

Year 2, Organic Chemistry, Chapter 16:

The basics of Organic Synthesis

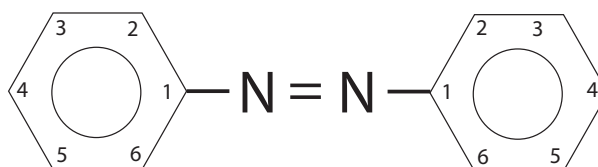
as exemplified by Azo Reactions

(Azo compounds are compounds bearing the functional group $R-N=N-R'$, in which R and R' can be either aryl or alkyl.)

NB For you, everything in this Chapter will (at 'A' Level) be just theory because in English schools you will NOT be allowed to go anywhere near Benzene. Not only is Benzene toxic and carcinogenic – but if you do not know what you are doing you could blow up your lab in one or more of your experiments and kill all your classmates.

- Most 'A' Level examining boards require you to know something about Organic Synthesis, and right at the end of this Section on Organic Chemistry I will talk about Organic Synthesis. Some exam boards (such as AQA) **do** require you to have a basic knowledge of the reactions that I am going to talk about in this Chapter.
- However, since we have been examining the reactions of Benzene in some detail, let me use this opportunity to introduce you to the basics of “synthesis” i.e. **making something from something else**, or “How can I get to South Ken (Imperial) or Euston Square (UCL) or the Strand (King's) from Gerrards Cross?”
- Do you remember that I told you about stuff that was on the radio when I was shaving the other morning. Well here it is again: critical thinking/lateral thinking/**or in its most simple form, just using the brain that God gave you/the brain that you were born with.**
- The term “diazene” is used as a noun to describe the compound “ $HN=NH$ ”, and it is used adjectivally to describe any compound that contains the group $-N=N-$. The EU description of an ‘azo’ dye is one that contains one or more diazene “ $-N=N-$ ” species¹. **Diazenes** do not have to have Benzene rings attached to them, but here I am looking only at those compounds that do have Benzene rings attached to them. IUPAC defines azo compounds as derivatives of diazene wherein both hydrogens are substituted by *hydrocarbyl* groups, e.g. diazene ($HN=NH$), or diphenyldiazene $C_6H_5.N=N.C_6H_5$ which is now no longer called azobenzene. (NB “=” represents a double bond.)

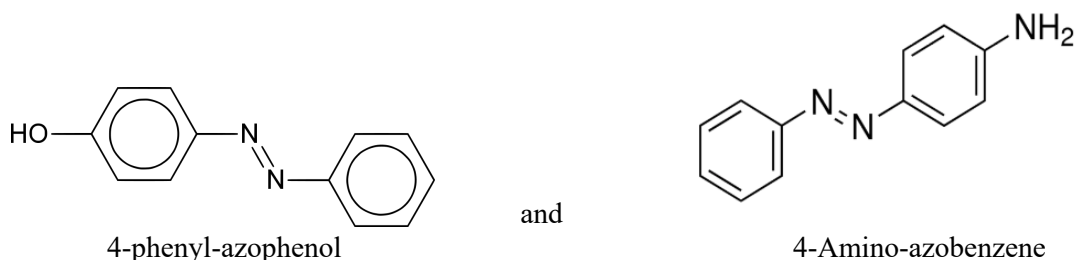
“Diphenyl” refers to the two “ $-C_6H_5$ ” species, and “diazene” refers to the two Nitrogen atoms i.e. the “ $-N=N-$ ” bit. Numbering should start at the C atom attached to the N atom (and should reflect the lowest numbering system possible).



$C_6H_5.N=N.C_6H_5$ is **Diphenyldiazene**

¹ “Azote” from the French name for Nitrogen.

- The IUPAC naming rules run to 400 pages and every chemist seems to interpret the rules in his/her own way. At its simplest, to name a diazo compound, one lot of C_6H_5- will (where required) be termed R and the other one be called R'. You start the numbering from the C atom linked to the N atom. I do not like the name, but the compound on the right below is called 4-Amino-azobenzene/ 4-Aminoazobenzene. It is also known as Aniline Yellow. The compound on the left is called 4-phenylazophenol or 'p' for 'para' "*p*-(phenylazo)phenol". (NB The term "phenyl" stands for the species C_6H_5- .)
- Azo derivatives are best summed up in the two little representations of just two of the hundreds if not even thousands of Azo compounds that there are viz.



- In fact, I believe that azo species are better referred to as "**di-azo**" compounds (because there are two Nitrogen atoms involved).
- What we are considering here are mainly "dyes" – and, in the lab, you encounter them all the time in the form of the indicators that you use in titration. The one below is methyl orange, and in acidic conditions it is red and in an alkali environment it is yellow.
- If an acid were added to the left hand species, can you see how an H^+ would join the left hand species to form the right hand species? For example, if HNO_3 had been added, the positively charged sodium cation would have bonded with the NO_3^- anion to form $NaNO_3$, while the H^+ cation would have bonded to the diazo species **via the lone pair on the N atom**. If you did not understand that, then please read the statement again and again and again until you do understand it. (After all, that is only first year stuff.)

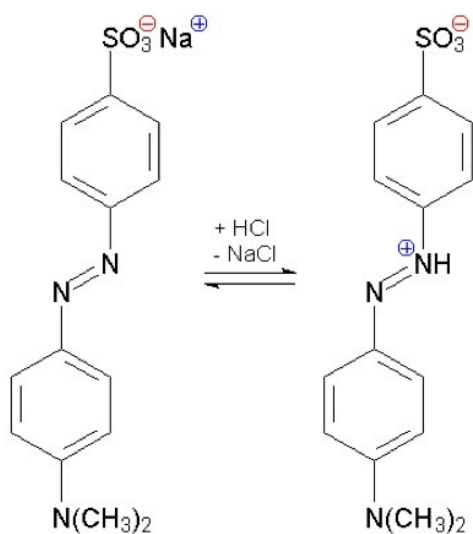
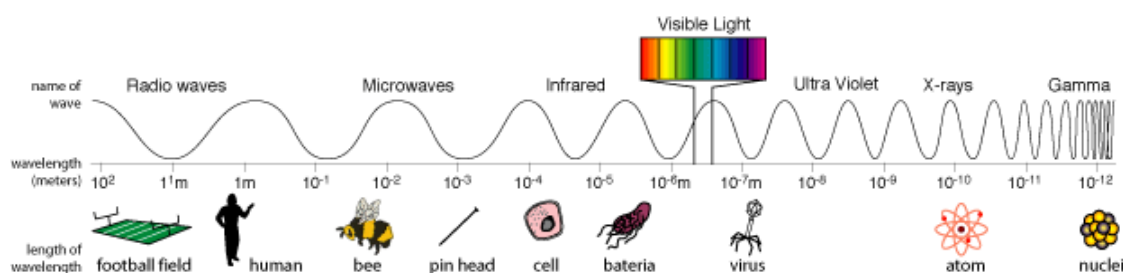
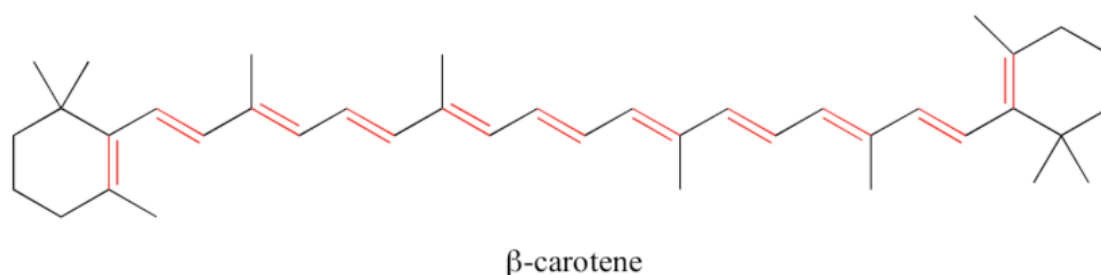


Fig.8 Methyl orange - an azo dye and acid-base indicator.

- When sunlight falls on an object, the object then absorbs certain wavelengths of light and reflects the remaining wavelengths – therefore the ‘colour’ of an object that is perceived by the brain of a human being is determined by the *reflected* wavelengths of light. However, if the sunlight is shining through the object, then the wavelengths that are perceived are determined by *transmittance* rather than by reflection – but whatever the technical situation involved, **objects absorb the wavelengths of light that are appropriate to themselves** and reflect or transmit the remaining wavelengths.
- However, it is sometimes the case that the energy that is absorbed by an object will cause changes in the object, and during the course of those changes photons of energy are emitted, and since energy and wavelength are correlated in electro-magnetic radiation, then this energy could also be perceived by human beings as “colour” provided that the wavelength falls within the ‘visible spectrum’ of electro-magnetic radiation (emr).²
- Because of evolutionary biological changes, different species “see” different wavelengths of emr. Human beings “see” only those parts of emr that fall in the category “visible to human beings” – but the human visible spectrum is just one minute fragment of the spectrum of all emr which ranges from long wavelength (low energy and thus harmless) radio waves to short wavelength (very high energy and thus harmful) gamma rays. NASA gives the following diagram

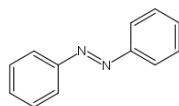


- In Chapter 4 we noted that conjugated compounds are best thought of as species that have a series of alternating double and single bonds, and that conjugated species are often highly coloured objects – and I showed you the skeletal structure of beta-carotene

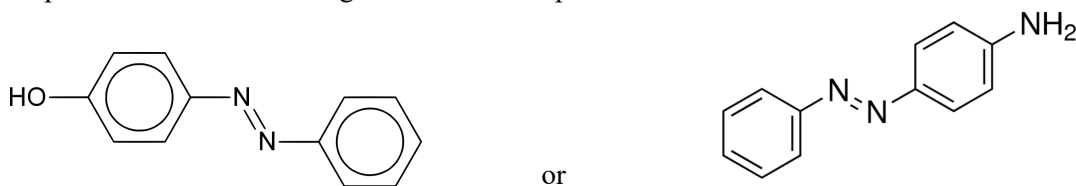


² Dr Helen (although, if you are reading this at some point of time in the future, she may by then well be Professor) Helen Czerski did an excellent series on “Colour” (and also other series) for BBC TV, and Prof Jim Al-Khalili has done numerous series for BBC TV and one of them was on electro-magnetic radiation. Besides being a competent physicist, Dr Czerski was also a gifted 1 and 3 metre springboard diver at Cambridge, and Prof Al-Khalili is an extremely gifted artist. [Interestingly, there are fewer gifted 1 and 3 metre springboard divers than there are people with PhDs.](#) (Diving is all to do with having the requisite spatial awareness.) There is thus no reason why **you** should not do other things besides developing your brain – and I would very much like you to do so. Instead of getting your parents to write a lovely fairy story for your UCAS Personal Statement, it would be much better if you actually *had done* something to distinguish yourself from other University applicants.

- Before we learnt how to extract crude oil from under the ground/sea/ice, i.e. prior to the 20th century, we human beings obtained nearly all our organic chemicals from doing things to coal tar, and (if you have the time) it is worth reading about the history of the dye “mauvine” (I presume that it was named after the colour mauve) that was formulated by the London chemist Sir William Henry Perkin. Sir William as an undergraduate (at what is now a part of Imperial College) was apparently experimenting with phenylamine/aniline to try to find a drug to combat malaria when he “discovered” mauvine. Sir William was not only an extremely competent chemist, but he obviously had a good brain for business because he immediately stopped his studies (much to the disappointment of his Prof) and set up a factory in Greenford (not far from where I grew up in Wembley) and thus he became both rich and famous.³
- Azo compounds viz. “azo dyes” (and two-thirds of all dyes are ‘azo’ compounds) are conjugated series and I am told that Azo compounds are today useful commercially because they are made at low temperatures and are water soluble. The chemistry of dyes had not even been born at the time that Sir William Perkin discovered the purple dye that he later called “aniline purple”, and he was totally unaware that the Benzene that he was obtaining from coal tar contained methylbenzene and that his production process was therefore being contaminated by methylphenylamines. At that time nobody even knew about the existence of methylbenzene and methylphenylamine, *let alone knew how to spell the names of such compounds*. Remember that this was all before Kekulé came up with his brilliant idea for the ring structure for Benzene! It is very easy to talk glibly about how rich Perkin became – but that results from an ignorance of the very considerable difficulties that Perkin experienced in order to make his production process a viable one.
- As a chemist interested in theory (more than in practicalities), it is the *derivation* of azo compounds from Benzene that fascinates me, and it is the knowledge of this that is required for the ‘A’ Level syllabus – so let us look at it now.
- Diazo compounds have the basic form



and the problem is to see how to get from C₆H₆ to species such as



- The solution is all part of what the exam boards call *Organic Synthesis*.

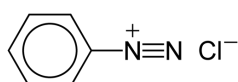
³ Being *rich* is of little importance, but ‘the dyes that Perkin subsequently produced were later used to stain previously invisible microbes and bacteria, thus allowing researchers to identify such bacilli as tuberculosis, cholera, and anthrax’. I tell you all this not because I want you to discover anything and become rich and famous, but because I want you to realise that it is important not to have tunnel vision and not to concentrate on *just* the task in hand (as poor Rosalind Franklin may have done and thereby missed the chance to be the discoverer of the double helix structure of DNA). A huge number of discoveries have been made by scientists purely by chance. However, “luck” is 99% sheer hard work and 1% being in the right place at the right time. If Perkin had not spent his boyhood studying extremely hard, he would not at the age of 18 have been struggling to find a drug to combat malaria – and thus would not have been in the right place at the right time when fate handed him “mauvine” on a (so to speak) petri dish. *Work hard*. That is how you have the best chance of having a happy and successful life. You may or you may not become rich in the process – but what does that matter compared to being happy and healthy.

- Almost by definition, if you look at the diagrams on page 4, you will immediately notice that an ideal starting point would be “C₆H₅.N=” because the compounds contain two such species, but the question in synthesis is “How do you get from C₆H₆” to the above?”
- The answer is (and don’t forget to memorise the reactions conditions involved in each transition)

Stage 1 Benzene (C₆H₆) —> Nitrobenzene (C₆H₅.NO₂) **using HNO₃ and 2H₂SO₄**

Stage 2 Nitrobenzene (C₆H₅.NO₂) —> Phenylamine (C₆H₅.NH₂) **using Tin and HCl**

Stage 3 Phenylamine (C₆H₅.NH₂) —> Benzenediazoniumchloride **using NaNO₂ and 2HCl**
(C₆H₅.N⁺ triple bond N) Cl⁻)



Stage 4 Now couple the C₆H₅.N⁺ triple bond N with whatever you need to get your end-product.

- In the ‘A’ Level exam, all that you need to do is to write down each of the above stages together with a reaction equation, and the Marking Scheme requires the markers to give you the maximum number of marks allotted to the question. You do **not** need to know any of the rest of this Chapter (but I would like you to know the Chemistry involved – stuff such as “could we therefore start with C₆H₆ and somehow stick an “-NH₂” species onto it in order to obtain phenylamine, C₆H₅.NH₂?”).

I believe that the following four slides come from (Knockhardy, in Ireland).

PHENOL

Structure

Preparation

phenol is an aromatic alcohol with formula C₆H₅OH
the OH group is attached directly to the benzene ring
it is an almost colourless crystalline solid

You cannot put an OH group directly onto a benzene ring by electrophilic substitution, so phenol has to be synthesised in a multi-stage process

Step 1 - Nitration of benzene

reagents	conc. nitric acid and conc. sulphuric acid (catalyst)
conditions	reflux at 55°C
equation	C ₆ H ₆ + HNO ₃ —> C ₆ H ₅ NO ₂ + H ₂ O
mechanism	electrophilic substitution

PHENOL

Structure

Preparation

phenol is an aromatic alcohol with formula C_6H_5OH
the OH group is attached directly to the benzene ring
it is an almost colourless crystalline solid

You cannot put an OH group directly onto a benzene ring by electrophilic substitution, so phenol has to be synthesised in a multi-stage process

Step 2 - Reduction of nitrobenzene

reagents	tin and conc. hydrochloric acid
conditions	reflux
equation	$C_6H_5NO_2 + 6 [H] \longrightarrow C_6H_5NH_2 + 2H_2O$
mechanism	reduction

There is a good video on this step by Frank Scullion at
<https://www.youtube.com/watch?v=62HL5vGcsos>

PHENOL

Structure

Preparation

phenol is an aromatic alcohol with formula C_6H_5OH
the OH group is attached directly to the benzene ring
it is an almost colourless crystalline solid

You cannot put an OH group directly onto a benzene ring by electrophilic substitution, so phenol has to be synthesised in a multi-stage process

Step 3 - Diazotisation of phenylamine

reagents	nitrous acid and hydrochloric acid (use sodium nitrite)
conditions	keep below $10^\circ C$
equation	$C_6H_5NH_2 + HNO_2 + HCl \longrightarrow C_6H_5N_2^+ Cl^- + 2H_2O$
reaction type	diazotisation

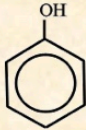
PHENOL

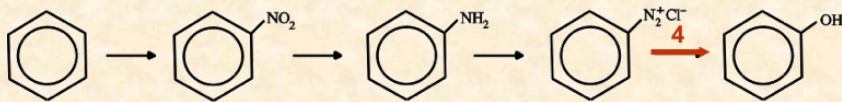
Structure phenol is an aromatic alcohol with formula C_6H_5OH the OH group is attached directly to the benzene ring it is an almost colourless crystalline solid

Preparation You cannot put an OH group directly onto a benzene ring by electrophilic substitution, so phenol has to be synthesised in a multi-stage process

Step 4 - Substitution of diazo group by OH

reagents	water
conditions	warm above $10^\circ C$
equation	$C_6H_5N_2^+ Cl^- + H_2O \longrightarrow C_6H_5OH + N_2 + HCl$
reaction type	hydrolysis / substitution





- However, let me take you through each step one by one.

The first stage (Benzene, $C_6H_6 \longrightarrow$ Nitrobenzene, $C_6H_5.NO_2$)

- Could we therefore start with C_6H_6 and somehow stick an “ $-NH_2$ ” species onto it in order to obtain phenylamine/aniline (*IUPAC name benzenamine*⁴)?
- The answer is “No”, because an “ $-NH_2$ ” species would be an “ NH_3 ” species (Ammonia) from which a proton (H^+) had broken away leaving behind the nucleophile “ $(-NH_2)^-$ ”, and **there is no (normal) way in which a nucleophile would react with another nucleophile** (in this case Benzene surrounded by/protected by/guarded by the huge π ring electron cloud above it and below it).
- Phenylamine/Aniline can be produced from Phenol and Ammonia using the ‘cumene’ process, but that is too complicated for ‘A’ Level purposes, therefore if the examiners ask you about this synthesis process⁵, then you have to start with something less complicated.
- In fact, what the examiners want you to say⁶ is that you start by nitrating C_6H_6 to obtain $C_6H_5.NO_2$ – and we have discussed this process already in Chapter 12, and remember to say that **the temperature must not be allowed to rise above $60^\circ C$** (otherwise a dinitro product could be produced). The next step would be to reduce the Nitrobenzene to Phenylamine.

⁴ The spelling is correct. An “e” in the middle of the name is omitted.

⁵ It is most unlikely that you will be asked a question about azo dyes that requires a *detailed* answer in the ‘A’ Level exams. My objective in taking you through this is twofold. First of all, I want to demonstrate how organic synthesis works, and then I want to get you to start thinking in the way that you will have to think when you become an undergrad next Autumn.

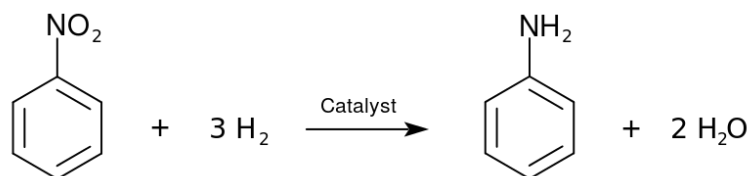
⁶ And in the exam please do **not** try to answer the question in perfect English. Do it in bullet point form: bang/bang/bang, and then move on to the next question. *You are not sitting for an ‘A’ Level English exam.*

The second stage⁷ (the Hydrogenation/Reduction of C₆H₅.NO₂ into C₆H₅.NH₂)

- The two most common methods of preparing Phenylamine from Nitrobenzene involve

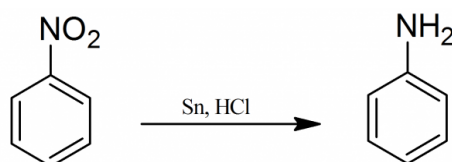
The reduction of Nitrobenzene by

- i) the catalytic hydrogenation of Nitrobenzene (where Platinum is a good catalyst to use)



or

- ii) reacting Nitrobenzene with Sn (Tin) and HCl, or Iron and HCl (where Sn²⁺ is oxidised to Sn⁴⁺, and the Sn²⁺ is thus the **reducing** agent in this reaction).⁸



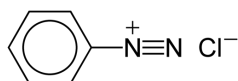
- Here you will use the widely-used (in acidic conditions) reducing agent Tin (II) Chloride, SnCl₂(aq) – and that is what needs to be done to get the Hydrogen that you require to hydrogenate C₆H₅.NO₂ (Nitrobenzene) to get the Phenylamine/Aniline/Benzenamine, (C₆H₅.NH₂) that is required.
- However, since I have already stated that I want to introduce you to how you have to start thinking when you get to University, let me go into it in just a bit more detail. [I do not want your first few weeks at University to be the dreadful shock for you that it was for me.](#)⁹

⁷ The stage is so complicated (and involves the formation of complex ions) that a detailed knowledge of the process is *no longer* required at 'A' Level – but if you are really interested, then you can read a simplified version of the process on Jim Clark's <http://www.chemguide.co.uk/organicprops/aniline/preparation.html>, or you could try <http://www.chegg.com/homework-help/write-balanced-half-reactions-reduction-nitrobenzene-5-anili-chapter-21.2-problem-13e-solution-9781111789268-exc> where you will get the diagram that I have shown in Appendix A.

⁸ Iron is much cheaper to use than Tin.

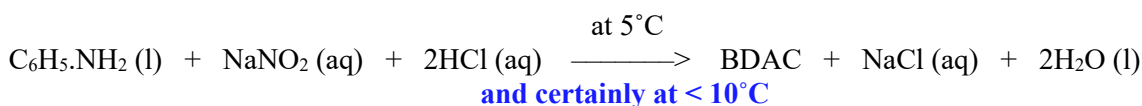
⁹ Just as you are clever (otherwise you would not be in the Science Upper Sixth), I also was considered to be modestly bright at school. However, when I got to University, in the very **first** lecture my Prof started writing Euler-Lagrange's equations on the blackboard – and I knew immediately that I did not know what on earth I had let myself in for! There is a huge jump from 'A' Levels to University – [but do not lose any sleep over it](#). Literally hundreds of thousands of 18-year olds (all over the world) make that leap every year. I survived *eventually*, and so will you. However, I hope that you will be better prepared for it than I was. The teachers in my school were good – but nobody prepared me for the massive difference that there is between **being taught** something and having [to learn about those things for yourself](#).

The third stage: the conversion of Phenylamine into Benzenediazoniumchloride (BDAC)



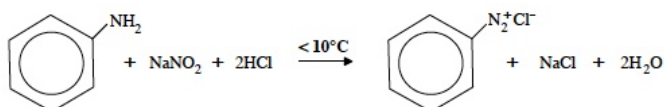
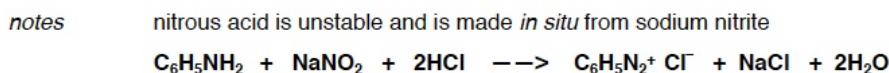
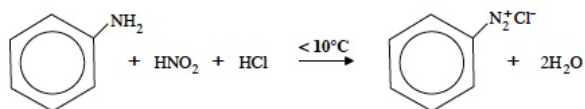
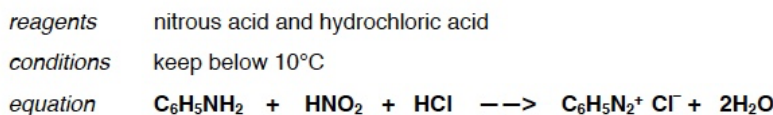
and let me draw your attention to the fact that the positive charge is on the N atom that is closer to the C₆H₅ species.

- Please do not be put off by the look of BDAC. After all, what conceptual difference is there between the salt that you have on your dining table (Na⁺Cl⁻) and any other salt? *None whatsoever*. The salt above is just more complex than (but conceptually no different from) table salt.
- BDAC can easily be obtained by reacting Phenylamine with “Nitrous acid” (HNO₂) – **but nitrous acid is very unstable and decomposes very quickly**, therefore the nitrous acid has to be made and used on-the-spot (*in situ*) by reacting NaNO₂(aq) with 2HCl(aq) and we would thus get



NB Please remember that in Organic Chemistry it is permissible to omit non-organic products in reaction equations (and that is why Organic equations sometimes do not always balance).

- Textbooks quote different temperatures ranging from 0°C to 10°C, and one of the reasons for keeping the temperature down is that Nitrous Acid is unstable and decomposes at higher temperatures – and it is the Nitrous Acid that is being made *in situ* and being utilised as soon as it is made. The table below shows the process of creating the benzenediazonium chloride (BDAC) diagrammatically, but please remember that I have told you the positive charge is on the N atom that is closer to the C₆H₅ species.

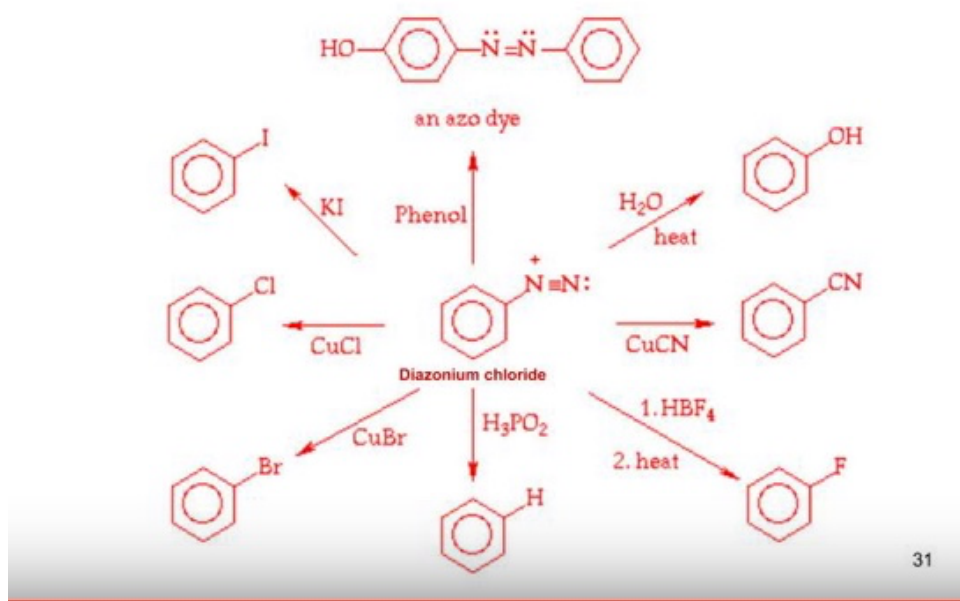


the solution is kept cold to slow down decomposition of the diazonium salt

Source: BDAC researchgate.net Module 7

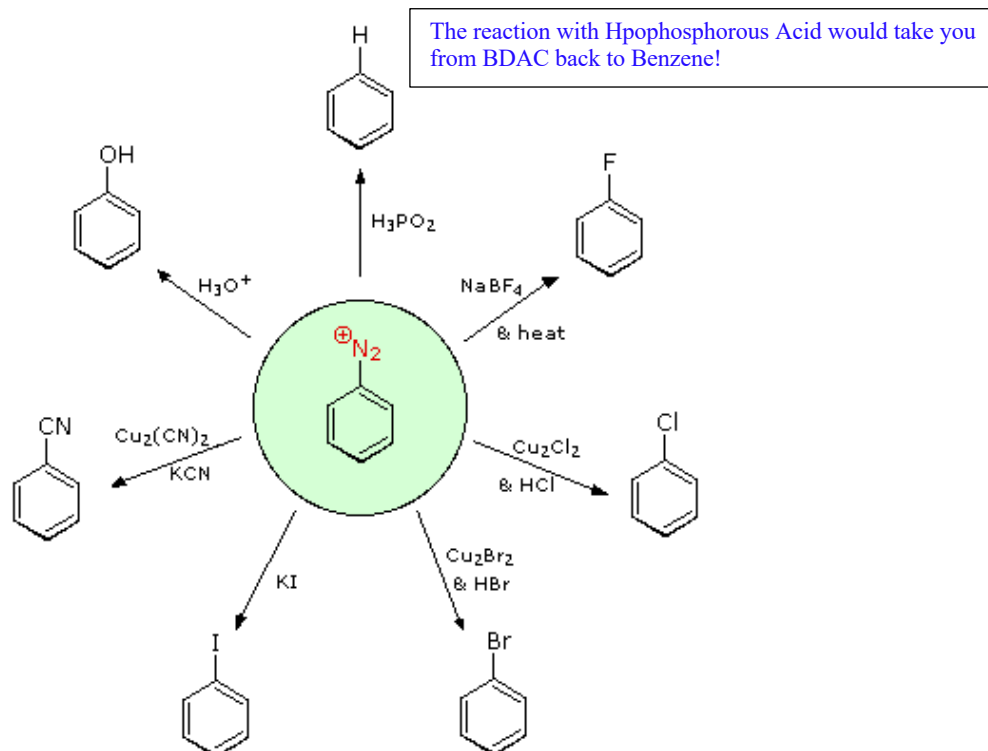
- BDAC is an extremely useful chemical precursor because a number of chemicals can be made easily from it. (The “diazonium chloride” below should really be called “benzenediazonium chloride”.) Most of the BDAC reactions take place in aqueous form and with the loss of Nitrogen in the form of $N_2(g)$, and without the need for heat.

Synthesis reactions involving diazonium chloride



Source: Unknown

- Prof Reusch shows the reactions slightly differently, but in effect they are the same reactions.



Source: Prof William Reusch, Michigan State University

The Fourth stage (coupling BDAC to the species required to form the end-product)

- The only thing left to do now is to join the BDAC to the appropriate species that will give the required end-product.
- “Aniline Yellow” was one of the earliest dyes to be made in modern times¹⁰, and let us now create it i.e. “4-(phenylazo)aniline” or “4-phenylazo phenylamine” yellow, $\text{C}_6\text{H}_5\text{.N=N-C}_6\text{H}_5\text{-NH}_2$. To get yellow $\text{C}_6\text{H}_5\text{.N=N-C}_6\text{H}_5\text{-NH}_2$ we now need to react $\text{-C}_6\text{H}_5\text{-NH}_2$ with $\text{C}_6\text{H}_5\text{.N}^+=\text{N-Cl}^-$, in mildly acidic conditions, and then we would get

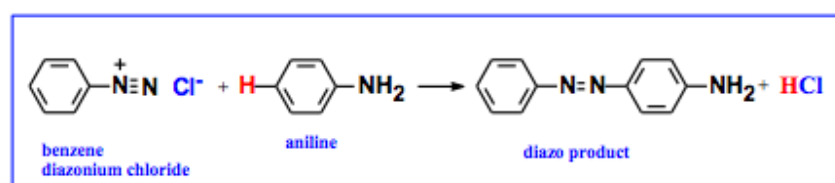
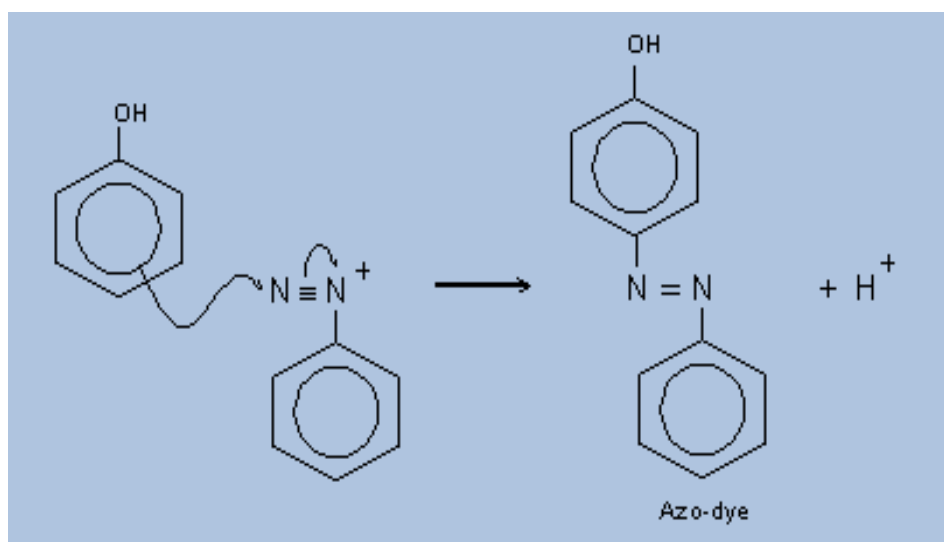


Figure 3. Coupling reaction with aniline.

Source: Researchgate.net

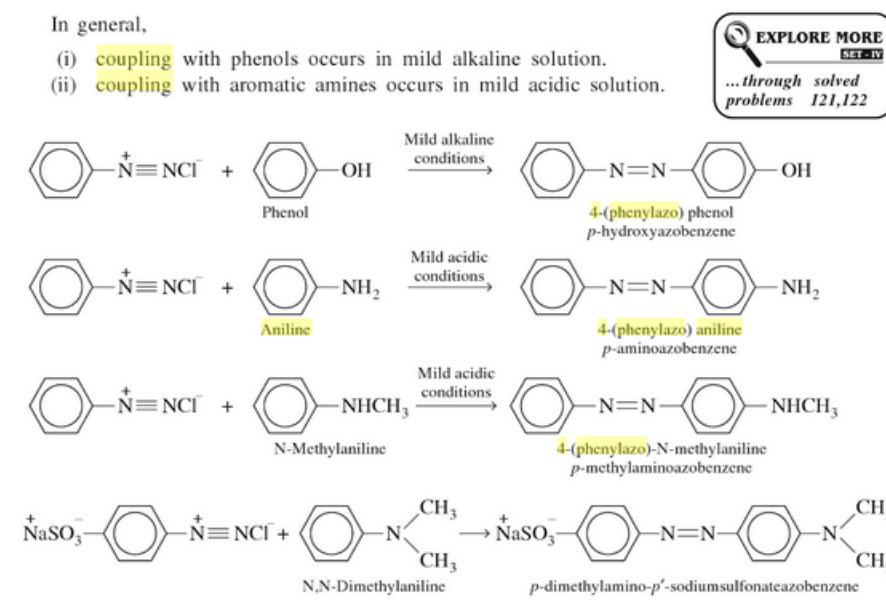
- The reaction would take place over about 20-30 minutes.
- avogadro.co.uk says that “In practice, a solution of a benzene diazonium salt is added to an alkaline solution of a phenol (or aromatic amine, such as phenylamine). The benzene diazonium cation behaves as an electrophile¹¹, but it is a weak electrophile and so the aromatic ring which it attacks must have attached to it an activating group such as -OH or -NH_2 . An electrophilic substitution reaction occurs to form an azo-dye.”
- As you can see from the diagram below, BDAC has carried out an electrophilic attack on Phenol, and HCl will be ejected/eliminated.



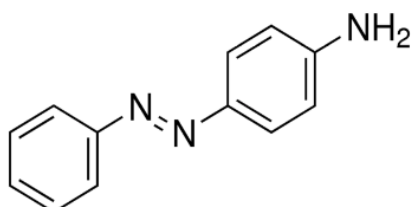
¹⁰ Dyes (chemicals made for colouring purposes) have been made for literally tens of thousands of years. Rock paintings have been discovered that were made by early man as long as 50,000 years ago. As human beings evolved, they travelled from the Rift valley in Africa across what is now called Saudi Arabia/Iraq/Iran/and India, and from there they (i) went down to Australia or (ii) went up and West into Northern Europe or (iii) went up into the Far East/China/across the Bering Straits/to North America/and then down into South America – and rock paintings have been found in ALL these places. Type “Rock paintings, Bradshaw” into your search engine and you can read about some of these discoveries.

¹¹ It does not “behave like an electrophile”. It is an electrophile!

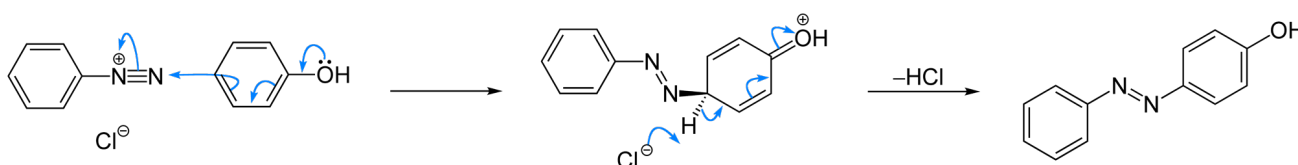
- To show you just how useful BDAC is, I will now show you how you can use it to create a number of different dyes. The diagram below is by Bhupinder and Manju Mehta.¹² In the diagram below, “p” stands for “para” as in ortho/meta/para (or numerically positions 2/3/4 on the Benzene ring), and the capital “N” represents the Nitrogen atom in the aniline.



NB The “p” in the “*p*-aminoazobenzene” stands for “para” as in OMP (‘Oh Mein Pappa’). The molecule is very often drawn as



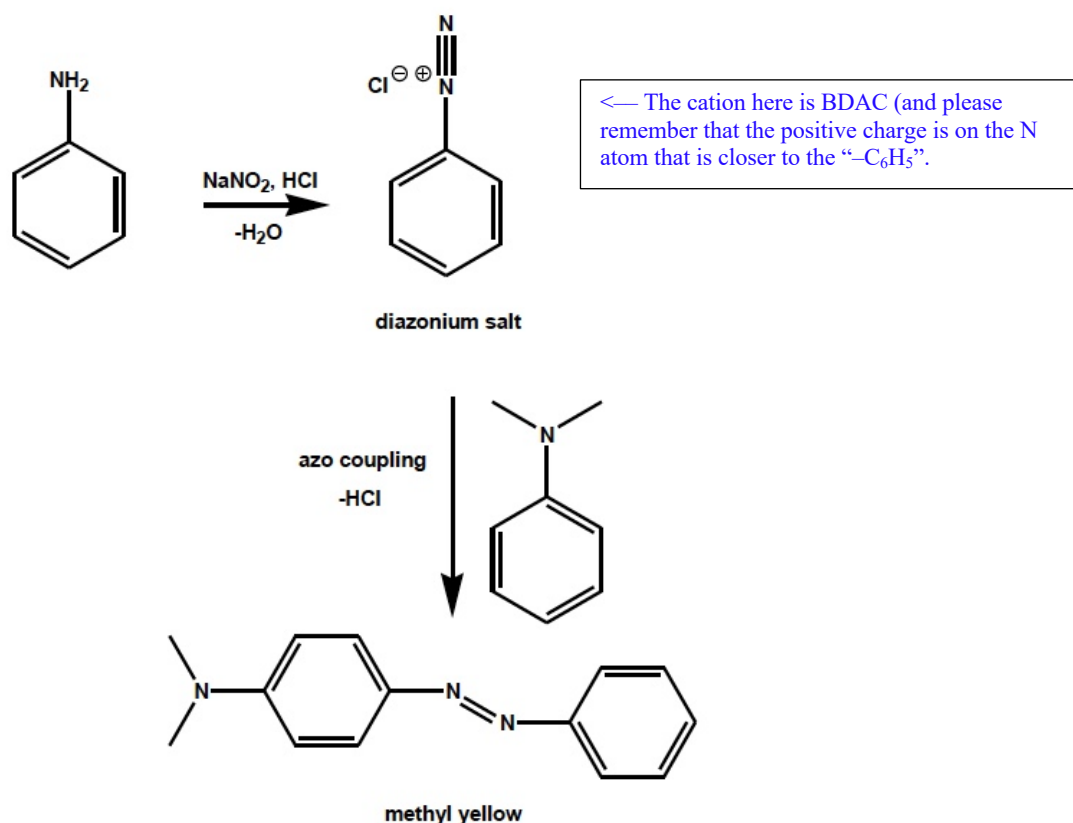
- If we had wanted to create 4-hydroxyphenylazobenzene (another yellow diazo compound and the first molecule in the diagram on page 11), we would have had to carry out the following



- In the diagram on the left above, the species on the left is $\text{C}_6\text{H}_5\cdot\text{N}^+\equiv\text{N}\cdot\text{Cl}^-$.

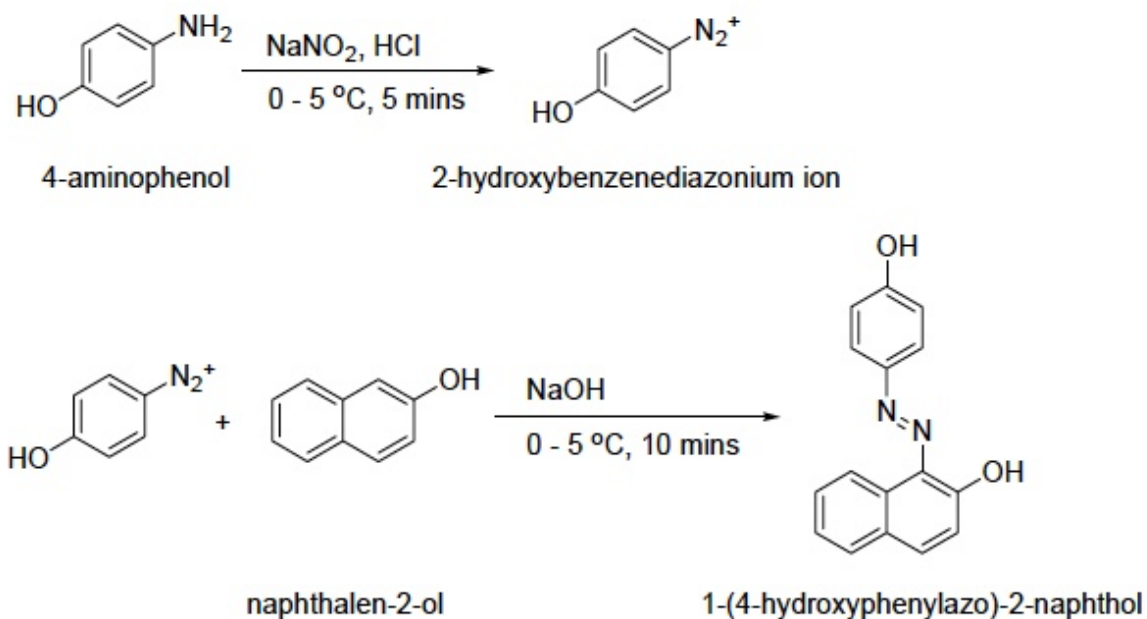
¹² To show you just how ignorant we in the West are (or perhaps I am), I could not tell you whether the authors are males or females! *Is that not sad.* Mind you, on occasions I have been respectfully addressed by foreigners as “Mr/Dr Agnes” (in some cultures apparently the surname/the familial name is put first, and Agnes may be more familiar to foreigners than “Angus”) so perhaps **all** of us human beings are woefully ignorant of each other’s cultures.

- I hope that you have noticed that very often we have started each name with the position involved (and in the compounds that I have used so far, the position has been “4”), and then there are many different conventions for naming. The molecule above is sometimes called “phenoldiazobenzene”.
- If we had wanted to get the indicator **Methyl Yellow**, $\text{C}_6\text{H}_5\text{.N=N-C}_6\text{H}_5\text{-N(CH}_3)_2$, then we would have had to do the following



- I show you this next diagram not so much to show you how useful BDAC is in Organic Synthesis, but to tell you that this is just a little fragment from something that was written **IN ENGLISH** (and not in one of the Chinese languages such as Mandarin or Cantonese) by the Hong Kong government for **Sixth Formers** in Hong Kong. If we are not careful, in this century we British will be left miles behind by scientists from the Far East.

To prepare the azo dye 1-(4-hydroxyphenylazo)-2-naphthol by the diazonium coupling reaction of naphthalen-2-ol with the benzenediazonium ion obtained from 4-aminophenol:



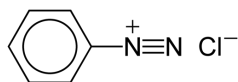
Source: Government of Hong Kong **brief for SIXTH formers.**

- To sum up therefore, I have tried to introduce you to the concept of Organic Synthesis by taking you through the synthesis of diazo compounds (via benzenediazonium chloride) viz.

Stage 1 Benzene (C_6H_6) \longrightarrow Nitrobenzene ($\text{C}_6\text{H}_5.\text{NO}_2$)

Stage 2 Nitrobenzene ($\text{C}_6\text{H}_5.\text{NO}_2$) \longrightarrow Phenylamine ($\text{C}_6\text{H}_5.\text{NH}_2$)

Stage 3 Phenylamine ($\text{C}_6\text{H}_5.\text{NH}_2$) \longrightarrow Benzenediazoniumchloride ($\text{C}_6\text{H}_5.\text{N}^+ \text{triple bond N}$)

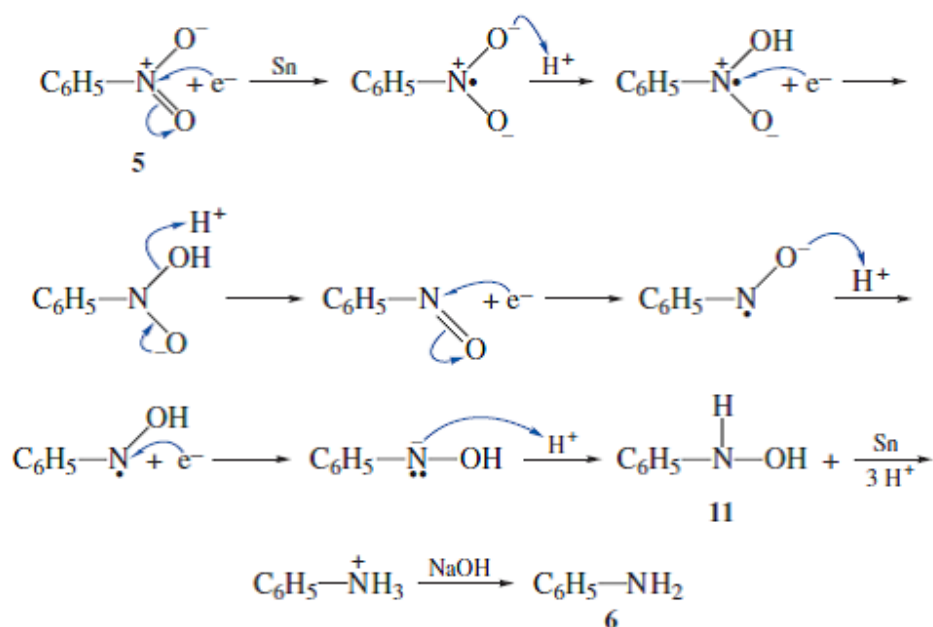


Stage 4 Now couple the $\text{C}_6\text{H}_5.\text{N}^+ \text{triple bond N}$ with whatever you need to get your end-product.

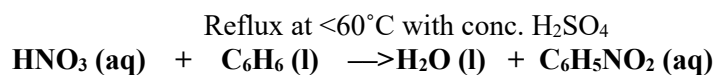
- OK, (other than for the Appendices) that concludes all the stuff that you are required to know about Benzene and its derivatives for 'A' Level purposes. Let us now talk about other organic species, and let us start with Carbonyl compounds in Chapter 17.

APPENDIX A

This is the reaction mechanism for the reduction of Nitrobenzene to Phenylamine.

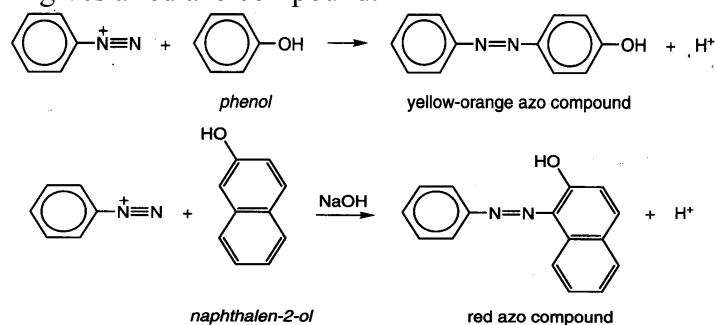


- You can see now why many UK exam boards have taken the conscious decision to accept the statement



Coupling with phenols

- Benzenediazonium salt and alkaline phenol gives a yellow orange azo compound
- Benzenediazonium salt and alkaline naphthalen-2-ol gives a red azo compound.



APPENDIX B

This is a hand-out for English schools from The Society of Dyers and Colourists.

Colours

Colours can be divided into two groups: Dyes, which are soluble in water and give clear solutions, such as inks, and pigments, which are insoluble in water and give hazy solutions or dispersions, such as paints.

Dyes

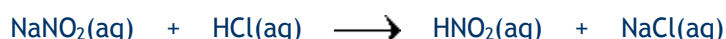
Many early dyes were made from plants. Alizarin is an example extracted from the madder root. Alizarin only colours cloth with fastness to water if it has been treated with a metal compound such as aluminium sulphate. The process is called mordanting. The colour obtained depends on the mordant used. An aluminium mordant gives a red colour, tin gives a pink colour and iron gives a brown colour.

The soluble dye reacts with the mordanting metal to produce an insoluble colour by the chelation of the metal ions and within the fibre structure gives a level of water fastness.

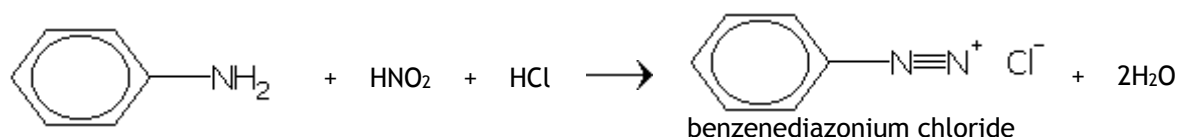
A range of synthetic colours have been developed based on phenylamine (aniline) and other similar chemicals to produce a whole family of azo colours and dyes.

Phenylamine reacts with a solution of sodium nitrite and hydrochloric acid at a temperature below 5°C (remember keeping that test-tube in ice?) to produce benzenediazonium chloride. This type of reaction is known as diazotisation and is used to produce azo linked compounds.

The hydrochloric acid first reacts with sodium nitrite to form unstable nitrous acid.



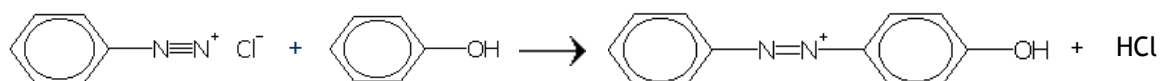
The nitrous acid then reacts with the amine.



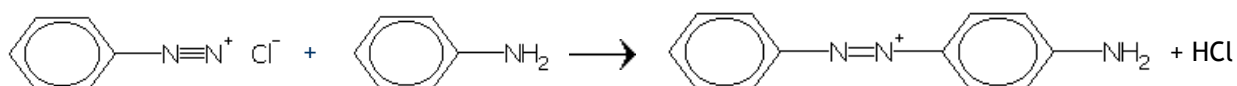
If the temperature is allowed to rise above 5°C, the benzenediazonium chloride decomposes to form phenol and nitrogen gas is given off.

If the benzenediazonium chloride is reacted with another compound containing a benzene ring, called a coupling agent, an azo compound is produced. The diazonium salt acts as an electrophile and is capable of reacting with other compounds containing benzene and similar ring structures. The reaction produces an azo linkage in the new compound. Phenols and amines are used as coupling agents and many are important colours both as soluble dyes and insoluble pigments.

With phenol the following reaction occurs:



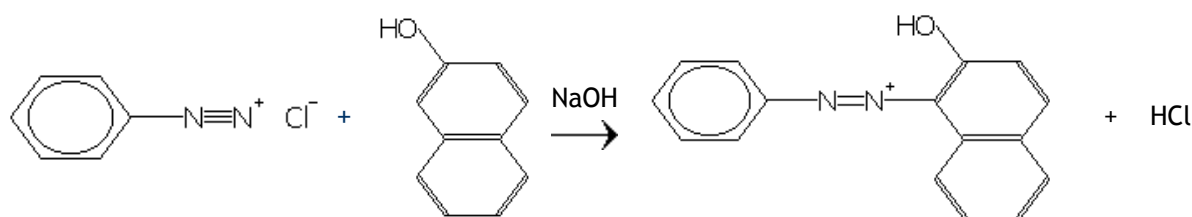
A similar reaction occurs with phenylamine:



The first dye is a yellow-orange shade, the second bright yellow. Many azo dyes are coloured in the range from red through to yellow. Some azo dyes are green, blue or even purple.

Many azo dyes are produced using a derivative of naphthalene, one example of which uses naphthalen-2-ol to produce a red azo dye. Notice how this compound is formed from two benzene rings joined (naphthalene differs since there is no hydroxy group present).

Also note that in this reaction Sodium Hydroxide is needed.

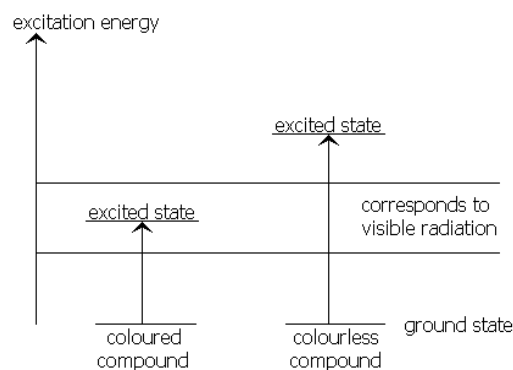


All coupling compounds contain a benzene ring that performs the coupling because it stabilises the delocalised electron structure. Without a coupled benzene ring the compound would remain unstable and break down at over 5°C like benzenediazonium chloride.

The Chemistry of Colour

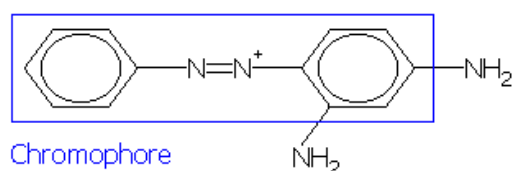
Coloured substances absorb radiation in the visible region of the spectrum. The energy absorbed causes changes in electronic energy. Electrons are promoted from a ground state to an excited state. The electrons excited in this case are the outer bonding electrons or lone pairs.

Not all electronic transitions are brought about by visible light as some require ultra-violet radiation. Those which absorb UV radiation appear colourless (unless they fluoresce). The energy needed to excite an electron in a coloured compound and in a colourless compound is shown below:



Coloured Organic Compounds

A dye molecule is built up from a group of atoms called a chromophore, which is largely responsible for its colour. Chromophores contain unsaturated groups such as $C=O$ and $-N=N-$, which are often part of an extended delocalised electron system involving arene rings. Chrysoidine is a basic dye shown below:



Attached to the chromophore are two NH_2 groups which interact with the chromophore to produce the orange colour.

Other functional groups may be added which can:

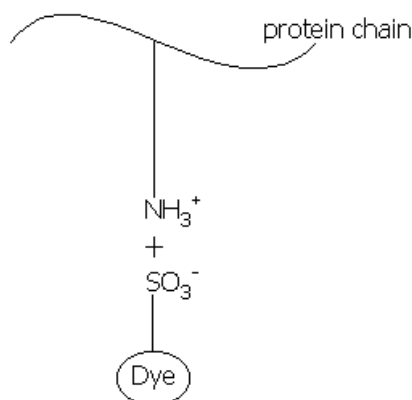
- modify or enhance the colour of the dye
- make the dye more soluble in water
- attach the dye molecule to the fibres of the cloth.

All azo dyes contain the $R-N=N-R'$ arrangement.

How do dyes stick to fibres?

This depends on the dye and the fibre to which the dye is attached.

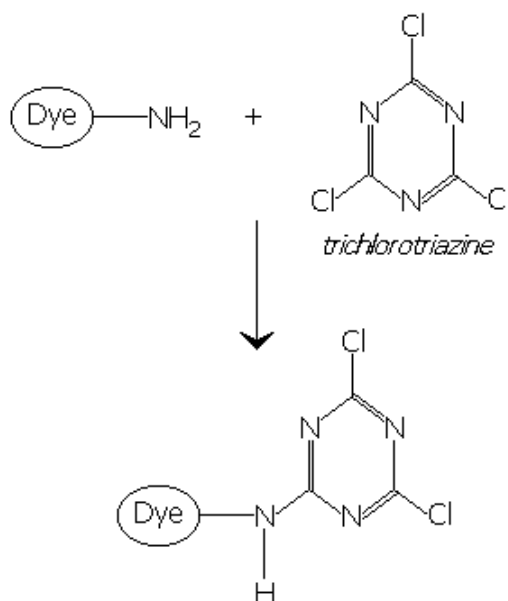
Protein-based fibres such as wool and silk have free ionisable CO_2H and NH_2 groups on the protein chains which can form an electrostatic attraction to parts of the dye molecule. For example the sulphonate group, SO_3^- , on a dye molecule can interact with a NH_3^+ group on the protein chain.



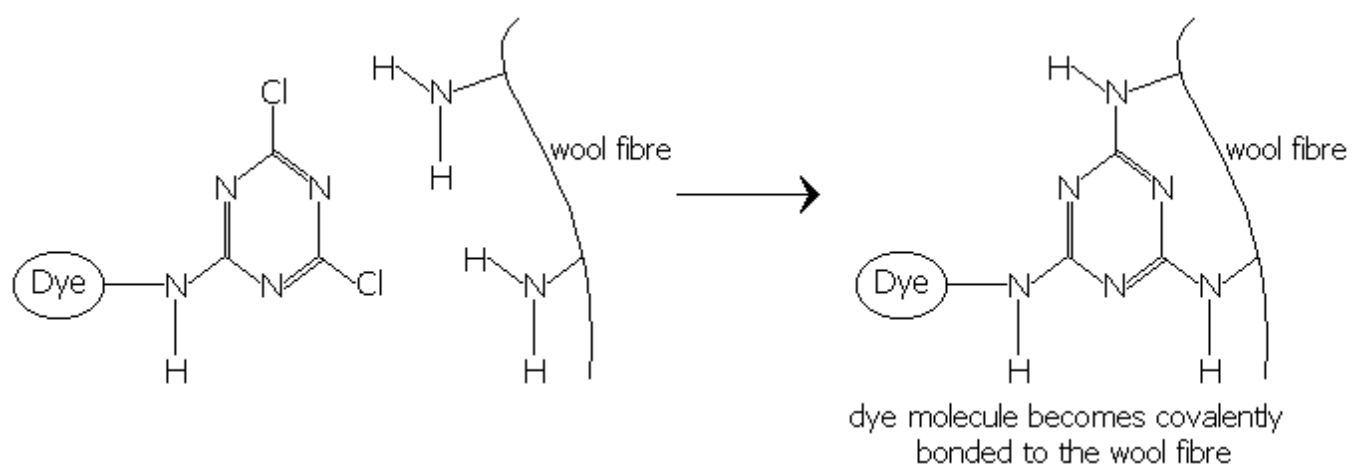
Cotton is a polymer with a string of glucose units joined together. Indigo which is used to dye denim jeans is a vat dye. Indigo is insoluble in water. The reduced form of indigo is soluble. Cotton is soaked in a colourless solution of the reduced form. This is then oxidised to the blue form of Indigo which precipitates in the fibres.

Direct dyes are applied from an aqueous solution and they are absorbed by the cotton cellulose structure. In the presence of sodium chloride salt solutions there is an attraction between the long chain dye molecules and ionic groups in the cotton, forming an ionic link via hydrogen bonds etc. These dyes have limited water fastness.

Fibre reactive dyes actually form covalent bonds with fibre molecules and are therefore extremely colour fast. A dye molecule is reacted with the molecule trichlorotriazine:



Trichlorotriazine can react with either -OH groups (present in cotton) or -NH groups (present in wool and nylons), thus effectively bonding the dye to the fabric.



Source: https://sdc.org.uk/.../2013/02/Azo_Dye_Synthesis_For_Schools.pdf