + 273)} = 2.0405\,\text{mol of } N_2$$

Here comes the tricky part: this total amount of N_2 comes from both sources (reaction (1) and (2)), albeit the majority is from the first one. The number of moles of N_2 generated from (1) is equal to $\frac{3}{2x}$, where x is the number of moles of NaN_3. In (2), however, the amount of N_2 formed is dependent on whether the reaction's limiting agent is sodium (fed-forward from reaction (1)), or KNO_3.

$$n_{KNO_3} = \frac{58.88}{39 + 14 + 3 \times 16} = 0.583\,\text{mol}$$

There are two scenarios:

- If $\frac{x}{5} > n_{\mathrm{KNO_3}}$ (therefore $x > 2.915\,\mathrm{mol}$), then $\mathrm{KNO_3}$ is limiting, and the moles of $\mathrm{N_2}$ generated in (2) are calculated based on $n_{\mathrm{KNO_3}}$. Therefore, $n^{(2)}_{\mathrm{N_2}} = \frac{1}{2}x \times 0.583 = 0.292\,\mathrm{mol}$, so that $\frac{3}{2}x + 0.292 = 2.0405$ and $x = 1.166\,\mathrm{mol}$. However, this does not satisfy the inequality $x > 2.915\,\mathrm{mol} \rightarrow$ This cannot be the solution.
- If $\frac{x}{5} < n_{\mathrm{KNO_3}}$ (therefore $x < 2.915\,\mathrm{mol}$), then Na is limiting, and the moles of $\mathrm{N_2}$ generated in (2) are calculated based on n_{Na} (which equals x). Therefore, $n^{(2)}_{(\mathrm{N_2})} = \frac{1}{10}x$, so that $\frac{3}{2}x + \frac{1}{10}x = \frac{8}{5}x = 2.0405\,\mathrm{mol}$ and $x = 1.275\,\mathrm{mol} < 2.915$ $\rightarrow$ Accept this solution.

Finally, $m_{\mathrm{NaN_3}} = 1.275 \times (22.99 + 3 \times 14.01) = 82.90\,\mathrm{g} \approx 83\,\mathrm{g}$.

Question K.5 (Rostislav Huňa)

When distilling home-made spirits (*domáca* in Slovakia, *moonshine* in the USA, *scumble* in Lancre, Discworld), it is necessary to be careful of methanol, which can be present in the distillate in a considerable amount. As a good chemist, you should be able to calculate the expected content of this dangerous substance to avoid various inconveniences. Methanol is produced in significantly higher quantities during the fermentation of fruit such as plums than, for example, during the fermentation of barley malt or other cereals because of the high amylopectin content. Now imagine that your plums produced a lot of pectin this year, and that after the first few distillations you got a mixture consisting of equal parts of ethanol and methanol by weight (neglect the water content). Determine the equilibrium molar composition of the distillate resulting from the distillation of this mixture (boiling point 69.1 °C at 100 000 Pa). The following formulae may be helpful:

Antoine's equation is one of the possible equations expressing the dependence of the partial pressure of a substance on temperature, for the i-th component it has the form:

$$\ln(p_i^{\mathrm{s}}) = A_i - \frac{B_i}{C_i + T}$$

Dalton's law $p_{\mathrm{total}} = \sum_{i=1}^{n} p_i = p_i + p_j + \ldots + p_n$ (where p_{i}, p_{j} are the partial pressures of individual components) and Raoult's law $p_i = x_i \cdot p_i^{\mathrm{s}}$.

Values of the parameters for
methanol: $A = 23.4803$, $B = 3626.55$, $C = -34.29$
ethanol: $A = 23.8047$, $B = 3803.98$, $C = -41.68$.

Solution:

Partial pressures can be calculated by substituting into the equation

$$p_i^{\mathrm{s}} = e^{A - \frac{B}{C+T}}$$

for the given temperature, to obtain $p_{\mathrm{m}}^{\mathrm{s}} = 121\,086\,\mathrm{Pa}$ and $p_{\mathrm{e}}^{\mathrm{s}} = 69\,481\,\mathrm{Pa}$.

The partial pressure of methanol is

$$p_{\mathrm{m}} = y_{\mathrm{m}} \cdot p$$

where y_{m} is the molar fraction of methanol in the gaseous mixture.

At the same time,

$$p_{\mathrm{m}} = x_{\mathrm{m}} \cdot p_{\mathrm{m}}^{\mathrm{s}}$$

applies.

Before substituting into the final form

$$x_{\mathrm{m}} \cdot p_{\mathrm{m}}^{\mathrm{s}} = y_{\mathrm{m}} \cdot p$$

we need to convert the mass fraction of methanol in the mixture to molar fraction:

$$x_{\mathrm{m}} = \frac{w_{\mathrm{m}}/M_{\mathrm{m}}}{w_{\mathrm{m}}/M_{\mathrm{m}} + w_{\mathrm{e}}/M_{\mathrm{e}}} = \frac{0.5/32.04}{0.5/32.04 + 0.5/46.068} = 0.59\ ,$$

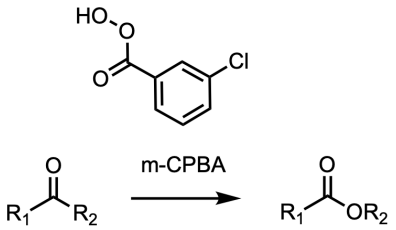
Then by substituting, we find

$$y_{\mathrm{m}} = \frac{0.59 \times 121\,086}{100\,000} = 0.715$$

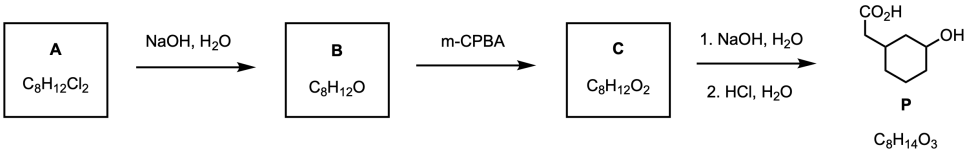
For ethanol, we might proceed similarly, but we don't need to, thanks to $y_{\mathrm{e}} = 1 - y_{\mathrm{m}}$. In fact, the first distillation would not succeed in removing the entire amount of water present, and we would have to deal with an azeotropic mixture afterwards.

Question K.6 (Richard Veselý)

The Baeyer-Villiger oxidation is a very useful synthetic transformation, coverting ketones to esters by inserting an oxygen atom next to the carbonyl group. The transformation is achieved by reacting a ketone with *meta*-chloroperoxybenzoic acid (mCPBA), generating the corresponding ester and *meta*-chlorobenzoic acid as a byproduct. A general scheme is shown below.

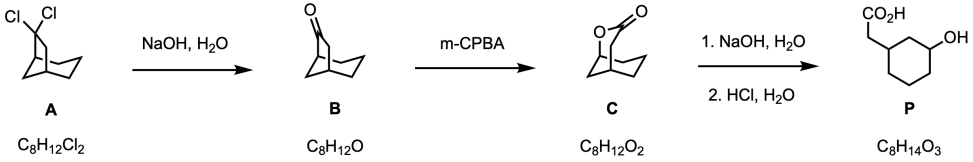


Substance **A** with the general formula $C_8H_{12}Cl_2$ was hydrolyzed in a basic environment to form substance **B** with the general formula $C_8H_{12}O$. **B** was then oxidized with *meta*-chloroperoxybenzoic acid to form substance **C** with the general formula $C_8H_{12}O_2$. Hydrolysis of **C** and subsequent treatment with dilute acid gave product **P** depicted below. Draw the formulas of molecules **A**, **B**, and **C**.



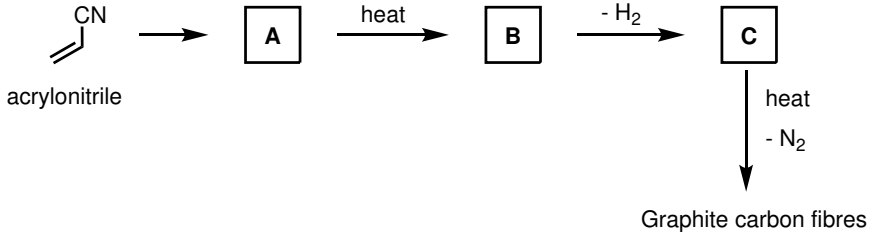
Solution:

The structures are in the picture. A water molecule is added at the C → P step, implying that the last step is hydrolysis of the ester. Step B → C: m-CPBA can do either Baeyer-Villiger oxidation or double bond epoxidation. In this case, we are hydrolyzing an ester, so this is a Bayer Villiger oxidation and molecule B must be the corresponding ketone. Even without knowledge of BV oxidation, it can be deduced that in step A → B a ketone is formed instead of two chlorides, because DBE does not change in the cork B→C and therefore the double bond C=O must already be present in B. Considering that C is an ester, so you can guess what happens in step B → C. We know that B must be a ketone and C is the same ketone, only with oxygen sandwiched between the neighboring carbon and the carbonyl carbon.



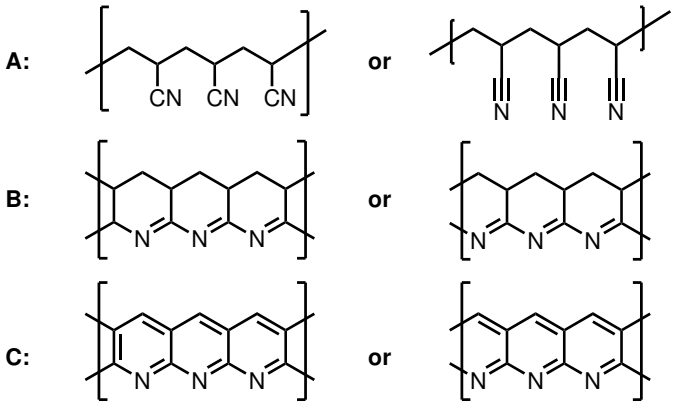
Question L.1 (Sam Holmes)

Carbon fibres are incredibly useful: they are added to many other materials to enhance their properties. They are generally made from acrylonitrile; a general scheme is shown below. Draw the structures of A, B, and C, showing three repeat units in each case.



Solution:

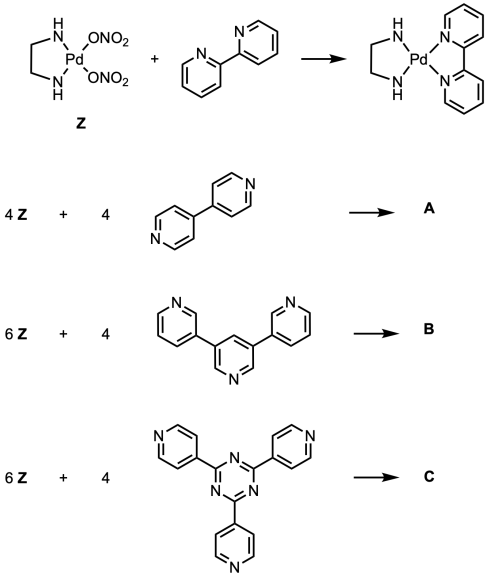
First, the radical polymerisation across the C-C double bond (this is straightforward). Then, a cyclisation reaction that makes the unsaturated chain **B**, which can be oxidised losing hydrogen to form the polyaromatic chain **C**. The pyrolysis of **C** to generate carbon fibres (with loss of nitrogen) is not important to the question.



We have neglected cross-linking here: The cyclisation step **A** → **B** may also occur between non-adjacent monomers, forming loops and cross-links which strengthen the material.

Question L.2 (Sam Holmes)

Metal complex **Z** can react with pyridine-based ligands to generate interesting structures. A simple 'chelating' ligand (the name derived from the Greek for claw), reacts with **Z** in a 1:1 ratio as shown, forming a new metal complex. When the nitrogen atoms in the (poly)pyridine ligand do not chelate, very interesting structures can be formed. Write down/sketch the shape of the molecule formed when these ligands react with 1, in the stoichiometries indicated. You are not required to draw the organic ligands in full. Hint: in all cases, palladium retains a square planar geometry with (close to) 90 degree angles between coordination sites.



Solution:

One way to approach this question would be to draw simplified diagrams of the ligands, marking the position of the nitrogen atoms, cut them out, and try and arrange them such that two nitrogen atoms always converge at 90 degrees. This is a very challenging problem! You can read more about it at doi.org/10.1039/B008684N.

A is a square: the bipyridine ligands form straight edges, and the palladium atoms sit at the corners. B is a rectangular prism (accept tube, as this is the name given by the authors) – each ligand 'panels' one of the faces, and the palladium atoms sit on the edges (with opposite pairs of edges having one and two palladium atoms respectively). C is an octahedron. This triangular ligands panel four of the faces of an octahedron, with the six palladium atoms sitting at the corners.

Question L.3 (Ladislav Prener)

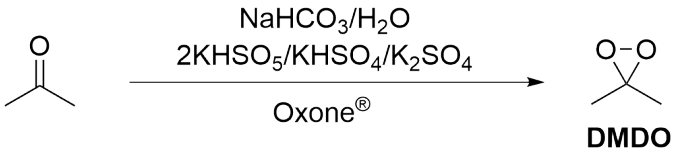
Murray's reagent (dimethyldioxirane, DMDO), which is a powerful, yet selective oxidising agent, can be prepared by oxidation of acetone by oxone. Since Sarah needed to epoxidise a substituted indole en route to hexacyclic pyrazinoquinazoline alkaloids, she prepared DMDO by the aforementioned method.

To determine the concentration of the DMDO solution, she ran an NMR titration as follows: In a 1 mℓ volumetric test tube, a 0.7 M solution of 1-methoxy-4-(methylthio)benzene (97 µℓ) in acetone-d_6 (903 µℓ) is prepared, to a total volume of 1 mℓ. A 0.6 mℓ portion of this solution is transferred to a 18 mℓ test tube and chilled to ca. 0 °C. Then, 3.3 mℓ of the prepared DMDO solution is added to the 1-methoxy-4-(methylthio)benzene solution in the test tube. After 10 minutes, a portion of the solution was analysed by 1H-NMR. Integration of the phenyl protons of the formed sulfoxide (RSOR) and sulfone (RSO_2R) products (see NMR data below) allows for determination of the ratio of these products to excess p-methoxythioanisole.

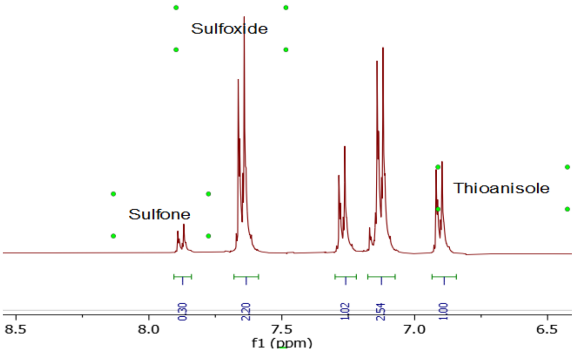
30 days later, she needed to use the DMDO solution again, which was stored in a −20 ℃ freezer. As a careful scientist, she re-ran the titration as before (see NMR data).

Calculate both the initial and final concentrations of the DMDO solution. Using the Arrhenius equation and an activation energy of 39.3 kJ mol^{-1}, calculate the final concentration of the DMDO solution had Sarah been lazy and stored it at 20 ℃ instead. (The decomposition of DMDO follows first order kinetics.)

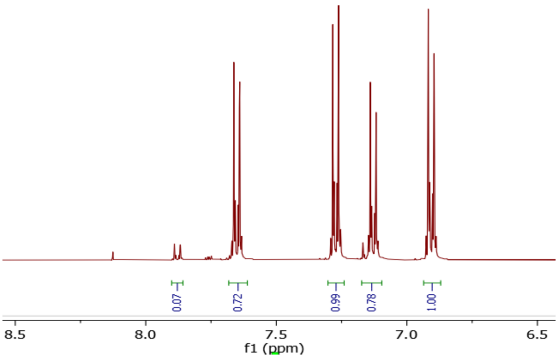
Hint: IUPAC name of p-methoxythioanisole is 1-methoxy-4-methylsulfanyl-benzene.



First spectrum:



Second spectrum:



Solution:

First we calculate the amount of substance of p-methoxysthioanisol in titrated volume:

$$n = c \times V = 0.7 \times 0.0006 = 0.00042\,\text{mol} = 0.42\,\text{mmol}$$

This amount of substance has to be the same as the sum of amounts of substance of p-methoxythioanisol, sulfoxide, and sulfon generated after the addition of DMDO:

$$n_{\text{p-methoxythioanisole}} + n_{\text{sulfoxide}} + n_{\text{sulfone}} = 0.42\,\text{mmol}$$

After the first titration is the ratio of amounts of substance $1 : 2{,}2 : 0.3$ —- this can be obtained from the relative integrals in the NMR spectrum. Molar fractions of

the substances are thus:

$$x_{\text{p-methoxythioanisole}} = 0.2857$$

$$x_{\text{sulfoxide}} = 0.6286$$

$$x_{\text{sulfone}} = 0.0857$$

And their amounts of substance are:

$$n_{\text{sulfoxide}} = 0.42 \times x_{\text{sulfoxide}} = 0.42 \times 0.6286 = 0.264012\,\text{mmol}$$

$$n_{\text{sulfone}} = 0.42 \times x_{\text{sulfone}} = 0.42 \times 0.0857 = 0.035994\,\text{mmol}$$

1 equivalent of DMDO is needed to oxidise the p-methoxythioanisole to the sulfoxide and two equivalents are needed to oxidise it to the sulfone. The total molar amount of DMDO in the 3.3 mL of the solution is thus:

$$n_{DMDO_0} = n_{\text{sulfoxide}} + 2 \times n_{\text{sulfone}} = 0.264012 + 2 \times 0.035994 = 0.336\,\text{mmol}$$

The concentration of the fresh DMDO solution is:

$$c_0 = \frac{n_{\text{DMDO}_0}}{V} = \frac{0,336}{3,3} = 0.1018\,\text{mol}\,\ell^{-1}$$

Going through the same calculations using the molar ratios from the second NMR spectrum gives us:

$$c_{30}(-20\ ^\circ\text{C}) = 0.06115\,\text{mol}\,\ell^{-1}$$

From these two concentrations and the information that DMDO decomposes through first order kinetics, we can calculate the rate constant of DMDO decomposition at -20 °C:

$$c_{30}(-20\ ^\circ\text{C}) = c_0 \times \exp -k(-20\ ^\circ\text{C}) \times t$$

Which can be rearranged to:

$$k(-20\ ^\circ\text{C}) = \frac{-\ln(\frac{c_{30}(-20\ ^\circ\text{C})}{c_0})}{t} = \frac{-\ln(\frac{0,06115}{0,1018})}{30} = 0.017056\,\text{day}^{-1}$$

We can then use this rate constant and the given activation energy to calculate the pre exponential factor in the Arrhenius equation:

$$k(-20\ ^\circ\text{C}) = A \times \exp(\frac{-E_A}{R \times 253,15})$$

$$A = \frac{k(-20\ ^\circ\text{C})}{\exp(\frac{-E_A}{R \times 253.15})} = \frac{0,017056}{\exp\frac{-39300}{R \times 253.15}} = 2\,191\,941.889\,\text{day}^{-1}$$

Now we can plug A back in and use the higher temperature lazy version of Sarah might be tempted to store the DMDO in to calculate the rate constant at +20 °C:

$$k(+20\ ^\circ\mathrm{C}) = A \times \exp\frac{-E_A}{R \times 293.15} = 2\,191\,941.889 \times \exp\frac{-39300}{R \times 293.15} = 0.21794\,\mathrm{day}^{-1}$$

And finally we can use this rate constant to calculate the leftover concentration of DMDO that would stay intact after 30 days at +20 °C

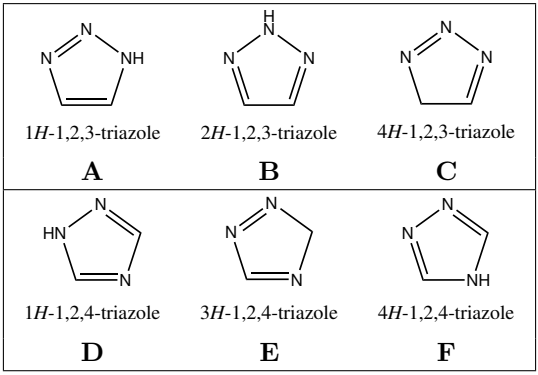
$$\begin{aligned} c_{30}(+20\ ^\circ\mathrm{C}) &= c_0 \times \exp\left(-k(+20\ ^\circ\mathrm{C}) \times t\right) = 0,1018 \times \exp\left(-0,21794 \times 30\right) \\ &= 1.476 \times 10^{-4}\,\mathrm{mol}\,\ell^{-1} = 0.1476\,\mathrm{mM} \end{aligned}$$

As it turns out, storing this oxidant in the freezer is in fact very important.

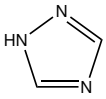
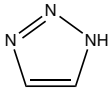
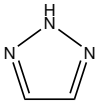
Question L.4 (Adam Tywoniak)

Triazole is a name shared by heterocyclic compounds with two constitutional isomers, each of which has three distinct tautomeric forms. Rank the molecular entities by their relative stability (measured by Gibbs free energy) by filling the symbols **A** – **F** into the bottom table. Consider isolated molecules or the gas phase.

Most stable		≈	
Second most stable		≈	
Second least stable			
Least stable			



Solution:

Most stable	 1*H*-1,2,4-triazole	≈	 4*H*-1,2,4-triazole
Second most stable	 1*H*-1,2,3-triazole	≈	 2*H*-1,2,3-triazole
Second least stable	 3*H*-1,2,4-triazole		
Least stable	 4*H*-1,2,3-triazole		

Aromaticity is the single most important contributor to the free energy of compounds of this type. Neither of the forms containing an sp^3 carbon atom meets Hückel's rule. Among those two, species **C** is higher in energy and thermodynamically less stable, as it contains a nitrogen-nitrogen double bond (instead of carbon-nitrogen), and two sets of neighbouring lone electron pairs lead to a higher repulsion than one such set.

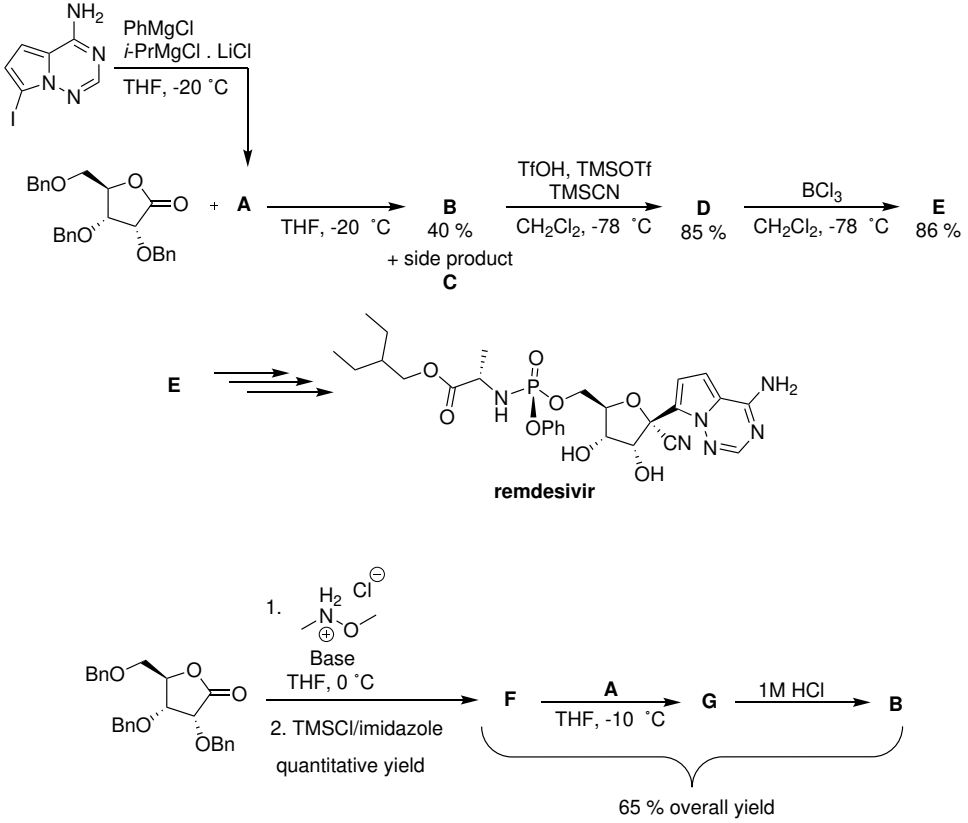
Question L.5 (Ondřej Daněk)

Remdesivir is an antiviral drug originally developed by Gilead Sciences for treatment of Ebola and Marburg virus infections. It later proved to be effective against other RNA viruses too, including its widespread use during the SARS-CoV-2 pandemic in recent years. In this question, we will take a look at the synthesis of remdesivir, some of its drawbacks and possible improvements.

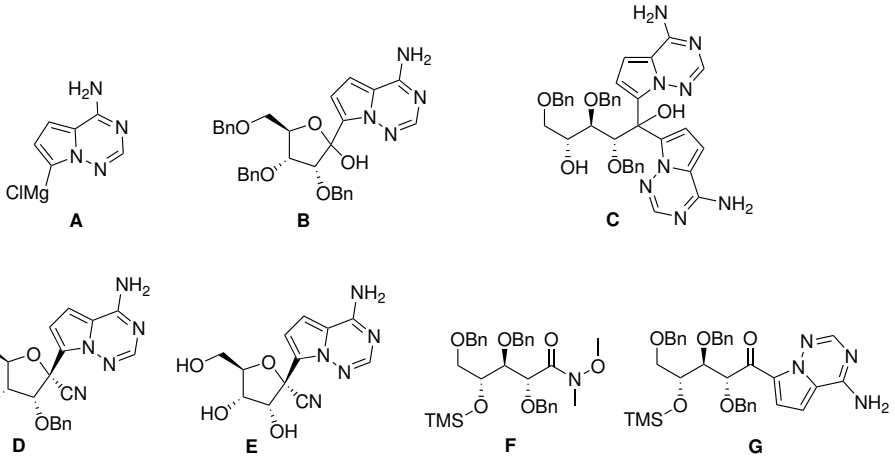
The method used by Gilead is shown in the scheme below. First, benzylated D-(+)-ribonic gamma-lactone is reacted with in situ generated reagent **A**. This step of the synthesis is quite inefficient and the desired product **B** is obtained in only 40 % yield.

The main side product **C** formed in this reaction shows up as a single charged ion with $m/z = 687.30$ in LCMS ESI+ analysis. Product **B** is then transformed to **D** by reaction with trimethylsilyl cyanide in presence of triflic acid and trimethylsilyl triflate, **D** is subjected to boron trichloride and after subsequent hydrolysis, compound **E** is obtained. **E** is then converted to final remdesivir through a series of reactions.

An improved synthesis of **B** was published in 2021. The same starting benzylated D-(+)-ribonic gamma-lactone is first reacted with *N*-methoxymethylamine hydrochloride in presence of a strong base to form **F** quantitatively, **F** is then reacted with in situ generated **A** in presence of trimethylsilyl chloride and the product **G** was subjected to 1M hydrochloric acid without prior purification. By using this one pot method, the researchers were able to improve the yield of **B** by 25%.



Solution:

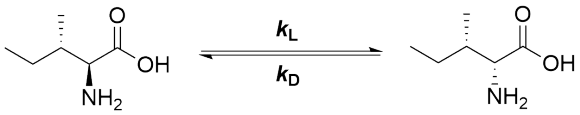


A is formed by halogen-metal exchange between the *turbo*-Grignard reagent (*i*-PrMgCl complex with LiCl) and then normal Grignard addition to the lactone proceeds. The desired lactol **B** can decyclize into a ketone similar to **G** that is then attacked by a second molecule of the Grignard reagent **A**. Because of that, the main side product **C** is the product of double Grignard addition. The stereochemistry of **B** is not clearly determined, because the Grignard reagent can approach the planar carbonyl from both sides, even though the attack from one side might be more probable, a mixture of diastereomers will form. In the next step, the reaction proceeds through a planar oxocarbenium intermediate that is formed after addition of the lewis acid (TMSOTf) and the cyanide ion from TMSCN can then attack from the sterically less hindered side. Determining which side that is would be very hard on paper, but the stereochemistry must be the same as in the final remdesivir, so in this question, it can be worked out backwards. Debenzylation with BCl_3 follows, it is noteworthy that more user friendly debenzylation procedure by Pd-C catalyzed hydrogenolysis cannot be used here because of the nitrile group that could be reduced as well under those conditions.

In the alternative synthesis of **B**, Weinreb amide is formed first from the lactone, and the now free OH group is protected with TMS group to not interfere with the Grignard reaction that follows. The Weinreb amide ensures that the reaction stops after the first Grignard addition and that the desired ketone **G** is formed. The TMS group is then removed by hydrochloric acid, and cyclization to the desired lactol **B** quickly proceeds.

Question L.6 (Agustín Lorusso)

To study old bone samples, archaeologists may choose to measure the progress of amino acid isomerization. Living organisms keep most amino acids in the 'L' configuration only. Upon death D-amino acids begin to form in a first-order, reversible racemization reaction. A popular choice to study is the L-isoleucine to D-alloisoleucine reaction.



L D

A shark vertebra was found in the Pacific ocean, in the core of a ferromanganese oxide nodule that accumulated in the deep-sea floor, with a roughly uniform thickness of 8mm. A sample of cartilage was extracted, washed and hydrolyzed. The 'diastereomeric excess' (de) of isoleucine was measured to be 12.4 %. Furthermore, ancient samples that have reached equilibrium will have $de = -16.0$ %.

$$de = \frac{[\mathrm{L}]-[\mathrm{D}]}{[\mathrm{L}]+[\mathrm{D}]} \times 100\ \%$$

Calculate the rate of deposition of ferromanganese oxides around the shark vertebra in nm/yr. We know that $k_{\mathrm{L}} = 9.3 \times 10^{-8}\,\mathrm{yr}^{-1}$ on the seafloor, at a temperature of 276 K.

Solution:

From the reaction diagram,

$$\frac{\mathrm{d}[L]}{\mathrm{d}t} = -k_L[L] + k_D[D]$$

because initially $[D] = 0$, we can say that $[L] + [D] = \text{constant}$, thus

$$-\frac{\mathrm{d}[L]}{\mathrm{d}t} = [L](k_L + k_D) - k_D \times \text{constant}$$

Integrate:

$$\ln\left(\frac{k_L[L] - k_D[D]}{k_L[L] + k_L[D]}\right) = -t \times (k_L + k_D)$$

Simplify:

$$\ln\left(\frac{1-K\times g}{1+g}\right) = -tk_L(1+K)$$

And even more useful simplification with $g = \frac{[D]}{[L]}$ and $K = \frac{k_D}{k_L}$
from

$$de = \frac{1-g}{1+g}\times 100$$

rearrange to

$$g = \frac{1-\left(\frac{de}{100}\right)}{1+\left(\frac{de}{100}\right)}.$$

So the sample has $g = 0.779$ and in equilibrium $g = 1.38$. At $t \to \infty$, $K = \frac{1}{g} = \frac{1}{1.38} = 0.724$ For the sample, $tk_L = 0.816$, therefore $t = 8.8\times 10^6$ years. Thus, rate of deposition is $\frac{8\times 10^6}{8.8\times 10^6} = 0.91\,\text{nm}$ yearly.

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