Singapore Chemistry League 2024

Catalytic Craze Problem and Solution

Problem Setter

Lin Bohan

Catalytic Craze: Eons of the Old Worm

Welcome, one and all! Allow me to explain the format of this question.

In this CC, you will solve for the identity of 9 different elements, which when taken together will reveal a certain pattern. The question sections are not arranged in any particular order.

For each element, there will be 3 part-questions and the answer to each part provides a clue related to the identity of the element. Some are more direct, some are a bit less obvious. In general, if you solve for all 3 clues, you should be able to unambiguously identify the element. With less clues it is still possible, but it may take some guesswork or sharp chemical intuition!

However, among the 9 elements, one of them is an imposter; This renegade element does not fit into the pattern that the other 8 follow, and your objective is to determine this element; the answer to this CC will be its atomic number.

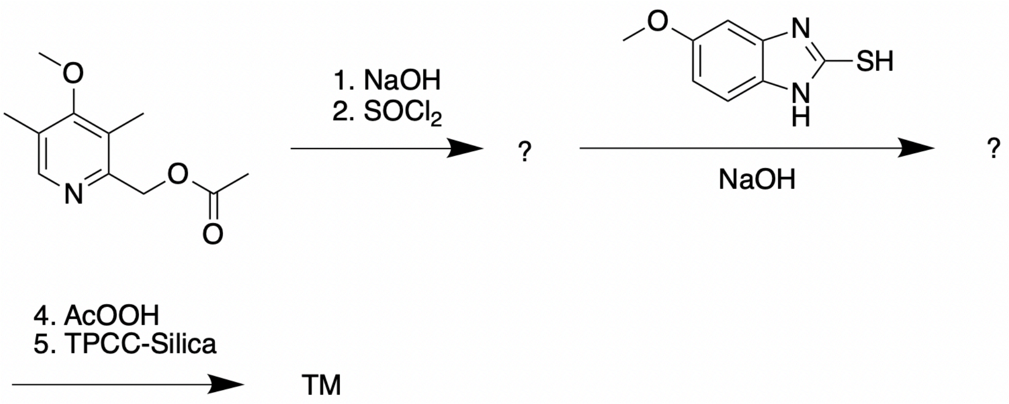
With that, I wish you the best of luck on this chemical odyssey.

Element 1

Part A: What is the identity of this famous transition metal complex?

This is a neutral complex with formula $ABC_3D_{45}E_{54}$, where each letter is just an arbitrary element and does not correspond to any actual elemental symbols. It's a 16-electron complex. The ^{31}P NMR shows a doublet of doublets and a doublet of triplets. The integration ratio is 1:2.

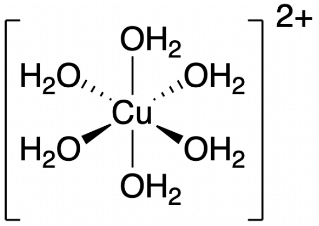
Part B: A pharmaceutical company made this drug. What does it do and how does it do it?

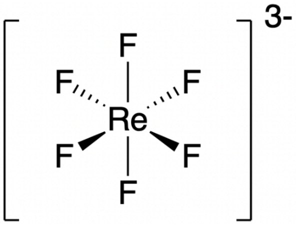


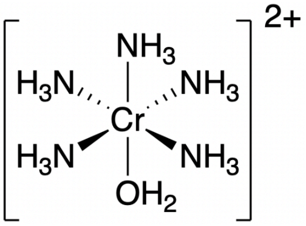
Once you have the identity of the target molecule (TM), try searching its molecular formula and the drug should turn up.

Part C: We're thinking of a martyred American scientist. What weapon was he the most famous for developing?

Think about what all three of these complexes have in common, apart from being octahedral.



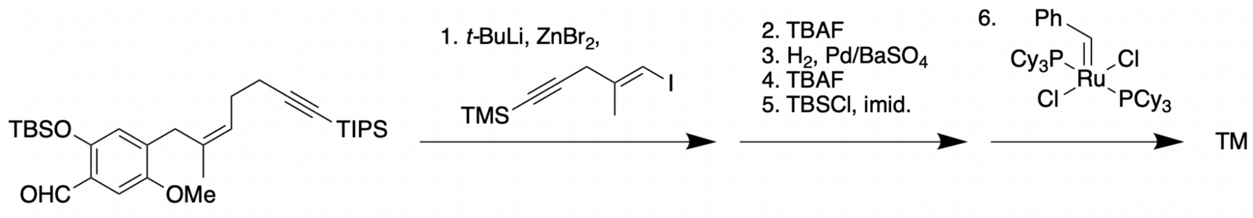




Element 2

Part A: How many stereoisomers are theoretically possible from this series of transformations?

Note: This means we don't take into account possible stereoisomers generated from past steps, only from this sequence. As a side note, all of the syntheses in this CC are actual syntheses, so if you're feeling really lucky you might try your luck guessing what it is!



The efficacy of the deprotection and reprotection steps aren't possible to predict *a priori*, so here are some pointers:

- The first TBAF deprotection removes only **one** silyl group, and the selectivity is determined primarily by sterics.
- The second TBAF step results in a global desilyation
- The reprotection appends only 1 equivalent of TBS

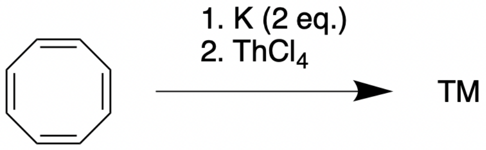
And some additional hints to help you along:

- Silylated alkynes tend to be less reactive than normal terminal alkynes
- The final step is an enyne metathesis during which no internal alkenes are affected, and produces a TM of molecular formula $C_{28}H_{42}O_3Si$.

Part B: We're looking at a lanthanide fluoride species. What are the coordination numbers in the crystal structure?

This LnF_n species has an unusual stoichiometry for a lanthanide species. On top of that, it's an early lanthanide, and other compounds of this lanthanide are commonly used as a single-electron oxidant in organic reactions.

Part C: Think of the point group of this organometallic compound


1. K (2 eq.)
2. $ThCl_4$
TM

Element 3

Part A: We can begin by obtaining an approximate ionic radius for this element.

It is given that the crystal structure of the iodide has a CsCl structure.

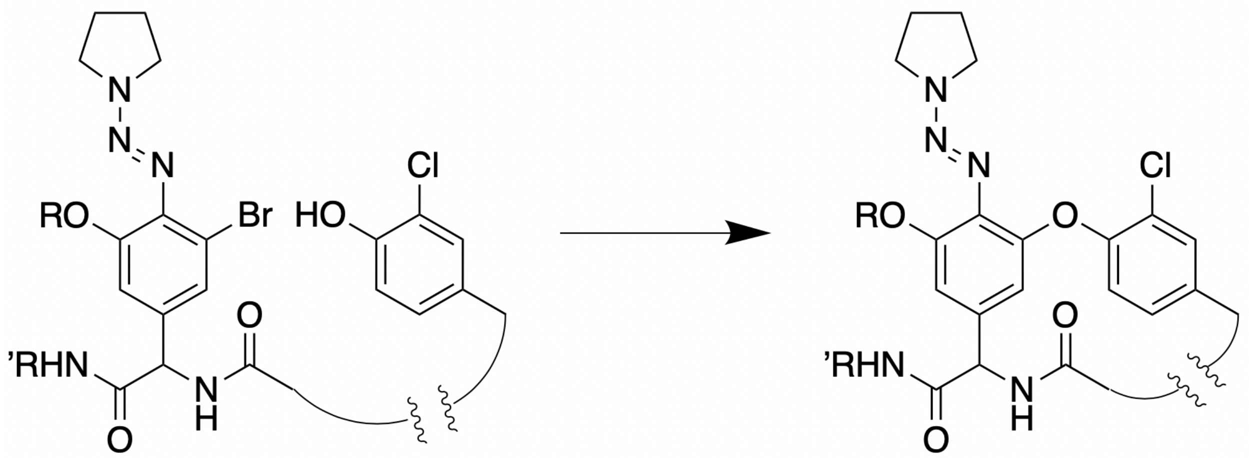
In 6-coordinate environments, I^- is found to have an average ionic radius of 2.2 Å. You may find it useful to use Shannon's ionic radii database.

Part B: As an element, it has something in common with these other two elements…

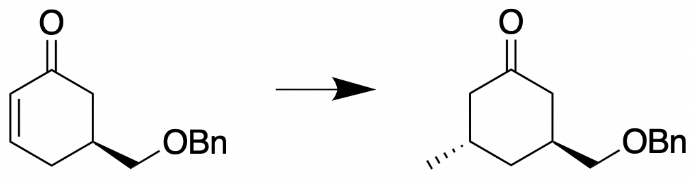
The following table gives a clue to the identity of the first element:

20nm	80nm	100nm
Red	Orange	Purple

And the second element plays a major role in both of the organic reactions shown below. The first is a Nicolaou classic, and this step is not a Pd-catalyzed coupling! However, it is still a well-known named reaction, and it far precedes the likes of the Suzuki, Negishi and Stille couplings. It is named after a German chemist who was active in the early 20th century.



The second organic reaction is a fair bit less intimidating, and is taught in most Gen Chem and Olympiad courses.



Part C: Radiochemistry at last

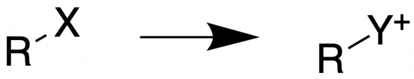
After an unknown number of alpha decays not exceeding five, ^{104}Sb is produced.

Element 4

Part A: Some blursed organic chemistry

In the reaction below, either X or Y can be the unknown element. For once, the lack of reaction conditions is not an omission - no reagents are added to effect this transformation! In addition no other isolable byproducts are formed.

This is a first-order reaction, and in order to obtain a theoretical 99% yield, it would have to sit for 81.9 years.



Part B: A good estimate for the Van der Waals radius

The Lennard-Jones potential describes how potential energy varies with the internuclear distance of two molecules or atoms:

$$U(x) = \epsilon((\frac{\sigma}{r})^{12} - (\frac{\sigma}{r})^{6})$$

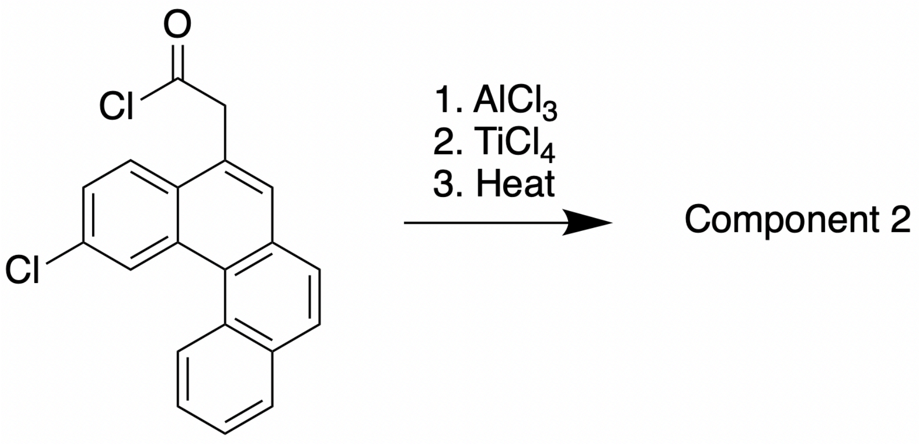
Where ϵ and σ are experimentally fitted constants. Usually, the VdW radius is simply expressed by σ, but in the case of the element at hand, it has been found that the equilibrium separation gives a better estimate of the VdW radius. It's given that $\epsilon = 1.36 \times 10^{-22}$ J and σ = 252 pm for the unknown element.

Part C: What could this supramolecular species be?

A supramolecular species is a chemical species of two distinct components that are not connected chemically, i.e via any ionic or covalent bonds, but are nonetheless found as a single unit.

This supramolecular assembly is synthesised by subjecting the reactants to high-pressure conditions, and without any chemical transformations taking place.

The first component is made of a single element. The second component can be synthesised via the following route:



The addition of $TiCl_4$ results in a product with molecular mass 852 g mol^{-1}.

Element 5

We're trying something a little different this time. Each of the three parts below give a 2-3 letter clue, and when all letters are assembled, they will be an anagram of the element name.

Part A: Find the identity of a binary compound

Element Y in XY_3 has a mass percentage of 61.7%. It is also given that XY_4 has molecular mass 746 g mol^{-1}.

Part B: A commonly used oxidising agent in organic chemistry

This is an ionic species.

The cation is composed of only two elements (note: metals coordinated to ligands are NOT considered cations). It can be used to make a buffer solution of pH = 10.0 if 339.6 g of NaOH is added to a 1 M concentration, 10 dm^3 aqueous solution of this cation.

The anion is a coordination complex $[M(NO_3)_6]^{n-}$, where, somewhat unusually, the nitrato ligand acts as a bidentate ligand. n represents an unknown integer.

Part C: It can be used to make a commonly used solvent

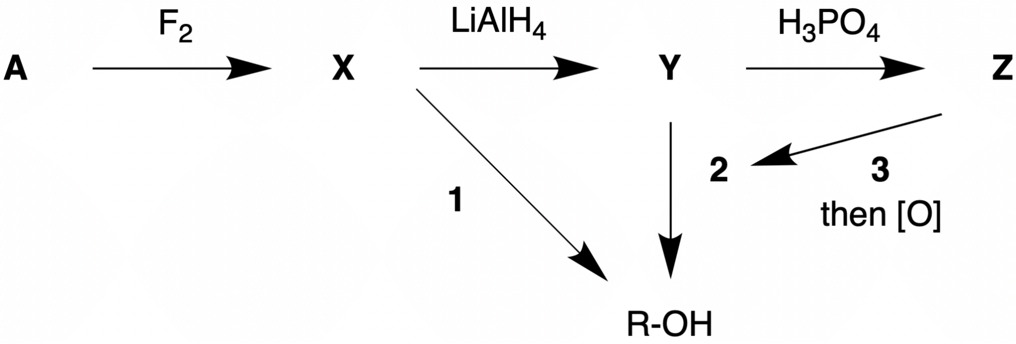
At 20°C, the solvent has a vapour pressure of 55.6 Pa. It is further given that it has $\Delta_{vap}H^{\ominus}$ = 50.0 kJ mol^{-1}. Assume that $\Delta_{vap}H$ does not vary over temperature. What is the normal boiling temperature?

The solvent is made from our chemical of interest on an industrial scale, by the reaction with molecular oxygen.

(Hint, the normal boiling point of a substance is defined as the temperature at which the vapour pressure is equal to the atmospheric pressure.)

Element 6

Compounds of this element are versatile organic reagents and also quite easily prepared. In the scheme below, A is the unknown element, and X, Y, Z are compounds containing the unknown element. 1, 2, and 3 are organic functional groups that can react with the respective compounds to eventually form an alcohol.



In this section, we will elucidate the functional groups 1, 2 and 3, and hence the identity of the element. Note that the transformations subsequently described do NOT correspond to the ones shown in the diagram above.

Part A: The identity of 1

An organic molecule is reacted to form the functional group. In the NMR analysis, it shows the disappearance of a singlet peak at 3.4 ppm and the appearance of a sharp singlet corresponding in intensity to 9 protons, at a chemical shift of ~ 0.2 ppm. The molecular mass of the organic molecule is also found to have increased by 72 g mol^{-1}.

Part B: The identity of 2

Tartaric acid is added to an excess of concentrated sodium hydroxide, and then mixed with an equimolar mixture of copper (II) sulfate. Immediately, an organic species containing the functional group of interest is added, resulting in the appearance of a red-brown precipitate which slowly turns into a black solid upon prolonged exposure to air.

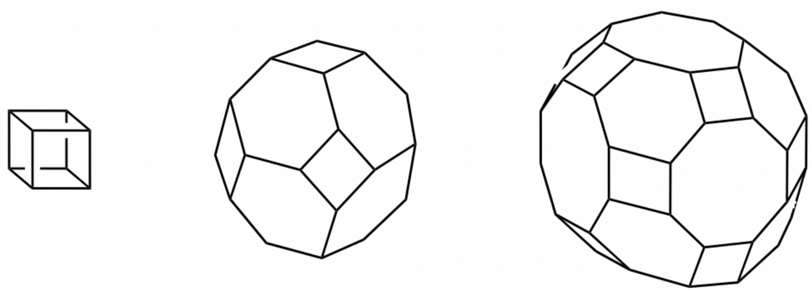
Part C: The identity of 3

Another organic molecule, $C_8H_4O_2$, contains two equivalents of the functional group in question (although, taken more liberally/generally, one might argue that it's three equivalents). It is subject to 120°C over the period of two days, in a solution of *t*BuOH. At the end, a sole major product, $C_{12}H_{14}O_3$, is obtained.

In another experiment, the same organic molecule is first reduced with 3 equivalents of hydrogen gas over a poisoned catalyst. Upon being kept at room temperature in the presence of *t*BuOH for a duration, it again forms only one major product, but with molecular formula $C_8H_{10}O_2$.

Element 7

Part A: These shapes may remind you of a certain material…



Physically, it often has the appearance of small, white granules. It's used as a solid-state reagent in organic synthesis. What are its main constituent elements?

Part B: The stoichiometry of the chloride

It's given that the chloride is able to bring out the maximum oxidation state of the element.

A mixture of the element and chlorine gas that stoichiometrically produces one mole of the chloride compound is heated from 172 K to 239 K. Over this temperature range, the unknown element exists as a solid. No chemical reaction or phase change takes place. After some calculations, ΔS was found to be +23.5 J K^{-1}.

The following data is given:

C_P[A (s)] / J mol^{-1} K^{-1}	25
C_P[Cl_2 (l)] / J mol^{-1} K^{-1}	31

Part C: Mystery organic reagent

A certain commonly used organic reagent is capable of converting both nitriles and carboxylic acids to the same functional group following workup. In addition, if more equivalents and more forcing conditions are used, carboxylic acids will be reacted to form the same substrate as can be achieved by using BH_3 in THF.

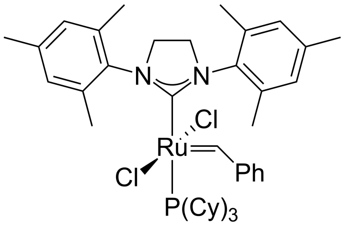
What are the elements present in this reagent?

Element 8

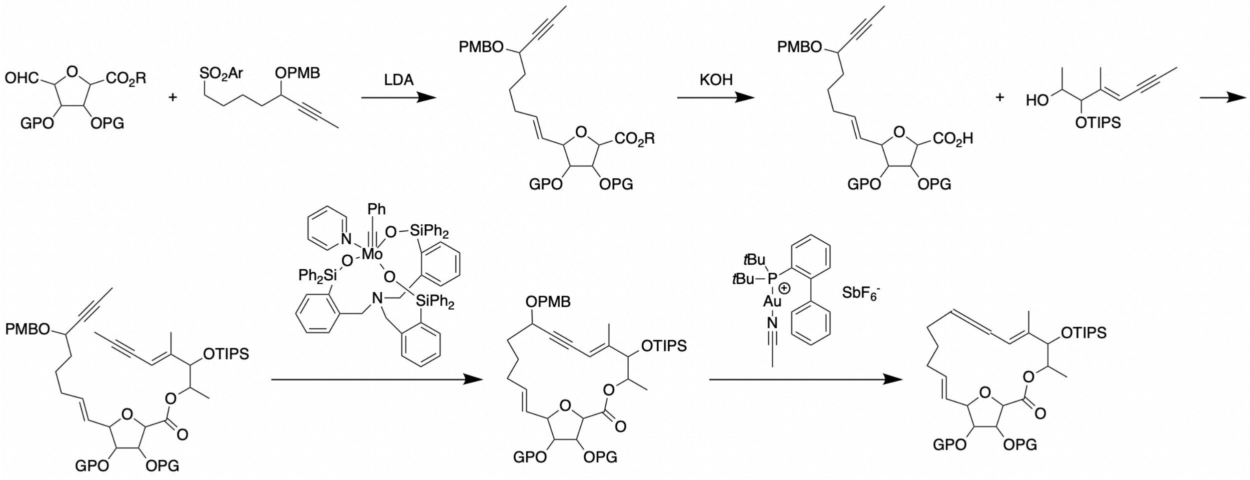
This element is a metal.

Part A: A mysterious unknown functional group!

Of the following four reagents and conditions, only two of them will react with the functional group, while the other two do not.

1. OsO_4, NMO
2. NCS, DMS; Et_3N
3. BH_3, THF; H_2O_2, NaOH
4. 

This functional group is involved in one of the steps in the synthetic transformation below, and that step involves a reactant bearing this element:



Part B: The identity of a certain acid, tying together two Nobel laureates with a small but fated connection

The first individual (b. 1879, d. 1960) was awarded the Nobel prize for foundational work in developing a well-used spectroscopy technique (among many others), which is compared against IR and NMR spectroscopy below. They are ranked 1-3 based on the extent to which they fulfil the criteria, 1 being the most and 3 being the least.

	Amount of information provided	Ease of sample preparation	Can differentiate between enantiomers*
IR	3	1	N
NMR	2	2	N
???	1	3	Y

* i.e between enantiomers, and not just enantiomerically pure vs racemic mixtures; also in the absence of any chiral additives.

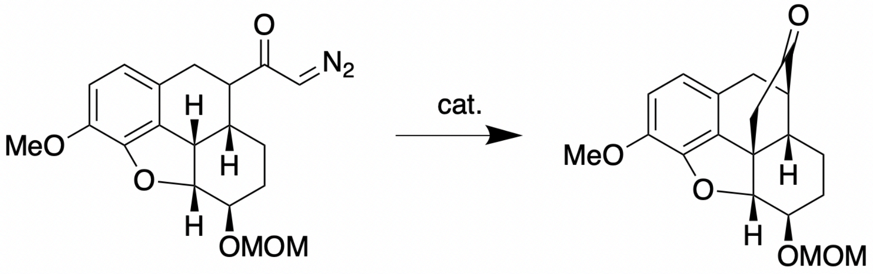
The second individual was awarded the Nobel Prize, alongside another scientist, for an experiment that laid the foundation of quantum mechanics by establishing the quantisation of energy. In addition, he also played a role in the nuclear politics of WWII, by producing a report that recommended against the use of atomic weapons in war.

The experiment involved the bombardment of Hg atoms with electrons. It was found that the emitted light was always of a certain wavelength - and hence energy.

Part C: The element can boast of membership in a certain snobby 8-element group…

…and here is a brief biography of some of the other members.

One of them is often associated with carbene insertion reactions and coordinates to the carbene to form a relatively stable species, for example the synthesis of morphine shown below. More generally, its compounds are powerful catalysts for various organic transformations, and have even been applied industrially to the synthesis of menthol via the Takasago process.



Another one of them can form a coordination complex $MCl_2(NH_3)_2$ (M denotes an arbitrary metal), which is perhaps one of the most famous chemotherapy agents. There are two possible isomeric forms, and only one of them is active.

Yet another member is a rather dense fellow; Its most synthetically useful compound is the oxide in the maximum oxidation state. Used alone it is able to synthesise diols, and when used in conjunction with an I(VII) species, it is capable of forming carbonyls.

Element 9

Part A: Many chemicals with this element, and indeed the whole group it belongs to, have something in common with the following three molecules!

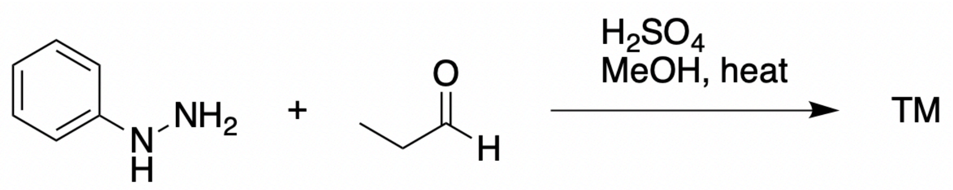
The first molecule has a stoichiometry of X_2Y, and the bond angle is found to be close to 90 degrees due to bonding involving the d orbitals on the central atom. This experimental finding is at odds with VSEPR theory, which would have predicted an angle of about 107.5 degrees. It also appears in the industrially important Claus process for the production of sulfuric acid.

The second molecule has a molecular mass $M_r = 88$ and shows the following peaks in its ^1H NMR spectrum when solvated in H_2O:

δ / ppm	Splitting	Integration
2.83	t	1
1.60	m	1

The ^{15}N NMR spectrum shows a single singlet peak. There are 4 carbon atoms in the molecule existing in 2 different chemical environments.

The third molecule can be quite readily generated from the following reactants:

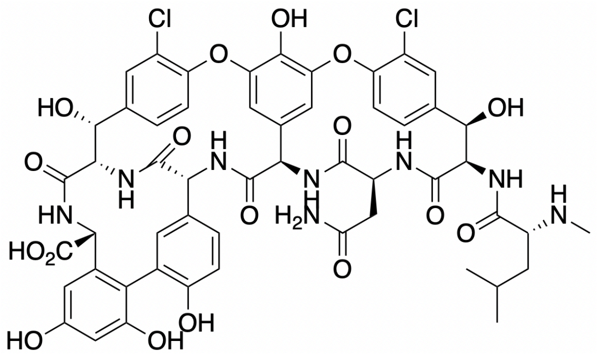


Part B: Its discoverer was a pioneer of chemistry as we know it today.

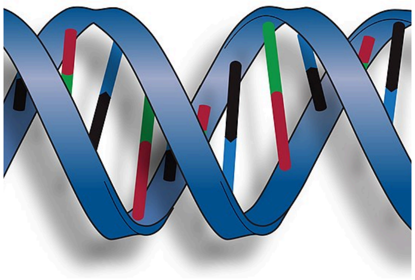
Indeed, discovering this element was only one of his many achievements spanning across the entirety of chemistry, from biochemistry to stoichiometry. He was active in the early 19th century, when it was still possible to have total knowledge of an entire scientific discipline.

He is credited with coining many terms that will be familiar to any high-schooler of today: the following is a selection.

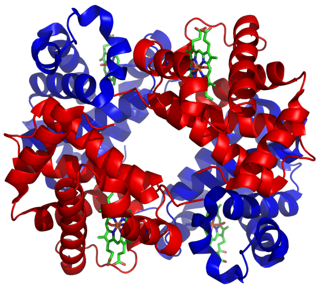
1. What type of biological macromolecule is derived from the same building blocks as this natural product?



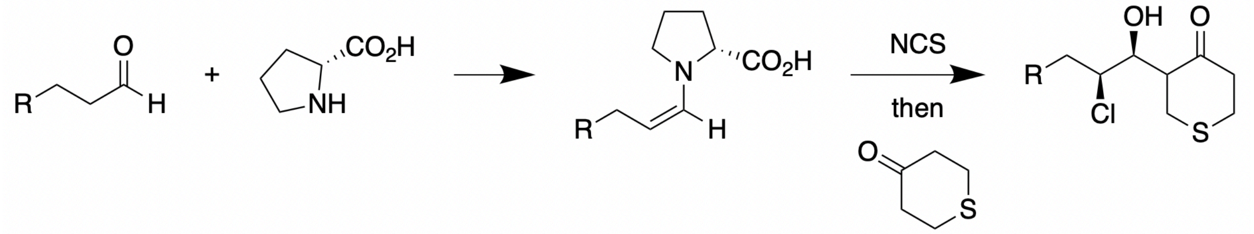
2. What do the following have in common? Think about their chemical structures.




[1]


[2]

3. What role does proline play in the following reaction?



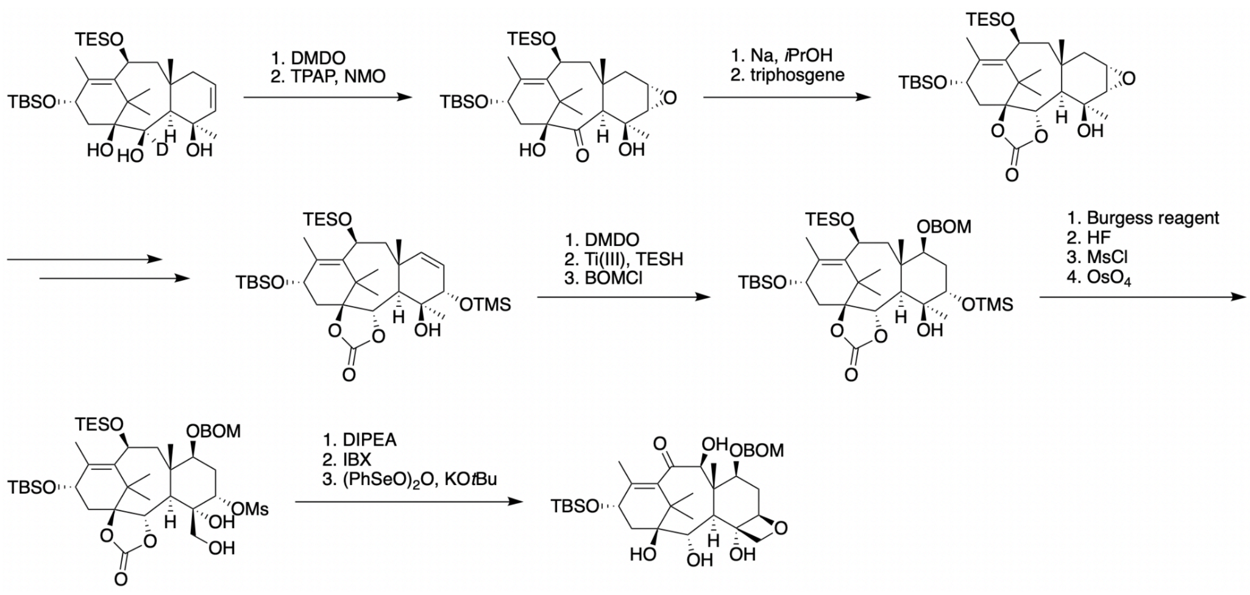
Part C: Finally, this element appears in reagents used in one of the oxidation steps in Baran's recent total synthesis of taxol.

So that you don't waste your time, it's none of the common organic elements - C, H, N, O.

---

[1] By StromBer - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=18580995

[2] By Zephyris at the English-language Wikipedia, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=2300973


TESO
TBSO
HO
HO
D
H
OH
1. DMDO
2. TPAP, NMO
O
1. Na, iPrOH
2. triphosgene
OTMS
1. DMDO
2. Ti(III), TESH
3. BOMCl
OBOM
1. Burgess reagent
2. HF
3. MsCl
4. OsO4
OMs
1. DIPEA
2. IBX
3. (PhSeO)2O, KOtBu

Catalytic Craze: Eons of the Old Worm

Solution:

79

A summary of the answers for each element:

#	Element	Atomic #	Part A	Part B	Part C
1	H	**1**	Wilkinson's catalyst, [$Rh(PPh_3)_3Cl$]	Omeprazole	They all exhibit Jahn-Teller distortion
2	O	**8**	8	CeF_4 (8:2 coordination)	D_8h
3	Cs	**55**	Ionic radius > 1.63 Å	The element is coloured (Au, Cu)	^{110}I, ^{114}Cs, ^{118}La, ^{122}Pr or ^{126}Pm
4	He	**2**	H or He		?@C_{60}
5	Sc	**21**	UI	CAN	DMS
6	B	**5**	−OTMS	−CHO	−C≡CH
7	Al	**13**	Zeolite	Trichloride	DIBAL-H
8	Au	**79**	Mo, Au or Sb	Aqua regia	Noble metals
9	Se	**34**	H_2S, putrescine, skatole	Jacob Berzelius	Ru, Os, I, Se

When their atomic numbers are arranged in increasing order: 1,2,5,8,13,21,34,55,79

This is awfully close to the fibonacci sequence: 1,1,2,3,5,8,13,21,34,55,89,... the only element that doesn't follow this order is Au, with atomic number 79!

By the way, the "Old Worm" in the title refers to the Worm God, Leto Atreides II from Dune, who spent 4 millenia (hence "eons") building the Golden Path to ensure humankind's survival - a small easter egg! Wonder if anyone might have guessed it?

Element 1: H

Taking every part into account, we may notice a common intersection point is the element hydrogen:

1. The Wilkinson's catalyst catalyses hydrogenation of olefins
2. Omeprazole works by inhibiting proton pumps
3. Edward Teller is known for developing the hydrogen bomb

Part A: Wilkinson's catalyst, $[Rh(PPh_3)_3Cl]$

A starting point can be to realise that in the stoichiometry given, C,D and E seem to be awfully convenient multiples of three, so we might guess that one of the components is a ligand, $CD_{15}E_{18}$. Again we observe that D and E are multiples of three, which might suggest that the ligand has a form $C(D_5E_6)$, which corresponds quite well to the triphenylphosphine ligand, $P(C_6H_5)_3$.

This is further corroborated by the fact that there are peaks in the ^{31}P NMR spectrum, strongly suggesting the presence of phosphorus-containing ligands. We now know that this is a tetracoordinate complex. The fact that there are two different peaks in the ^{31}P NMR spectrum, with integration ratio 1:2, suggests a square planar complex, with the alternative tetrahedral complex giving only one peak.

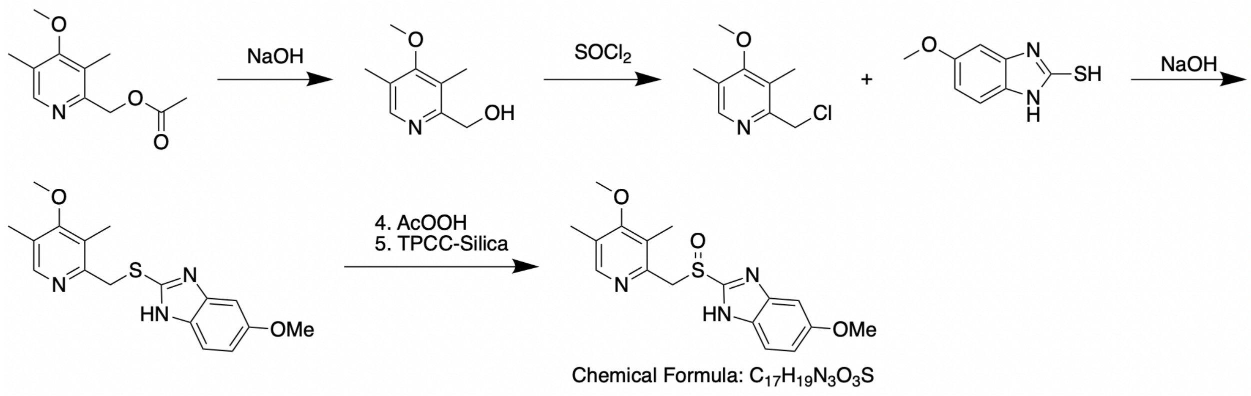
We also know that the last ligand is a single element. There is a limited range of such ligands, and O^{2-}, N^{3-} and halides are by far the most common. For each case, we can then deduce the group number of the metal:

Charge on ligand	Group number of metal	Possible metals
-1	16 - 3(2) - 2 + 1 = 9	Co, Rh, Ir
-2	16 - 3(2) - 4 + 2 = 8	Fe, Ru, Os
-3	16 - 3(2) - 6 + 3 = 7	Mn, Tc, Re

The square planar geometry strongly suggests a d^8 configuration, which would only be attainable in the first case, where the ligand is a halide. Since it is a famous catalyst, one may guess at Wilkinson's catalyst, named after Sir Geoffrey Wilkinson. This was a pioneering homogeneous catalyst and was used in the catalytic hydrogenation of alkenes.

Part B: Omeprazole

The synthetic transformations are shown:



This is a medication used to treat indigestion and heartburn, and it belongs to a broad class of drugs called proton pump inhibitors (PPIs). It works by blocking the action of the proton pumps in our cells, hence regulating the uptake of H^+ ions.

Part C: They all exhibit Jahn-Teller distortion

It takes some guesswork to start, but one may note the choice of ligands: two of them have weak-field ligands (H_2O, NH_3) while the last has a strong-field CN^- ligand. In addition, one may try to deduce the d^n configuration of the metal:

$[Cu(OH_2)_6]^{2+}$	$[Co(CN)_6]^{4-}$	$[Cr(NH_3)_5(OH_2)]^{2+}$
High-spin	Low-spin	High-spin
d^9	d^7	d^4

An astute student will realise these are the configurations for which Jahn-Teller distortions are the most readily apparent. The question prompts us that we're looking for the identity of a scientist, so why not take a look at the individuals that this phenomenon is named after?

1. **Hermann Arthur Jahn** was a British scientist of German descent, so he doesn't quite fit the description of a "martyred American scientist"
2. **Edward Teller,** on the other hand, was a Hungarian-born American scientist, as I am sure those who have watched *Oppenheimer* will be aware of. And he was indeed

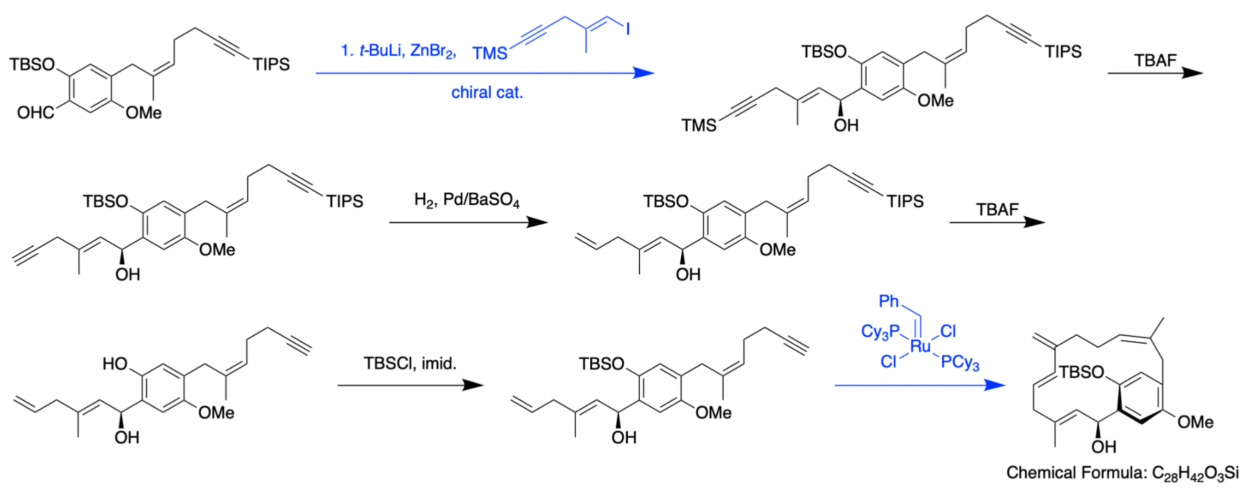
martyred for his relentless pursuit of the hydrogen bomb - he gives his name to the Teller-Ulam design upon which the pioneering thermonuclear weapons were built.

Element 2: O

The recurring theme of all 3 parts is the number 8, which is the atomic number of oxygen.

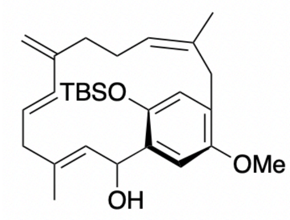
Part A: 8 possible stereoisomers

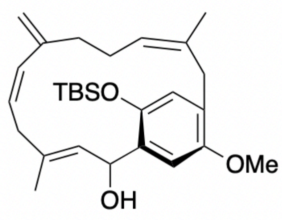
This is taken from the Shair synthesis of longithorone A in 2002, and the actual synthetic pathway is shown. You will note that in the first step, a chiral catalyst was used in reality, but it was removed in the synthetic scheme provided in the question to remove any potential ambiguity.

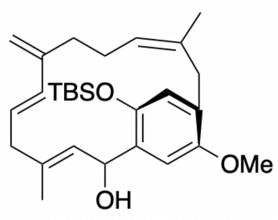


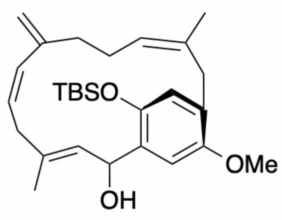
The steps where stereoisomers could be generated are marked in blue and discussed:

1. **Nucleophilic addition to the aldehyde.** In the absence of chiral control (and indeed also even in the presence thereof, if the chiral element doesn't impart sufficient stereo-differentiation), two enantiomers at the secondary alcohol can be formed as attack is equally likely from both sides of the planar carbonyl carbon.
2. **Enyne metathesis.** This step can give rise to a whopping 4 stereoisomers - 2 due to the cis/trans conformation of the newly-formed internal alkene, and 2 due to atropisomeric products with respect to the aromatic ring. They are drawn explicitly below. In the actual synthesis this step, and a subsequent TBAF deprotection, were achieved in a very respectable 42% combined yield.









The atropisomerism is somewhat harder to visualise, but imagine holding the aromatic ring stationary in space, and then closing the macrocycle either "above" or "below" the ring. Overall, as there are 3 new stereoelements in the final molecule, we can expect $2^3 = 8$ possible theoretical isomers.

Some additional notes about the deprotection / reprotection steps:

1. The choice of silyl group removed in the first deprotection is dictated by steric bulk, with TMS $<$ TBS $\approx$ TIPS. Hence we should expect the acetylenic TMS group to be removed.
2. The regioselectivity of the reprotection depends primarily on which position is the most acidic. The pKa of a phenol is about 10, while the pKa of a terminal alkyne and an alcohol are about 25 and 20, respectively, making them much less acidic.

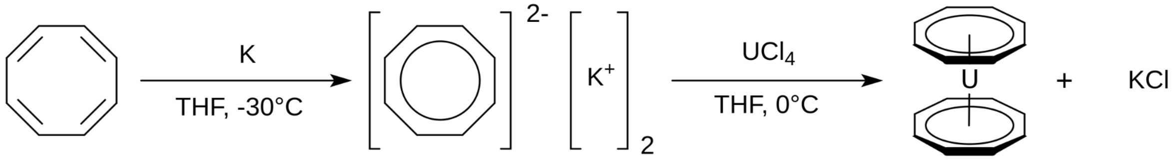
Part B: CeF_4, with 8:2 coordination

Lanthanides generally exhibit a +3 charge, so an "unusual" stoichiometry could mean either a +2 or a +4 charge. Given that it's used as a single-electron oxidant, we can deduce that it is a Ln(IV) species, as they would be readily reduced back to Ln(III). The principal lanthanide that exhibits this behaviour is Ce, with Pr and Nd also exhibiting such behaviour but to a much more limited extent. More unambiguously, Ce is the only lanthanide that forms a tetrahalide.

The CeF_4 species consists of vertex-sharing antiprisms (https://www.chemtube3d.com/ss-cef4/ for a 3D model), hence has an 8-coordinate Ce and 2-coordinate F.

Part C: D_8h symmetry

This is the synthesis of thorocene, a close relative to the more well-known uranocene, for whom the entirely analogous preparation is shown:



[3]

The K is an oxidant, which transfers 2 electrons (1 per K) to form the aromatic COT^{2-} ligand (there are 10 pi electrons, hence fulfilling Huckel's 4n+2 rule). They then undergo a ligand exchange with U/Th to form the uranocene/thorocene complex.

This is a linear complex, with the COT^{2-} ligands parallel to each other and with the vertices directly in line. This is a result of the interactions with the f-orbitals on the central metal, where this configuration allows for maximum orbital overlap. Indeed, this is one of the few examples of true phi-bonding.

---

[3] By Cmoarl - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=37755151

Element 3: Cs

Part A: Ionic radius > 1.63 Å

In a bcc unit cell, the cationic radius / anion radius ratio should not be smaller than 0.732, or an octahedral coordination would occur instead of a cubic coordination. Further using the Goldschmidt radius to adjust for the different coordination environments, we deduce that the ionic radius of the cation is not smaller than 0.732 x 2.2 x 0.97/0.96 = 1.63 Å in an 8-coordinate environment.

Furthermore, having a CsCl structure means it is single charged. Using Shannon's ionic radii (http://abulafia.mt.ic.ac.uk/shannon/radius.php) the possible identities are narrowed down to Rb^+, Cs^+, Fr^+, Tl^+.

Part B: The element is coloured in its elemental form

Element 1 is Au: the table lists the colours of gold nanoparticles (AuNPs) of different diameters. AuNPs have a variety of uses from catalysis to medical imaging and specific drug delivery, and is a hot area of research right now. Indeed, Au is perhaps the most famous coloured element - since gold is… gold coloured.

Element 2 is Cu: The first reaction is the Ullmann biaryl ether coupling, which uses Cu(0) or Cu(I) species as catalysts. The scheme is taken from the Nicolaou synthesis of vancomycin. The second reaction is a conjugate addition by use of a Gilman reagent, Me_2CuLi, which also contains Cu. There are other possible reagents but this is the only one commonly taught in undergraduate classes. Cu itself has a reddish-brown colour, which has been exploited since antiquity.

There are few other elements which are coloured. Among the metals, Cs has a slight yellowish lustre, and Os is ever so slightly blue. Among the non-metals, there are C (although, as an artist, I insist that black is not a colour), P, S, liquid O_2 and the halides.

Part C: ^{110}I, ^{114}Cs, ^{118}La, ^{122}Pr or ^{126}Pm

An alpha-decay is merely the loss of a helium-4 (alpha particle) from the isotope, so we need to work backwards by adding the proton number in steps of 2 and the nucleon number in steps of 4 (although for the purposes of the question, we don't even need the nucleon number). Given a maximum of 5 possible alpha-decays, this gives us 5 possible elements.

Element 4: He

Part A: H or He

This is a first-order reaction, which, combined with the lack of reagents (along with the title of Part A), might suggest that this is a radioactive decay. To obtain the half-life:

$$(\frac{1}{2})^n = 1 - 0.99 = 0.01$$
$$n = \frac{ln(0.01)}{ln(1/2)} = 6.6439$$
$$n \times t_{1/2} = 81.9 \text{ yr}$$
$$t_{1/2} = \frac{81.9}{6.6439} = 12.3 \text{ yr}$$

Using a database like Wikipedia (https://en.wikipedia.org/wiki/List_of_radioactive_nuclides_by_half-life) we can see that this corresponds to the half-life of ^{3}H, which beta decays to ^{3}He.

Part B: 141 pm

We want to use the Lennard-Jones potential to find the equilibrium separation. To do that, we have to find the global minima, so we begin by finding $\frac{dU}{dr} = 0$:

$$\epsilon(\sigma^{12}(\frac{-12}{r^{13}}) - \sigma^6(\frac{-6}{r^7})) = 0$$
$$6\epsilon\frac{\sigma^6}{r^7}(-2(\frac{\sigma}{r})^6 + 1) = 0$$
$$(\frac{\sigma}{r})^6 = 1/2$$
$$r = 2^{1/6}\sigma$$

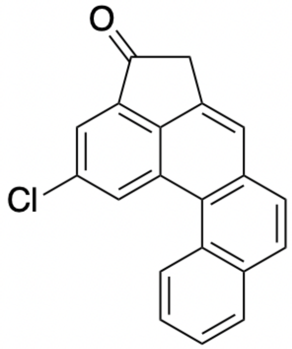
This would give twice of the VdW radius, so we have to divide by two then substitute the values:

$$r = 2^{-5/6}(252) \text{ pm} = 141 \text{ pm}$$

Some possible elements (https://en.wikipedia.org/wiki/Van_der_Waals_radius) are He (140 pm), F (147 pm), Cu (140 pm) and Zn (139 pm).

Part 3: ?@C_{60}

Let us start with the second component. In the first step of the synthesis, a Lewis acid is added which likely interacts with the acyl chloride. In conjunction with the presence of phenyl rings, we deduce that an S_EAr reaction has occurred, producing:



The second step is a bit mysterious, and our only clue is that the product has $M_r = 852$. So we might try calculating the M_r of the intermediate at hand - which turns out to be 302. One might notice $302 * 3 = 906 = 852 + 3 * 18$ - this suggests a trimerisation reaction with loss of 3 molecules of water. This fits a triple aldol condensation to form a central benzene ring.

The result of the final step cannot be predicted *a priori* but given the plethora of phenyl rings, the presence of 5-membered rings and the total of 60 carbons within the structure, one could guess buckminsterfullerene to be the product. Indeed, this is Scott synthesis of buckminsterfullerene (https://synarchive.com/syn/100).

Fullerenes have a versatile supramolecular chemistry, generally classified into types where another chemical species encloses the fullerene (exohedral fullerenes), or when the fullerene itself encloses a chemical species (endohedral fullerenes). The fact that the first component comprises a single element strongly suggests an endohedral fullerene. As it is synthesised by high-pressure methods, this suggests a non-metallo endohedral fullerene as metallo-endohedral fullerenes are generally made in an arc reactor or via laser evaporation. $H_2@C_{60}$ and $Ng@C_{60}$ stand out as possible structures, where Ng = noble gas.

Element 5: Sc

The letters collected are u, i (part A), c, a, n (part B) and d, m, s (part C), which together give scandium.

Part A: UI_3

Let the atomic mass of the element X be M_X and element Y be M_Y.

Then we can form the following two equations:

$$\frac{3M_X}{3M_X+M_Y} = 0.617$$

$$4M_X + M_Y = 746$$

Rearranging the first equation, we get:

$$\frac{3M_X+M_Y}{3M_X} = 1 + \frac{1}{3}\left(\frac{M_Y}{M_X}\right) = \frac{1}{0.617}$$

$$M_Y = 1.86M_X$$

Substituting into the second equation:

$$5.86M_X = 746$$

$$M_Y = 127$$

$$M_X = 237$$

Which matches to iodine (M_r = 126.9) and uranium (M_r = 238.0). Given that we were working with 3s.f., the value of M_X is within the plausible error margins.

Part B: CAN

First, we find the identity of the cation. We need to use the Henderson-Hasselbalch equation to find its pKa:

$$pH = pKa + log\frac{[A-]}{[HA]}$$

$$pKa = pH - log\frac{[A-]}{[HA]}$$

$$= 10.0 - log\frac{[NaOH]}{[HA]_{initial}-[NaOH]}$$

$$= 10.0 - log\frac{0.1\times\frac{339.6}{22.99+16.00+1.008}}{1-0.1\times\frac{339.6}{22.99+16.00+1.008}}$$

$$= 9.25$$

A search such as “what acid has pKa of 9.25”, or scouring through a comprehensive pKa table, will return NH_4^+ as the answer.

As the nitrate acts as a bidentate ligand, the coordination number of the central atom is 12 - an anomalously large number that points to its possible identity as a lanthanide! Coupled with the fact that this is used as an oxidising agent, ceric ammonium nitrate, CAN, is the answer we seek.

Part C: DMS

At the heart of solving this question lies the Clausius-Clapeyron equation, which tells us the temperature dependence of the vapour pressure of a particular chemical:

$$ln\frac{P2}{P1} =- \frac{\Delta_{vap}H}{R}(\frac{1}{T2} - \frac{1}{T1})$$

At boiling temperature, we have P = 1 atm = 101325 Pa. Sub T1 = 293.15 K, P1 = 55.6 Pa, T2 = b.p, P2 = 101325 Pa and $\Delta_{vap}H = 50.0$ kJ mol^{-1}:

$$ln\frac{101325}{55.6} =- \frac{50.0(1000)}{8.3145}(\frac{1}{b.p} - \frac{1}{293.15})$$

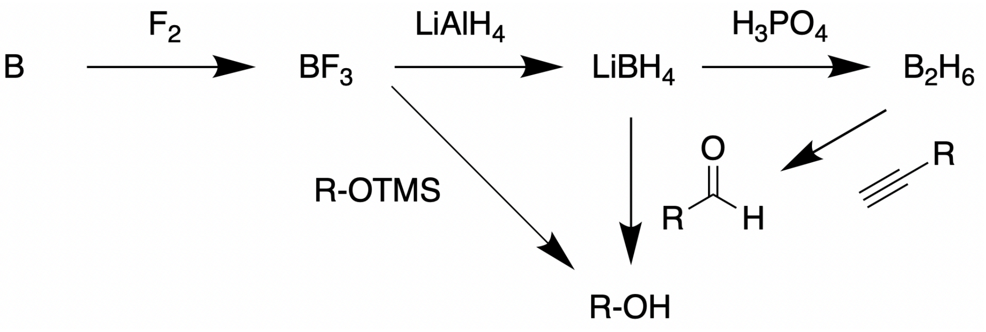
B.p = 462.38 K = 189 °C

Using a database (e.g. https://organicchemistrydata.org/solvents/) the solvent is found to be DMSO, which is indeed made from DMS industrially by reaction with O_2 or NO_2.

Element 6: B

To complete the table, the easiest place to start, perhaps, is Y → R-OH. The commonly encountered reagents to effect this transformation are $[AlH_4]^-$ and $[BH_4]^-$, giving B or Al as the possible identity of the element. H_3PO_4 serves to generate AlH_3 or BH_3, and both could theoretically undergo 1,2 addition onto an alkyne (via either hydroalumination or hydroboration) and then be oxidised to an enol which tautomerizes to an aldehyde, so Z → 2 doesn't quite help us decide.

However, we note that A is likely the trifluoride, and that BF_3 are known reagents for silyl ether deprotection. Hence, the completed scheme is:



Part A: −OTMS

The giveaway clue is the appearance of the 0.2 ppm singlet. No conventional organic functional groups are shielded enough to be so upfield, but one might note that the commonly used standard, tetramethylsilane, has a very similar chemical shift (0.0 ppm by definition). So perhaps a silyl group is at play? 9 equivalent protons suggest a trimethylsilyl group, which is often used to protect alcohols. This is further corroborated by the increase of 72 g mol^{-1}. Indeed, now the disappearance of the signal at 3.4 ppm can be explained to be the loss of an alcoholic proton.

Part B: −CHO

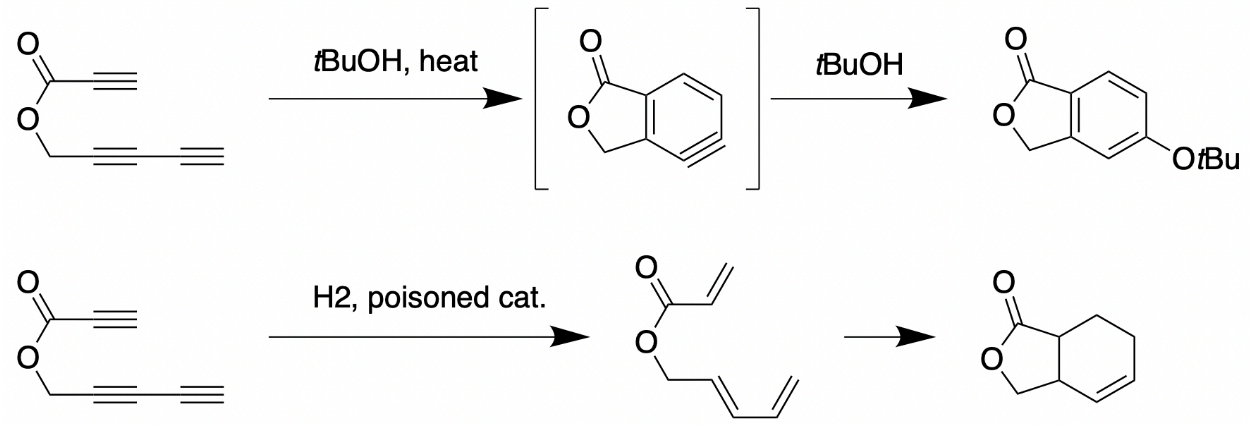
The procedure described is in fact the preparation of Fehling's solution, and indeed the positive test of a reddish brown ppt of Cu_2O is observed, which points at an aldehyde functional group. The Cu_2O can be further oxidised to CuO, which is a black solid.

Part C: −C≡C-H

We may begin by comparing how the product has changed, and we observe an increase in molecular formula by $C_4H_{10}O$, which is incidentally the molecular formula of *t*BuOH, so we may be reasonably confident that a net addition of a *t*BuOH has resulted. However, this is not a condensation reaction or a substitution, as we would usually expect it to react - strange!

To make further progress we might turn to the second experiment. This time we observe an increase of 6 hydrogens, which likely occurs as a result of the aforementioned addition of 3 equivalents of H_2 and not the subsequent reaction. This would point at a pericyclic reaction, as they are one of few reaction types that do not change the molecular formula. We observe that, given it is pericyclic, we may reasonably hypothesise the presence of alkene functionalities, and that they have likely been reduced from alkynes via a poisoned catalyst.

Hence, this strongly suggests the initial product had three alkynes - a deduction till this point is already sufficient to solve this part, but for the interested student, the first reaction is a hexadehydro-Diels-Alder (HDDA), while the second is simply a DA.

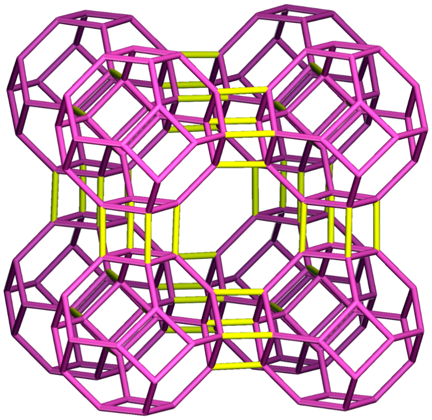


Element 7: Al

From part B, we know that this is likely to be a group 3, group 13, or f block element. From part A, the constituent elements are Al, Si, O and either a metal or H. From part C, the elements are Al, C and H. Hence, the common intersection point of all three parts is aluminium, Al.

Part A: Zeolites

When the shapes are pieced together, you get the LTA framework of zeolites, which are aluminosilicates. Each of the three shapes represents one of the holes that occur in this structure. They are often used as molecular sieves in organic synthesis, for example for the uptake of protons.


[4]


[5]

Part B: ACl_3

We need to use the equation for the entropy change of a system on heating:

$$\Delta S = \int_{T1}^{T2} nC_{p,m} dT$$

As C_p is assumed to be independent on temperature, this is simplified to:

---

[4] By Nao1958 - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=75387204

[5] By Smokefoot - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=44351968

$$\Delta S = nC_{p,m} ln\frac{T2}{T1}$$

For multiple species present:

$$\Delta S = ln\frac{T2}{T1}\sum_{i=1}^{N} n_i C_{p,m,i}$$

In this case, let the unknown chloride formed be ACl_n. Thus:

$$23.5 = (25 + 31\frac{n}{2})ln\frac{239}{172}$$

n = 3

Part C: DIBAL-H

Carboxylic acids, when reacted with BH_3 in THF, can be reduced to alcohols, so we know that our mystery reagent is capable of the same. It is, however, also capable of reducing it to only aldehydes, and the most prominent example of such a reagent is DIBAL-H, which does indeed also effect the reduction of nitriles to aldehydes.

Element 8: Au

Part A: Mo, Au, Sb

Rather than take a purely iterative approach through all of the functional groups in existence (a brobdingnagian task), we can use the synthetic scheme to narrow the possibilities. The functional groups that are involved in a transformation are:

Step	FGs
1	Aldehyde, sulfone, alkene
2	Ester, carboxylic acid
3	Carboxylic acid, alcohol, ester
4	Alkyne
5	Alkyne, allene

And running an iterative check on each of these functionalities:

	OsO_4, NMO	NCS, DMS; Et_3N*	BH_3, THF; H_2O_2, NaOH	Hoveyda-Grubbs catalyst
Aldehyde	🟥	🟥	🟥	🟥
Sulfone	🟥	🟥	🟥	🟥
Alkene	🟩	🟥	🟥	🟥
Ester	🟥	🟥	🟥	🟥
Carboxylic acid	🟥	🟥	🟥	🟥
Alcohol	🟥	🟩	🟥	🟥
Alkyne	🟥	🟥	🟩	🟩
Allene	🟩	🟥	🟩	🟩

* This is the Corey-Kim oxidation, which is an alternative to the Swern oxidation.

The only FG that matches the requirements is the alkyne, which, in the synthetic scheme, reacts in two steps: The alkyne metathesis, and the alkyne-allene isomerisation.

Part B: Aqua regia

To begin, the condition that this spectroscopic technique can differentiate between enantiomers greatly limits the possible choices, since more routinely used methods like mass and UV-Vis spectrometry are excluded. On top of that, we are told that it provides even more detail than a NMRS - a tall barometer indeed!

The spectroscopic technique that fulfils these requirements best is **x-ray crystallography**. Searching online gives various sources with a compilation of Nobel Prizes awarded for work in X-ray crystallography (e.g. this open-source article, https://pubs.acs.org/doi/10.1021/ed500343x or the Wikipedia page https://en.wikipedia.org/wiki/X-ray_crystallography#Nobel_Prizes_involving_X-ray_crystallography). The process becomes a bit more tedious here, but also straightforward as it is just a matter of verifying the birth and death date to arrive at the identity of Max von Laue.

The identity of the second individual is much easier to arrive at, for example, by simply searching “what experiment involved bombarding Hg atoms with electrons and confirmed quantisation of energy” in ChatGPT, the **Franck-Hertz experiment** is given. Which of the two individuals, James Franck or Gustav Hertz, are we interested in?

Again we can use AI resources e.g. by searching “What report recommended against using atomic weapons in war?” - the answer is the **Franck report**, which lends its name from James Franck, who spearheaded the initiative.

These two scientists are connected by the acid **aqua regia**. During the Nazi occupation, they sent their Nobel Prizes to George de Hevesy for protection, who promptly dissolved it in aqua regia to disguise it as a simple shelf chemical. Aqua regia literally means “regal water”, and is most notable for its ability to dissolve gold.

Part C: Noble metals

The first member is Rh, which indeed is often used in carbene insertion reactions. The synthesis shown is taken from the White synthesis of morphine. In the Takasago menthol synthesis, it appears in a Noyori hydrogenation reaction, where it appears as a BINAP complex to enable the asymmetric step.

The second member is Pt, as cisplatin, $PtCl_2(NH_3)_2$ has been in use as an anticancer agent since 1978.

The third member is Os. OsO_4 is well-known as a reagent for Upjohn dihydroxylation, and when used with $NaIO_4$, it cleaves alkenes via the Lemieux-Johnson oxidation.

Element 9: Se

Part A: They are all smelly!

The first molecule is H_2S, which has been described to have the smell of rotten eggs.. A predicated VSEPR model of 107.5 degrees suggests a tetrahedral electron-pair geometry / pseudostructure, and that this is a divalent group 16 element. That it is involved in the Claus process, as well as its true geometry, suggests H_2S.

The second molecule is putrescine, $H_2N(CH_2)_3NH_2$, which smells like rotten meat/fish. The existence of ^{15}N NMR peaks, along with an even-numbered molecular mass, tells us there is an even number of N. If there were to be 4 N atoms, there is not quite enough mass left over for 4 C atoms, so it must have 2 N atoms. This gives us the molecular formula $C_4H_{12}N_2$. The 3.04 ppm signal in the ^{1}H NMR must be the amine protons, so we know there are two equivalent primary amines. The triplet splitting gives us two -CH_2NH_2 moieties, and balance has to be fulfilled by a connecting -CH_2CH_2- chain.

The third molecule is skatole, which is responsible for the smell of faeces. The reaction shown is none other than the venerable Fischer Indole Synthesis.

Part B: Jacob Berzelius

1. This natural product is, at its core, a polypeptide with the side chains forming additional complicated ring systems. The building block of a polypeptide is an amino acid, which is the monomer of proteins.
2. They are all polymers. DNA is a polymer of nucleoside triphosphates, which condense via formation of a phosphodiester backbone. The plastic container is usually made of polypropylene, a polymer of (you guessed it) propylene. The strange squiggly structure is human haemoglobin - this is a common representation of enzymes that most biologists will be familiar with. Enzymes are polymers of amino acids.
3. Proline is a catalyst here, as it is regenerated in the final step (although it is not shown) chemically unaltered and also serves to accelerate the first step by the formation of an enamine. This is one example of asymmetric organocatalysis, for which the 2022 Nobel Prize was awarded to List and Sharpless.

The man who introduced all of these terms was Jacob Berzelius, a 19th century Swedish chemist and a contemporary of other mighty figures like Robert Boyle. He was credited with discovering both cerium and selenium.

Part C: Ru, Os, I or Se

The oxidation steps, and the non-organic elements are:

DMDO	-
TPAP, NMO	Ru
OsO_4	Os
IBX	I
$(PhSeO)_2O$, KO^tBu	Se

Problem prepared by: Lin Bohan

Solution:

79

A summary of the answers for each element:

#	Element	Atomic #	Part A	Part B	Part C
1	H	**1**	Wilkinson's catalyst, [$Rh(PPh_3)_3Cl$]	Omeprazole	They all exhibit Jahn-Teller distortion
2	O	**8**	8	CeF_4 (8:2 coordination)	D_8h
3	Cs	**55**	Ionic radius > 1.63 Å	The element is coloured (Au, Cu)	^{110}I, ^{114}Cs, ^{118}La, ^{122}Pr or ^{126}Pm
4	He	**2**	H or He		$?@C_{60}$
5	Sc	**21**	UI	CAN	DMS
6	B	**5**	-OTMS	-CHO	-C≡CH
7	Al	**13**	Zeolite	Trichloride	DIBAL-H
8	Au	**79**	Mo, Au or Sb	Aqua regia	Noble metals
9	Se	**34**	H_2S, putrescine, skatole	Jacob Berzelius	Ru, Os, I, Se

When their atomic numbers are arranged in increasing order: 1,2,5,8,13,21,34,55,79

This is awfully close to the fibonacci sequence: 1,1,2,3,5,8,13,21,34,55,89,... the only element that doesn't follow this order is Au, with atomic number 79!

By the way, the "Old Worm" in the title refers to the Worm God, Leto Atreides II from Dune, who spent 4 millenia (hence "eons") building the Golden Path to ensure humankind's survival - a small easter egg! Wonder if anyone might have guessed it?

Element 1: H

Taking every part into account, we may notice a common intersection point is the element hydrogen:

1. The Wilkinson's catalyst catalyses hydrogenation of olefins
2. Omeprazole works by inhibiting proton pumps
3. Edward Teller is known for developing the hydrogen bomb

Part A: Wilkinson's catalyst, [Rh(PPh$_3$)$_3$Cl]

A starting point can be to realise that in the stoichiometry given, C,D and E seem to be awfully convenient multiples of three, so we might guess that one of the components is a ligand, $CD_{15}E_{18}$. Again we observe that D and E are multiples of three, which might suggest that the ligand has a form $C(D_5E_6)$, which corresponds quite well to the triphenylphosphine ligand, $P(C_6H_5)_3$.

This is further corroborated by the fact that there are peaks in the ^{31}P NMR spectrum, strongly suggesting the presence of phosphorus-containing ligands. We now know that this is a tetracoordinate complex. The fact that there are two different peaks in the ^{31}P NMR spectrum, suggests a square planar complex. Each peak is split into a double by $^{1}J_{Rh\text{-}P}$ coupling. The peaks of the P *trans* to the last ligand B are split further into triplets due to coupling to the other two P. The peaks of the two P *cis* to B are split further into doublets due to coupling to the last P.

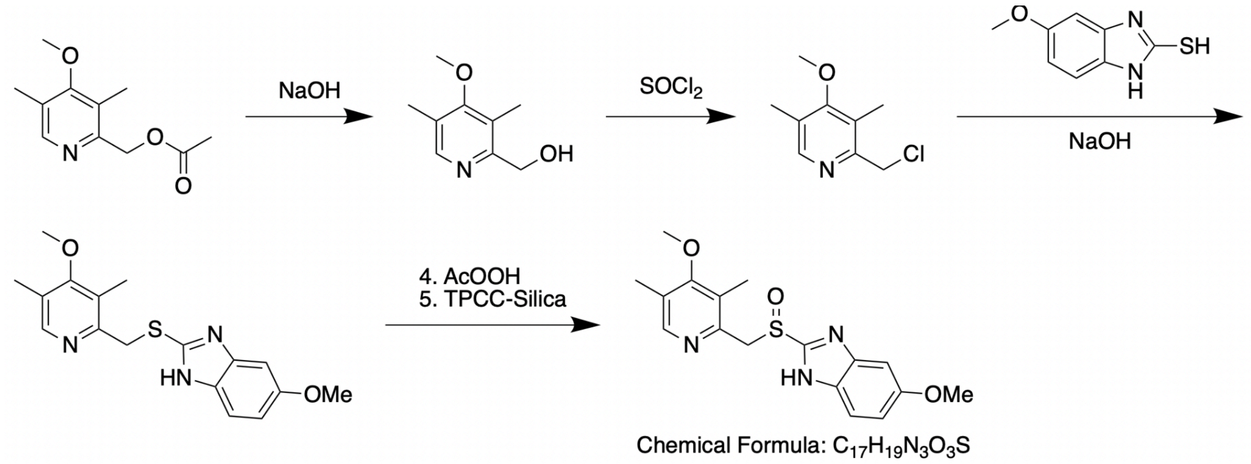
We also know that the last ligand is a single element. There is a limited range of such ligands, and O^{2-}, N^{3-} and halides are by far the most common. For each case, we can then deduce the group number of the metal:

Charge on ligand	Group number of metal	Possible metals
-1	16 - 3(2) - 2 + 1 = 9	Co, Rh, Ir
-2	16 - 3(2) - 4 + 2 = 8	Fe, Ru, Os
-3	16 - 3(2) - 6 + 3 = 7	Mn, Tc, Re

The square planar geometry strongly suggests a d^8 configuration, which would only be attainable in the first case, where the ligand is a halide. Since it is a famous catalyst, one may guess at Wilkinson's catalyst, named after Sir Geoffrey Wilkinson. This was a pioneering homogeneous catalyst and was used in the catalytic hydrogenation of alkenes.

Part B: Omeprazole

The synthetic transformations are shown:



This is a medication used to treat indigestion and heartburn, and it belongs to a broad class of drugs called proton pump inhibitors (PPIs). It works by blocking the action of the proton pumps in our cells, hence regulating the uptake of H^+ ions.

Part C: They all exhibit Jahn-Teller distortion

It takes some guesswork to start, but one may start by deducing some of the basic properties of the complex, such as the d^n configuration of the metal:

$[Cu(OH_2)_6]^{2+}$	$[Re(F)_6]^{3-}$	$[Cr(NH_3)_5(OH_2)]^{2+}$
High-spin	High-spin	High-spin
d^9	d^4	d^4

An astute student will realise these are the configurations for which Jahn-Teller distortions are the most readily apparent. The question prompts us that we're looking for the identity of a scientist, so why not take a look at the individuals that this phenomenon is named after?

1. **Hermann Arthur Jahn** was a British scientist of German descent, so he doesn't quite fit the description of a "martyred American scientist"

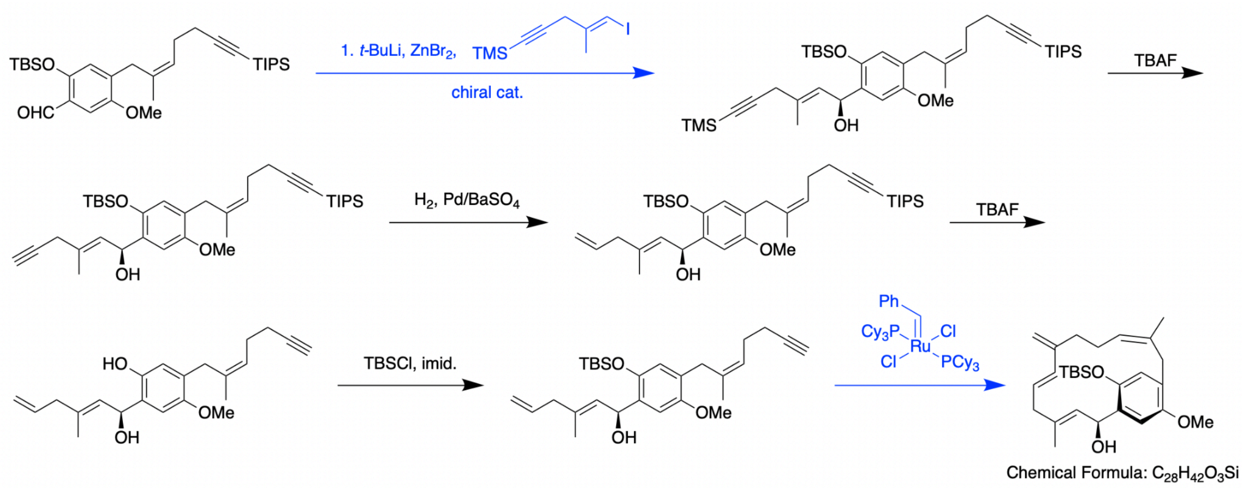
2. **Edward Teller,** on the other hand, was a Hungarian-born American scientist, as I am sure those who have watched *Oppenheimer* will be aware of. And he was indeed *martyred* for his relentless pursuit of the hydrogen bomb - he gives his name to the Teller-Ulam design upon which the pioneering thermonuclear weapons were built.

Element 2: O

The recurring theme of all 3 parts is the number 8, which is the atomic number of oxygen.

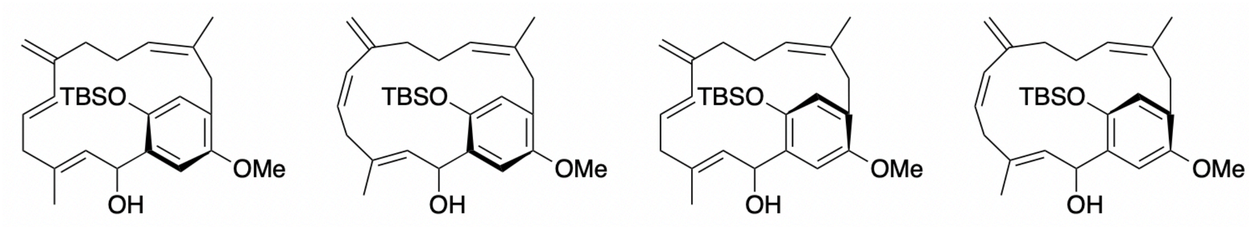
Part A: 8 possible stereoisomers

This is taken from the Shair synthesis of Longithorone A in 2002, and the actual synthetic pathway is shown. You will note that in the first step, a chiral catalyst was used in reality, but it was removed in the synthetic scheme provided in the question to remove any potential ambiguity.



The steps where stereoisomers could be generated are marked in blue and discussed:

1. **Nucleophilic addition to the aldehyde.** In the absence of chiral control (and indeed also even in the presence thereof, if the chiral element doesn't impart sufficient stereo-differentiation), two enantiomers at the secondary alcohol can be formed as attack is equally likely from both sides of the planar carbonyl carbon.
2. **Enyne metathesis.** This step can give rise to a whopping 4 stereoisomers - 2 due to the cis/trans conformation of the newly-formed internal alkene, and 2 due to atropisomeric products with respect to the aromatic ring. They are drawn explicitly below. In the actual synthesis this step, and a subsequent TBAF deprotection, were achieved in a very respectable 42% combined yield.



The atropisomerism is somewhat harder to visualise, but imagine holding the aromatic ring stationary in space, and then closing the macrocycle either "above" or "below" the ring. Overall, as there are 3 new stereoelements in the final molecule, we can expect $2^3 = 8$ possible theoretical isomers.

Some additional notes about the deprotection / reprotection steps:

1. The choice of silyl group removed in the first deprotection is dictated by steric bulk, with TMS $<$ TBS $\approx$ TIPS. Hence we should expect the acetylenic TMS group to be removed.
2. The regioselectivity of the reprotection depends primarily on which position is the most acidic. The pKa of a phenol is about 10, while the pKa of a terminal alkyne and an alcohol are about 25 and 20, respectively, making them much less acidic.

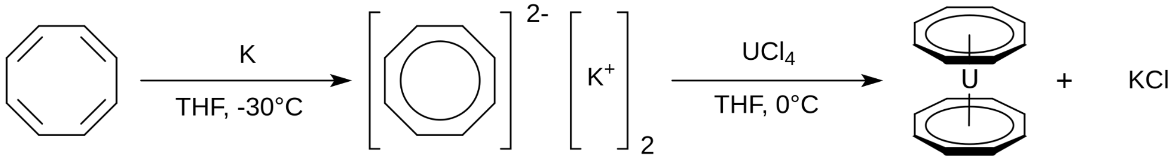
Part B: CeF_4, with 8:2 coordination

Lanthanides generally exhibit a +3 charge, so an "unusual" stoichiometry could mean either a +2 or a +4 charge. Given that it's used as a single-electron oxidant, we can deduce that it is a Ln(IV) species, as they would be readily reduced back to Ln(III). The principal lanthanide that exhibits this behaviour is Ce, with Pr and Nd also exhibiting such behaviour but to a much more limited extent. More unambiguously, Ce is the only lanthanide that forms a tetrahalide.

The CeF_4 species consists of vertex-sharing antiprisms (https://www.chemtube3d.com/ss-cef4/ for a 3D model), hence has an 8-coordinate Ce and 2-coordinate F.

Part C: D_8h symmetry

This is the synthesis of thorocene, a close relative to the more well-known uranocene, for whom the entirely analogous preparation is shown:



[6]

The K is an oxidant, which transfers 2 electrons (1 per K) to form the aromatic COT^{2-} ligand (there are 10 pi electrons, hence fulfilling Huckel's 4n+2 rule). They then undergo a ligand exchange with U/Th to form the uranocene/thorocene complex.

This is a linear complex, with the COT^{2-} ligands parallel to each other and with the vertices directly in line. This is a result of the interactions with the f-orbitals on the central metal, where this configuration allows for maximum orbital overlap. Indeed, this is one of the few examples of true phi-bonding.

---

[6] By Cmoarl - Own work, Public Domain, https://commons.wikimedia.org/w/index.php?curid=37755151

Element 3: Cs

Part A: Ionic radius > 1.63 Å

In a bcc unit cell, the cationic radius / anion radius ratio should not be smaller than 0.732, or an octahedral coordination would occur instead of a cubic coordination. Further using the Goldschmidt radius to adjust for the different coordination environments, we deduce that the ionic radius of the cation is not smaller than 0.732 x 2.2 x 0.97/0.96 = 1.63 Å in an 8-coordinate environment.

Furthermore, having a CsCl structure means it is single charged. Using Shannon's ionic radii (http://abulafia.mt.ic.ac.uk/shannon/radius.php) the possible identities are narrowed down to Rb^+, Cs^+, Fr^+, Tl^+.

Part B: The element is coloured in its elemental form

Element 1 is Au: the table lists the colours of gold nanoparticles (AuNPs) of different diameters. AuNPs have a variety of uses from catalysis to medical imaging and specific drug delivery, and is a hot area of research right now. Indeed, Au is perhaps the most famous coloured element - since gold is… gold coloured.

Element 2 is Cu: The first reaction is the Ullmann biaryl ether coupling, which uses Cu(0) or Cu(I) species as catalysts. The scheme is taken from the Nicolaou synthesis of vancomycin. The second reaction is a conjugate addition by use of a Gilman reagent, Me_2CuLi, which also contains Cu. There are other possible reagents but this is the only one commonly taught in undergraduate classes. Cu itself has a reddish-brown colour, which has been exploited since antiquity.

There are few other elements which are coloured. Among the metals, Cs has a slight yellowish lustre, and Os is ever so slightly blue. Among the non-metals, there are C (although, as an artist, I insist that black is not a colour), P, S, liquid O_2 and the halides.

Part C: ^{110}I, ^{114}Cs, ^{118}La, ^{122}Pr or ^{126}Pm

An alpha-decay is merely the loss of a helium-4 (alpha particle) from the isotope, so we need to work backwards by adding the proton number in steps of 2 and the nucleon number in steps of 4 (although for the purposes of the question, we don't even need the nucleon number). Given a maximum of 5 possible alpha-decays, this gives us 5 possible elements.

Element 4: He

Part A: H or He

This is a first-order reaction, which, combined with the lack of reagents (along with the title of Part A), might suggest that this is a radioactive decay. To obtain the half-life:

$$(\frac{1}{2})^n = 1 - 0.99 = 0.01$$
$$n = \frac{ln(0.01)}{ln(1/2)} = 6.6439$$
$$n \times t_{1/2} = 81.9\text{ yr}$$
$$t_{1/2} = \frac{81.9}{6.6439} = 12.3\text{ yr}$$

Using a database like Wikipedia (https://en.wikipedia.org/wiki/List_of_radioactive_nuclides_by_half-life) we can see that this corresponds to the half-life of ^{3}H, which beta decays to ^{3}He.

Part B: 141 pm

We want to use the Lennard-Jones potential to find the equilibrium separation. To do that, we have to find the global minima, so we begin by finding $\frac{dU}{dr} = 0$:

$$\epsilon(\sigma^{12}(\frac{-12}{r^{13}}) - \sigma^6(\frac{-6}{r^7})) = 0$$
$$6\epsilon\frac{\sigma^6}{r^7}(-2(\frac{\sigma}{r})^6 + 1) = 0$$
$$(\frac{\sigma}{r})^6 = 1/2$$
$$r = 2^{1/6}\sigma$$

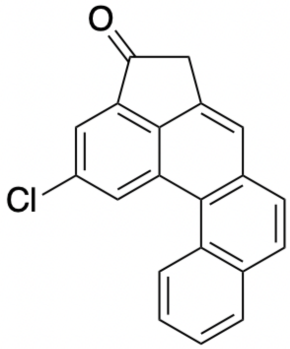
This would give twice of the VdW radius, so we have to divide by two then substitute the values:

$$r = 2^{-5/6}(252)\text{ pm} = 141\text{ pm}$$

Some possible elements (https://en.wikipedia.org/wiki/Van_der_Waals_radius) are He (140 pm), F (147 pm), Cu (140 pm) and Zn (139 pm).

Part 3: ?@C_{60}

Let us start with the second component. In the first step of the synthesis, a Lewis acid is added which likely interacts with the acyl chloride. In conjunction with the presence of phenyl rings, we deduce that an S_EAr reaction has occurred, producing:



The second step is a bit mysterious, and our only clue is that the product has $M_r = 852$. So we might try calculating the M_r of the intermediate at hand - which turns out to be 302. One might notice $302 * 3 = 906 = 852 + 3 * 18$ - this suggests a trimerisation reaction with loss of 3 molecules of water. This fits a triple aldol condensation to form a central benzene ring.

The result of the final step cannot be predicted *a priori* but given the plethora of phenyl rings, the presence of 5-membered rings and the total of 60 carbons within the structure, one could guess buckminsterfullerene to be the product. Indeed, this is Scott synthesis of buckminsterfullerene (https://synarchive.com/syn/100).

Fullerenes have a versatile supramolecular chemistry, generally classified into types where another chemical species encloses the fullerene (exohedral fullerenes), or when the fullerene itself encloses a chemical species (endohedral fullerenes). The fact that the first component comprises a single element strongly suggests an endohedral fullerene. As it is synthesised by high-pressure methods, this suggests a non-metallo endohedral fullerene as metallo-endohedral fullerenes are generally made in an arc reactor or via laser evaporation. H_2@C_{60} and Ng@C_{60} stand out as possible structures, where Ng = noble gas.

Element 5: Sc

The letters collected are u, i (part A), c, a, n (part B) and d, m, s (part C), which together give scandium.

Part A: UI_3

Let the atomic mass of the element X be M_X and element Y be M_Y.

Then we can form the following two equations:

$$\frac{3M_X}{3M_X+M_Y} = 0.617$$

$$4M_X + M_Y = 746$$

Rearranging the first equation, we get:

$$\frac{3M_X+M_Y}{3M_X} = 1 + \frac{1}{3}\left(\frac{M_Y}{M_X}\right) = \frac{1}{0.617}$$

$$M_Y = 1.86M_X$$

Substituting into the second equation:

$$5.86M_X = 746$$

$$M_Y = 127$$

$$M_X = 237$$

Which matches to iodine (M_r = 126.9) and uranium (M_r = 238.0). Given that we were working with 3s.f., the value of M_X is within the plausible error margins.

Part B: CAN

First, we find the identity of the cation. We need to use the Henderson-Hasselbalch equation to find its pKa:

$$pH = pKa + log\frac{[A-]}{[HA]}$$

$$pKa = pH - log\frac{[A-]}{[HA]}$$

$$= 10.0 - log\frac{[NaOH]}{[HA]_{initial}-[NaOH]}$$

$$= 10.0 - log\frac{0.1\times\frac{339.6}{22.99+16.00+1.008}}{1-0.1\times\frac{339.6}{22.99+16.00+1.008}}$$

$$= 9.25$$

A search such as "what acid has pKa of 9.25", or scouring through a comprehensive pKa table, will return NH_4^+ as the answer.

As the nitrate acts as a bidentate ligand, the coordination number of the central atom is 12 - an anomalously large number that points to its possible identity as a lanthanide! Coupled with the fact that this is used as an oxidising agent, ceric ammonium nitrate, CAN, is the answer we seek.

Part C: DMS

At the heart of solving this question lies the Clausius-Clapeyron equation, which tells us the temperature dependence of the vapour pressure of a particular chemical:

$$ln\frac{P2}{P1} =- \frac{\Delta_{vap}H}{R}(\frac{1}{T2} - \frac{1}{T1})$$

At boiling temperature, we have P = 1 atm = 101325 Pa. Sub T1 = 293.15 K, P1 = 55.6 Pa, T2 = b.p, P2 = 101325 Pa and $\Delta_{vap}H$ = 50.0 kJ mol^{-1}:

$$ln\frac{101325}{55.6} =- \frac{50.0(1000)}{8.3145}(\frac{1}{b.p} - \frac{1}{293.15})$$

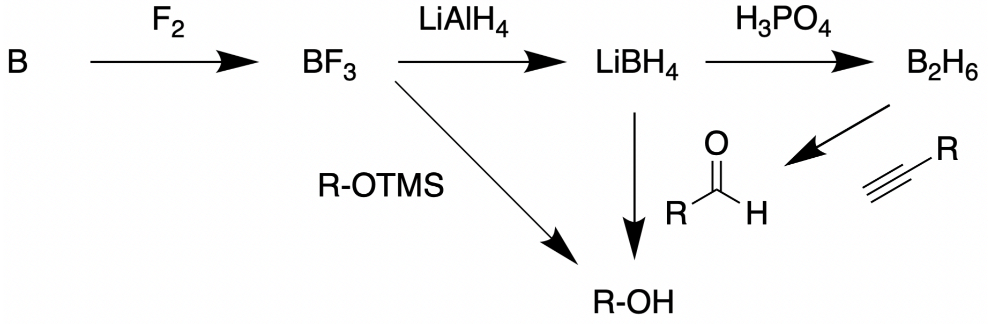
B.p = 462.38 K = 189 °C

Using a database (e.g. https://organicchemistrydata.org/solvents/) the solvent is found to be DMSO, which is indeed made from DMS industrially by reaction with O_2 or NO_2.

Element 6: B

To complete the table, the easiest place to start, perhaps, is Y → R-OH. The commonly encountered reagents to effect this transformation are $[AlH_4]^-$ and $[BH_4]^-$, giving B or Al as the possible identity of the element. H_3PO_4 serves to generate AlH_3 or BH_3, and both could theoretically undergo 1,2 addition onto an alkyne (via either hydroalumination or hydroboration) and then be oxidised to an enol which tautomerizes to an aldehyde, so Z → 2 doesn't quite help us decide.

However, we note that A is likely the trifluoride, and that BF_3 are known reagents for silyl ether deprotection[7]. Hence, the completed scheme is:



Part A: -OTMS

The giveaway clue is the appearance of the 0.2 ppm singlet. No conventional organic functional groups are shielded enough to be so upfield, but one might note that the commonly used standard, tetramethylsilane, has a very similar chemical shift (0.0 ppm by definition). So perhaps a silyl group is at play? 9 equivalent protons suggest a trimethylsilyl group, which is often used to protect alcohols. This is further corroborated by the increase of 72 g mol^{-1}. Indeed, now the disappearance of the signal at 3.4 ppm can be explained to be the loss of an alcoholic proton.

Part B: -CHO

The procedure described is in fact the preparation of Fehling's solution, and indeed the positive test of a reddish brown ppt of Cu_2O is observed, which points at an aldehyde functional group. The Cu_2O can be further oxidised to CuO, which is a black solid.

---

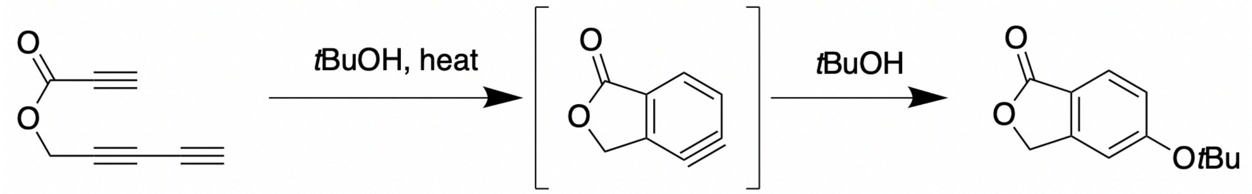
[7] *Journal of the Chemical Society, Chemical Communications,* no. 24, Jan. 1993, pp. 1823–25.

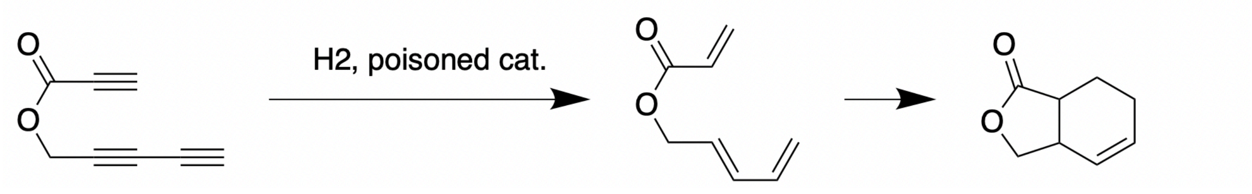
Part C: -C≡C-H

We may begin by comparing how the product has changed, and we observe an increase in molecular formula by $C_4H_{10}O$, which is incidentally the molecular formula of *t*BuOH, so we may be reasonably confident that a net addition of a *t*BuOH has resulted. However, this is not a condensation reaction or a substitution, as we would usually expect it to react - strange!

To make further progress we might turn to the second experiment. This time we observe an increase of 6 hydrogens, which likely occurs as a result of the aforementioned addition of 3 equivalents of H_2 and not the subsequent reaction. This would point at a pericyclic reaction, as they are one of few reaction types that do not change the molecular formula. We observe that, given it is pericyclic, we may reasonably hypothesise the presence of alkene functionalities, and that they have likely been reduced from alkynes via a poisoned catalyst.

Hence, this strongly suggests the initial product had three alkynes - a deduction till this point is already sufficient to solve this part, but for the interested student, the first reaction is a hexadehydro-Diels-Alder (HDDA), while the second is simply a DA.



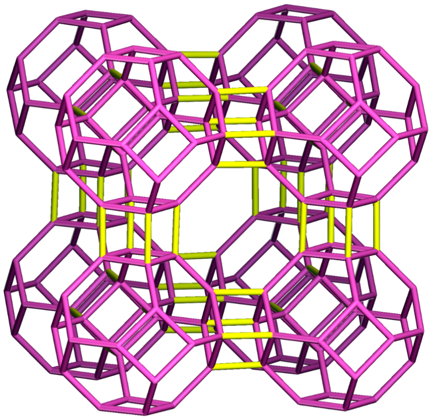


Element 7: Al

From part B, we know that this is likely to be a group 3, group 13, or f block element. From part A, the constituent elements are Al, Si, O and either a metal or H. From part C, the elements are Al, C and H. Hence, the common intersection point of all three parts is aluminium, Al.

Part A: Zeolites

When the shapes are pieced together, you get the LTA framework of zeolites, which are aluminosilicates. Each of the three shapes represents one of the holes that occur in this structure. They are often used as molecular sieves in organic synthesis, for example for the uptake of protons.



[8]

[9]

Part B: ACl_3

We need to use the equation for the entropy change of a system on heating:

$$\Delta S = \int_{T1}^{T2} nC_{p,m} dT$$

As C_p is assumed to be independent on temperature, this is simplified to:

---

[8] By Nao1958 - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=75387204

[9] By Smokefoot - Own work, CC BY-SA 4.0, https://commons.wikimedia.org/w/index.php?curid=44351968

$$\Delta S = nC_{p,m} ln\frac{T2}{T1}$$

For multiple species present:

$$\Delta S = ln\frac{T2}{T1}\sum_{i=1}^{N} n_i C_{p,m,i}$$

In this case, let the unknown chloride formed be ACl_n. Thus:

$$23.5 = (25 + 31\frac{n}{2})ln\frac{239}{172}$$

n = 3

Part C: DIBAL-H

Carboxylic acids, when reacted with BH_3 in THF, can be reduced to alcohols, so we know that our mystery reagent is capable of the same. It is, however, also capable of reducing it to only aldehydes, and the most prominent example of such a reagent is DIBAL-H, which does indeed also effect the reduction of nitriles to aldehydes.

Element 8: Au

Part A: Mo, Au, Sb

Rather than take a purely iterative approach through all of the functional groups in existence (a brobdingnagian task), we can use the synthetic scheme to narrow the possibilities. The functional groups that are involved in a transformation are:

Step	FGs
1	Aldehyde, sulfone, alkene
2	Ester, carboxylic acid
3	Carboxylic acid, alcohol, ester
4	Alkyne
5	Alkyne, allene

And running an iterative check on each of these functionalities:

	OsO_4, NMO	NCS, DMS; Et_3N*	BH_3, THF; H_2O_2, NaOH	Hoveyda-Grubbs catalyst
Aldehyde	🟥	🟥	🟥	🟥
Sulfone	🟥	🟥	🟥	🟥
Alkene	🟩	🟥	🟥	🟥
Ester	🟥	🟥	🟥	🟥
Carboxylic acid	🟥	🟥	🟥	🟥
Alcohol	🟥	🟩	🟥	🟥
Alkyne	🟥	🟥	🟩	🟩
Allene	🟩	🟥	🟩	🟩

* This is the Corey-Kim oxidation, which is an alternative to the Swern oxidation.

The only FG that matches the requirements is the alkyne, which, in the synthetic scheme, reacts in two steps: The alkyne metathesis, and the alkyne-allene isomerisation.

Part B: Aqua regia

To begin, the condition that this spectroscopic technique can differentiate between enantiomers greatly limits the possible choices, since more routinely used methods like mass and UV-Vis spectrometry are excluded. On top of that, we are told that it provides even more detail than a NMRS - a tall barometer indeed!

The spectroscopic technique that fulfils these requirements best is **x-ray crystallography**. Searching online gives various sources with a compilation of Nobel Prizes awarded for work in X-ray crystallography (e.g. this open-source article, https://pubs.acs.org/doi/10.1021/ed500343x or the Wikipedia page https://en.wikipedia.org/wiki/X-ray_crystallography#Nobel_Prizes_involving_X-ray_crystallography). The process becomes a bit more tedious here, but also straightforward as it is just a matter of verifying the birth and death date to arrive at the identity of Max von Laue.

The identity of the second individual is much easier to arrive at, for example, by simply searching "what experiment involved bombarding Hg atoms with electrons and confirmed quantisation of energy" in ChatGPT, the **Franck-Hertz experiment** is given. Which of the two individuals, James Franck or Gustav Hertz, are we interested in?

Again we can use AI resources e.g. by searching "What report recommended against using atomic weapons in war?" - the answer is the **Franck report**, which lends its name from James Franck, who spearheaded the initiative.

These two scientists are connected by the acid **aqua regia**. During the Nazi occupation, they sent their Nobel Prizes to George de Hevesy for protection, who promptly dissolved it in aqua regia to disguise it as a simple shelf chemical. Aqua regia literally means "regal water", and is most notable for its ability to dissolve gold.

Part C: Noble metals

The first member is Rh, which indeed is often used in carbene insertion reactions. The synthesis shown is taken from the White synthesis of morphine. In the Takasago menthol synthesis, it appears in a Noyori hydrogenation reaction, where it appears as a BINAP complex to enable the asymmetric step.

The second member is Pt, as cisplatin, $PtCl_2(NH_3)_2$ has been in use as an anticancer agent since 1978.

The third member is Os. OsO_4 is well-known as a reagent for Upjohn dihydroxylation, and when used with $NaIO_4$, it cleaves alkenes via the Lemieux-Johnson oxidation.

Element 9: Se

Part A: They are all smelly!

The first molecule is H_2S, which has been described to have the smell of rotten eggs. A predicated VSEPR model of 107.5 degrees suggests a tetrahedral electron-pair geometry / pseudostructure, and that this is a divalent group 16 element. That it is involved in the Claus process, as well as its true geometry, suggests H_2S.

The second molecule is putrescine, $H_2N(CH_2)_4NH_2$, which smells like rotten meat/fish. The existence of ^{15}N NMR peaks, along with an even-numbered molecular mass, tells us there is an even number of N. If there were to be 4 N atoms, there is not quite enough mass left over for 4 C atoms, so it must have 2 N atoms. This gives us the molecular formula $C_4H_{12}N_2$. As the solvent is in water, no -NH or -OH peaks will appear, so the protons in the ^1H NMR must be C-H protons. The two chemical environments and the shifts suggest an aliphatic $-(CH_2)_4-$ chain connecting the $-NH_2$. See footnote for original NMR data.[10]

The third molecule is skatole, which is responsible for the smell of faeces. The reaction shown is none other than the venerable Fischer Indole Synthesis.

Part B: Jacob Berzelius

1. This natural product is, at its core, a polypeptide with the side chains forming additional complicated ring systems. The building block of a polypeptide is an amino acid, which is the monomer of proteins.
2. They are all polymers. DNA is a polymer of nucleoside triphosphates, which condense via formation of a phosphodiester backbone. The plastic container is usually made of polypropylene, a polymer of (you guessed it) propylene. The strange squiggly structure is human haemoglobin - this is a common representation of enzymes that most biologists will be familiar with. Enzymes are polymers of amino acids.
3. Proline is a catalyst here, as it is regenerated in the final step (although it is not shown) chemically unaltered and also serves to accelerate the first step by the formation of an enamine. This is one example of asymmetric organocatalysis, for which the 2022 Nobel Prize was awarded to List and Sharpless.

---

[10] *Chemical Physics Letters*, vol. 466, no. 4, Dec. 2008, pp. 219–22.

The man who introduced all of these terms was Jacob Berzelius, a 19th century Swedish chemist and a contemporary of other mighty figures like Robert Boyle. He was credited with discovering both cerium and selenium.

Part C: Ru, Os, I or Se

The oxidation steps, and the non-organic elements are:

DMDO	-
TPAP, NMO	Ru
OsO_4	Os
IBX	I
$(PhSeO)_2O$, KO^tBu	Se