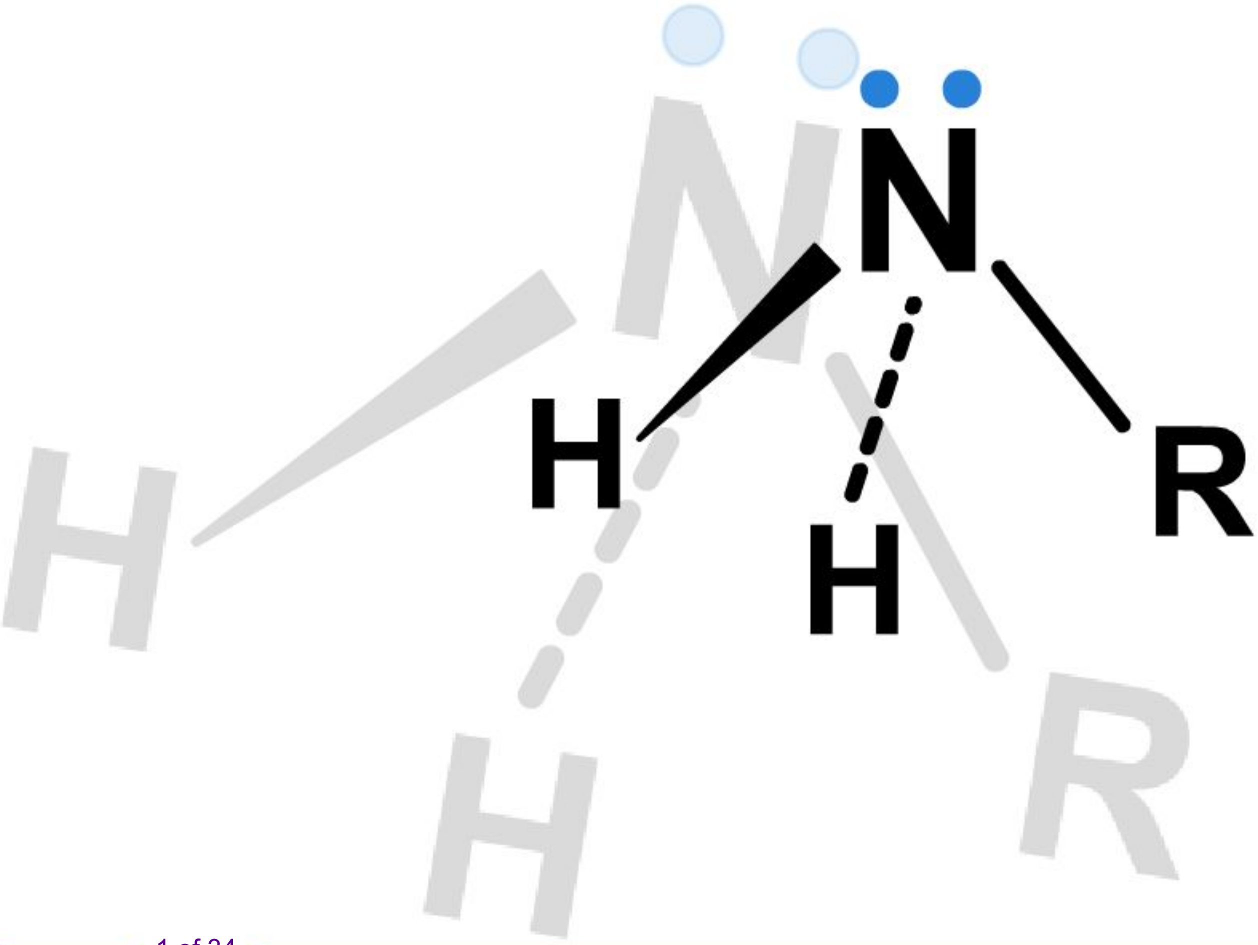
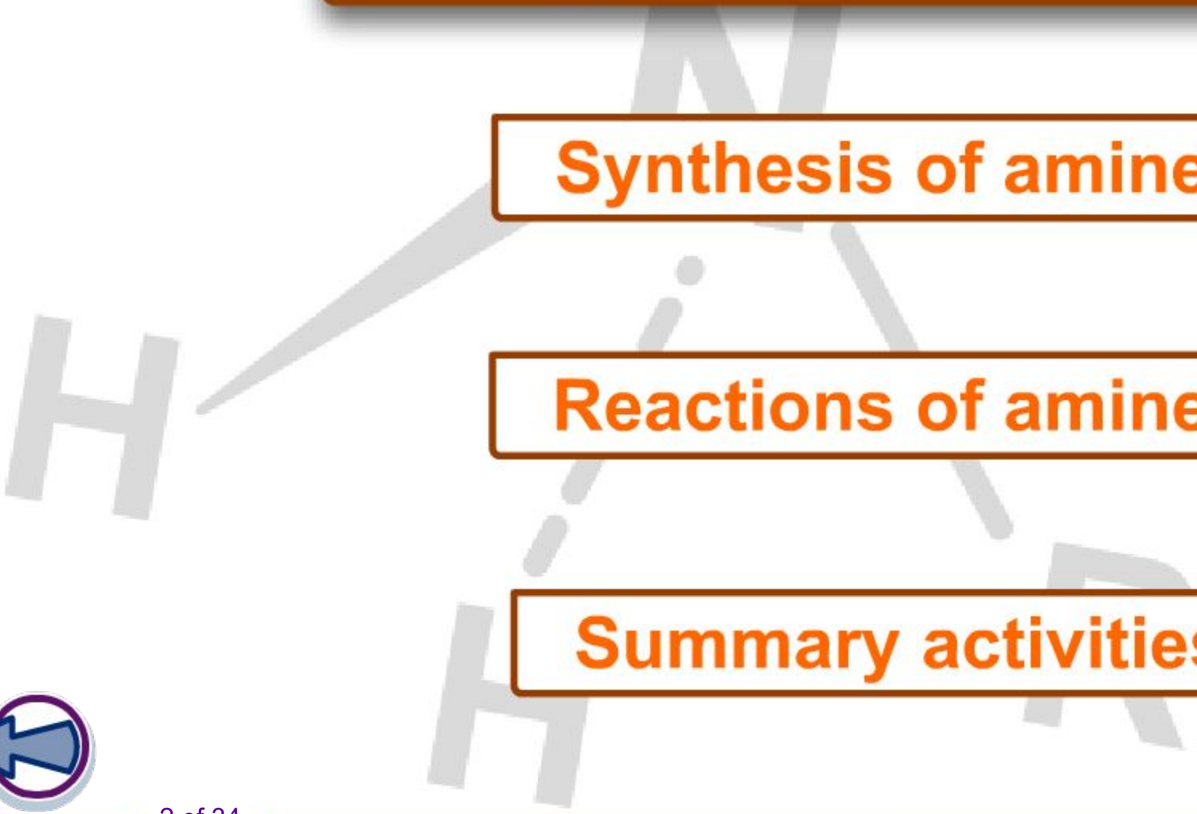
Amines



A2 Chemistry

Amines

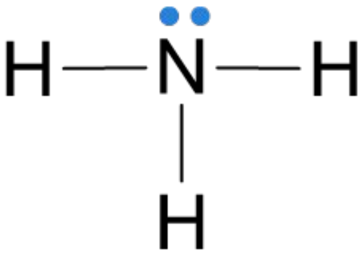


Properties of amines

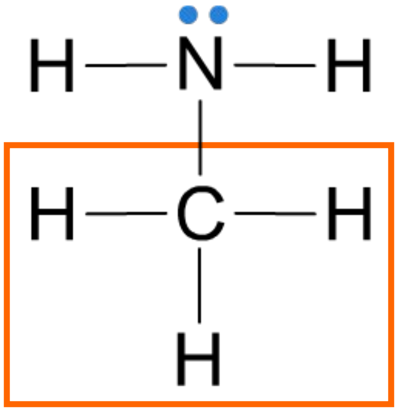
- Synthesis of amines
- Reactions of amines
- Summary activities

Ammonia and amines

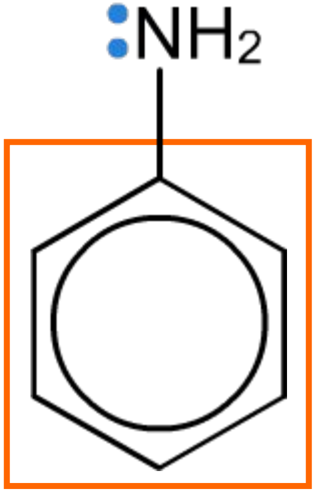
Amines are nitrogen-containing organic compounds derived from ammonia, where one or more of the hydrogen atoms has been replaced by an **alkyl** or **aryl** group.



ammonia



methylamine



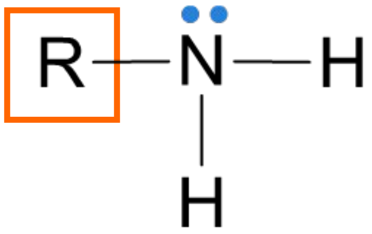
phenylamine

Amines have unpleasant odours: those with low boiling points smell like ammonia, whereas those that are liquid at room temperature have fishy aromas.

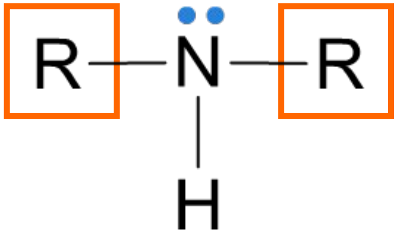
Structure of amines

An alkyl or aryl group can be represented by an R when drawing a chemical structure. This is referred to as an **R group**.

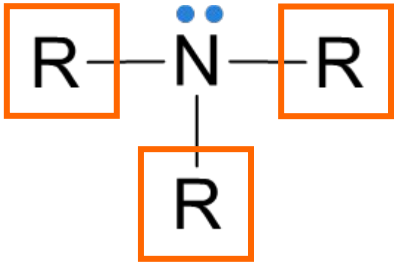
- **Primary (1°) amines** have one R group attached to the nitrogen atom.



- **Secondary (2°) amines** have two R groups attached to the nitrogen atom.

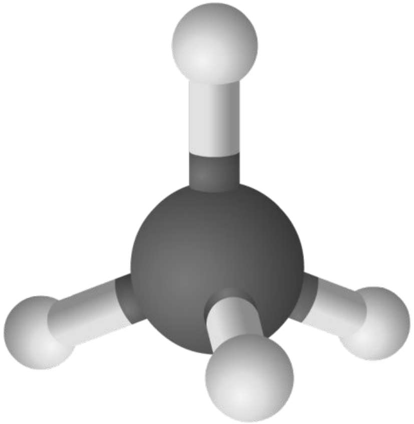


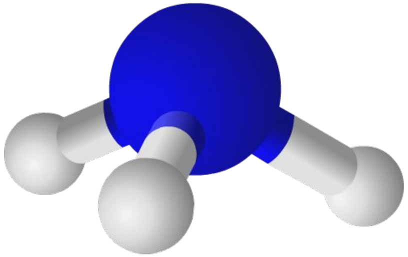
- **Tertiary (3°) amines** have three R groups attached to the nitrogen atom.



Shape of amines

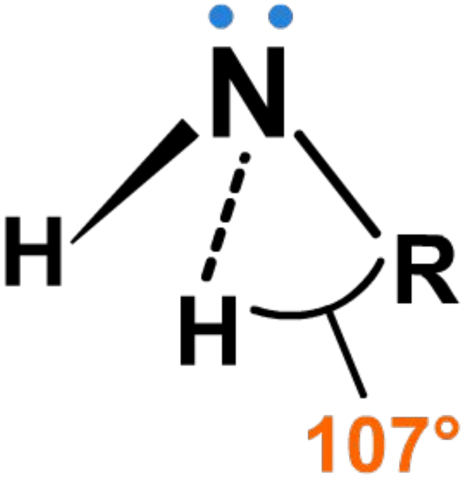
The ammonium ion (NH_4^+) is **tetrahedral** in shape, as the four bonding pairs of electrons (which repel each other) spread out equally around the central nitrogen atom.



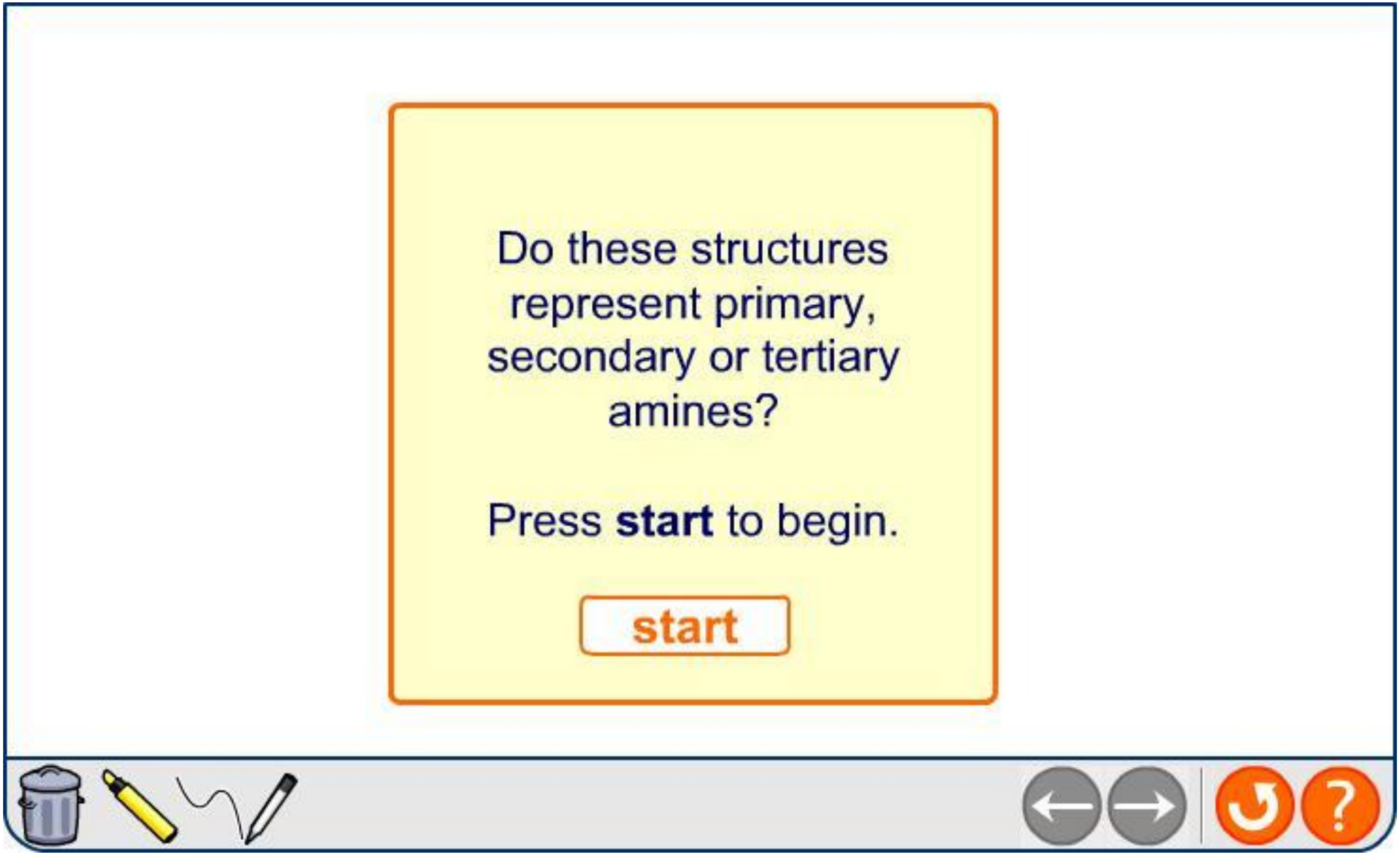


Ammonia (NH_3) is **pyramidal** in shape, as it has a lone pair in place of one bonding pair, which exerts a stronger repulsive force.

The amines are shaped similarly to ammonia, with a bond angle of 107° between groups on the nitrogen atom.



Identifying amines

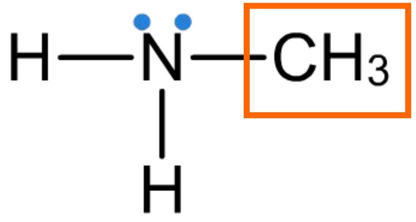


Do these structures represent primary, secondary or tertiary amines?

Press **start** to begin.

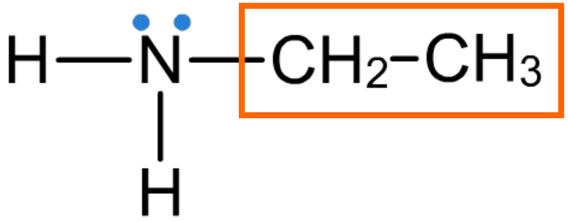
Naming amines (1/3)

Amines are named using the suffix *–amine*.



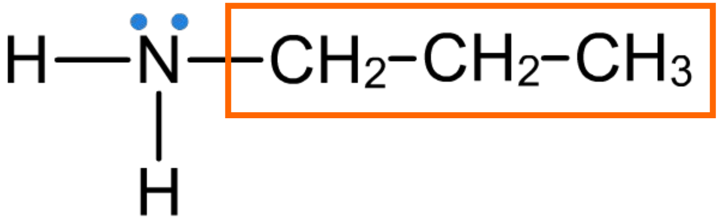
$$\mathrm{H-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-\boxed{CH_3}}$$

methylamine



$$\mathrm{H-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-\boxed{CH_2-CH_3}}$$

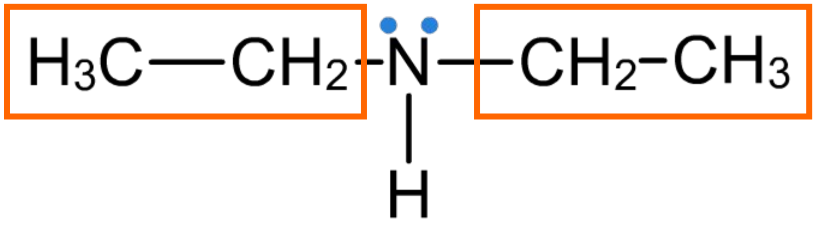
ethylamine



$$\mathrm{H-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-\boxed{CH_2-CH_2-CH_3}}$$

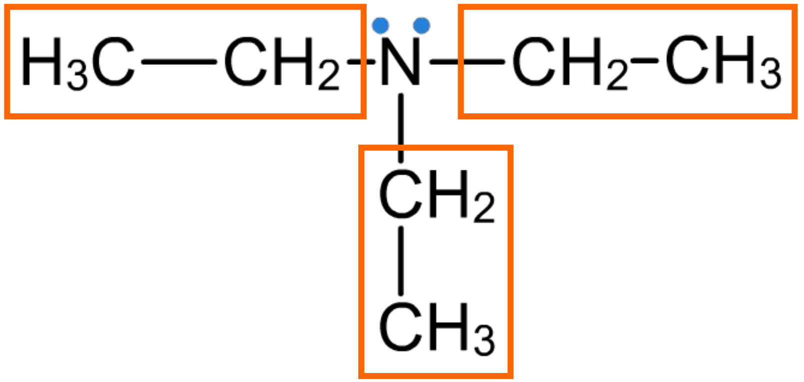
propylamine

If two identical R groups are attached, the prefix *di*– is used, and if three identical groups are present, then *tri*– is used.



$$\mathrm{\boxed{H_3C-CH_2}-\overset{\cdot\cdot}{\underset{\underset{H}{|}}{N}}-\boxed{CH_2-CH_3}}$$

diethylamine

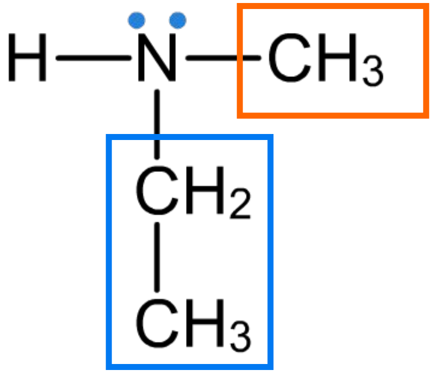


$$\mathrm{\boxed{H_3C-CH_2}-\overset{\cdot\cdot}{\underset{\underset{\boxed{\begin{matrix}CH_2\\|\\CH_3\end{matrix}}}{|}}{N}}-\boxed{CH_2-CH_3}}$$

triethylamine

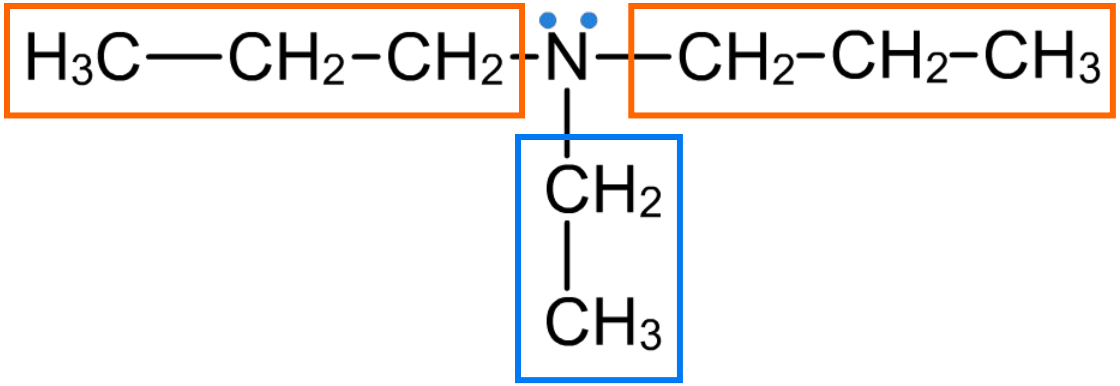
Naming amines (2/3)

If two different alkyl or aryl groups are present, they are listed alphabetically.



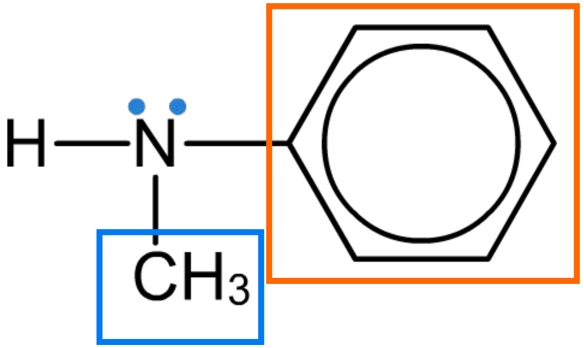
$\mathrm{H{-}\ddot{N}(CH_2CH_3){-}CH_3}$

ethylmethylamine

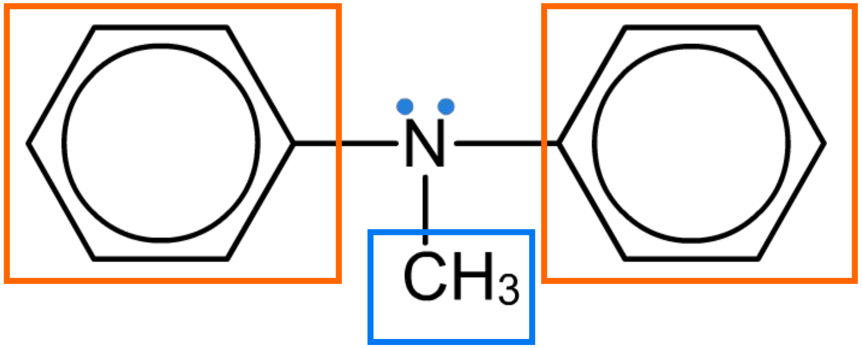


$\mathrm{H_3C{-}CH_2{-}CH_2{-}\ddot{N}(CH_2CH_3){-}CH_2{-}CH_2{-}CH_3}$

ethyldipropylamine



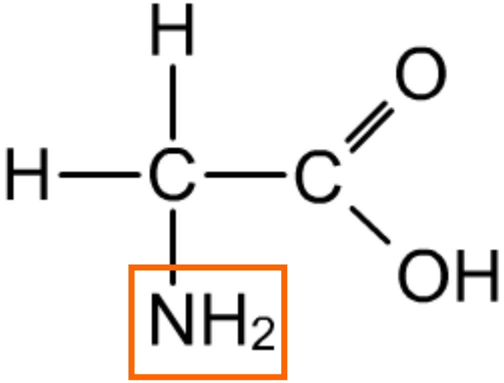
methylphenylamine



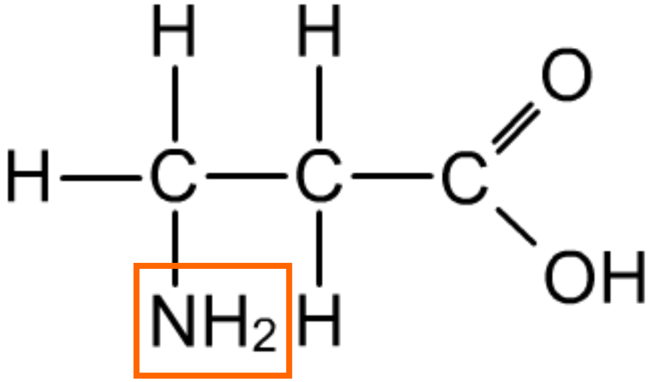
methyldiphenylamine

Naming amines (3/3)

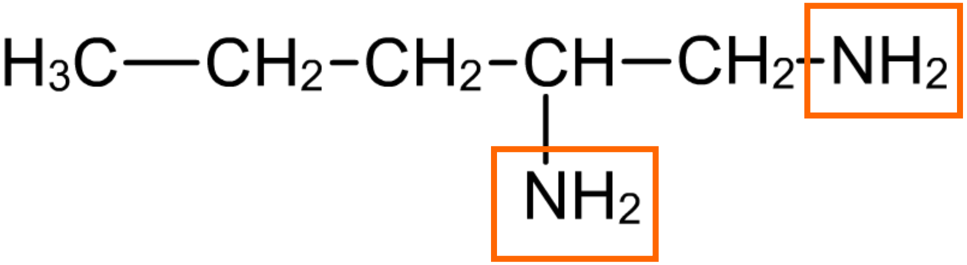
If other functional groups are present in the molecule, the presence of amine groups is denoted using the *amino*– prefix.



2-aminoethanoic acid



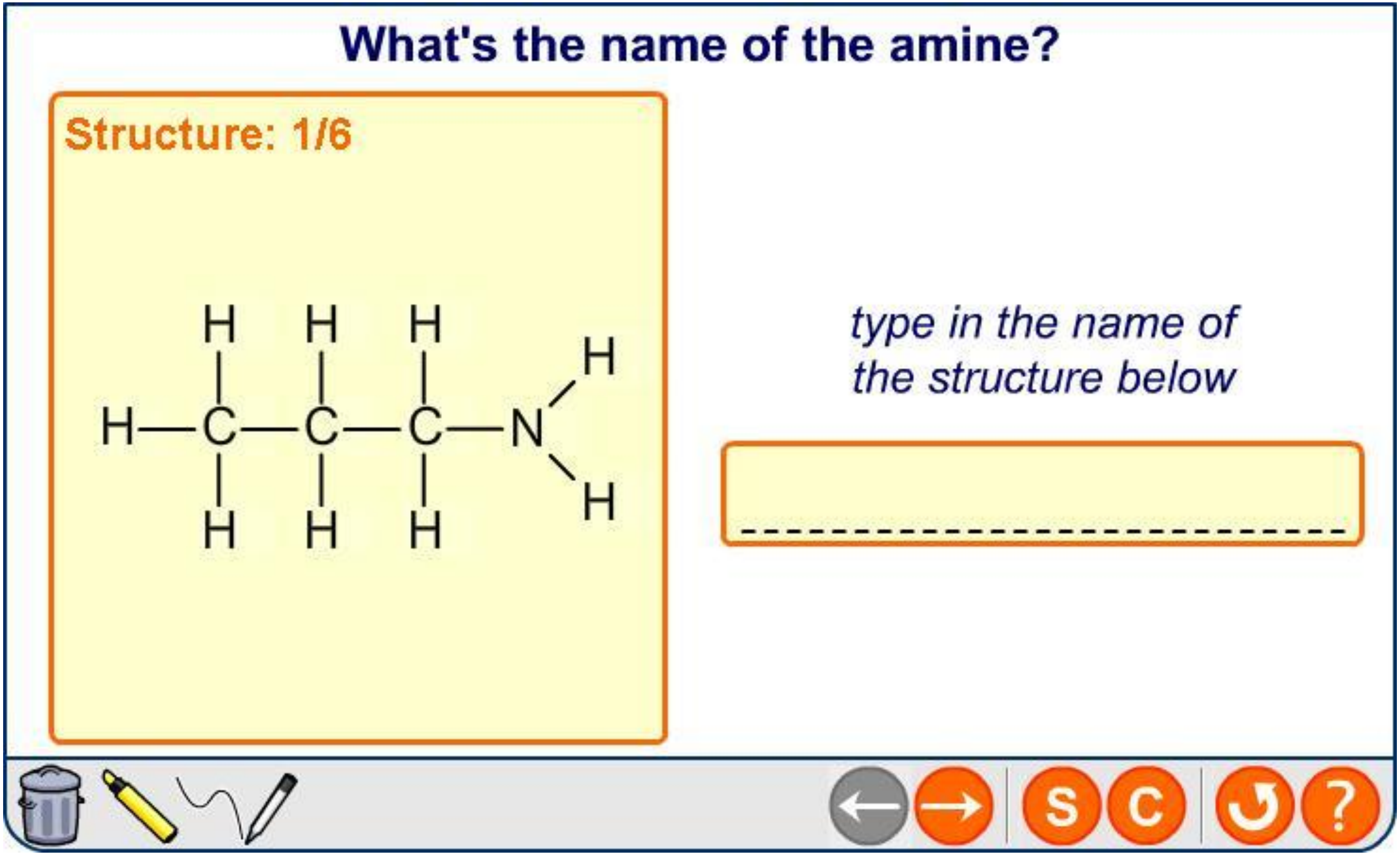
3-aminopropanoic acid



$H_3C-CH_2-CH_2-CH(NH_2)-CH_2-NH_2$

1,2-diaminopentane

Naming amines activity



What's the name of the amine?

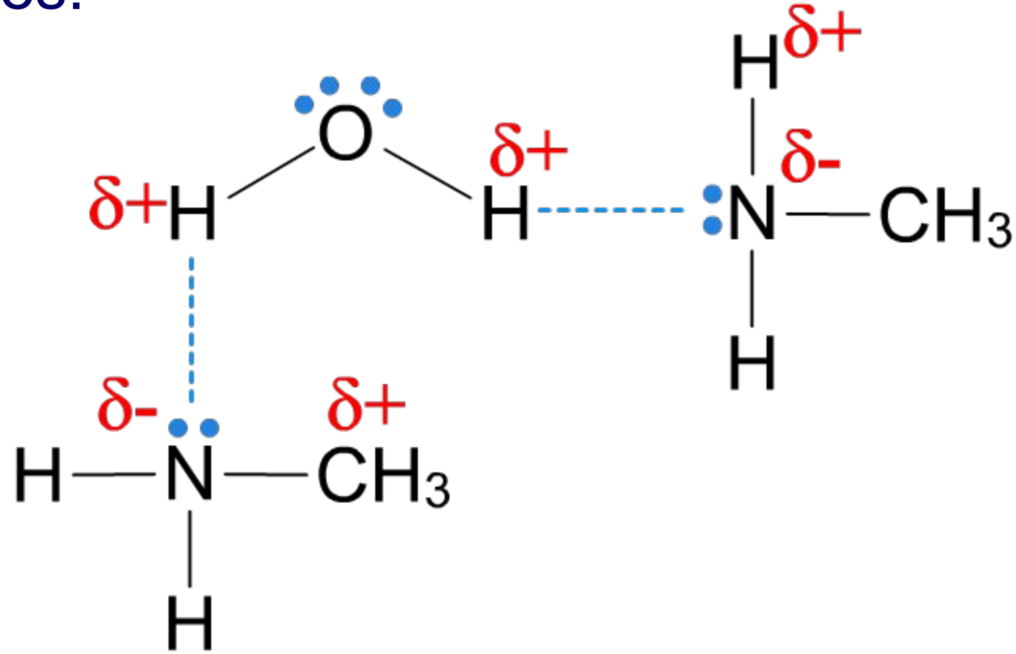
Structure: 1/6

type in the name of the structure below

Solubility of primary amines

Shorter chain amines are soluble in water, as the lone pair of electrons on the nitrogen atom allows them to form hydrogen bonds with water molecules.

Longer chain amines are only sparingly soluble, as the larger R groups interfere with the hydrogen bonds.



In aqueous solution, amine molecules are able to accept an H^+ ion from the water molecules, resulting in an alkaline solution due to the remaining OH^- ions.

Boiling points of primary amines

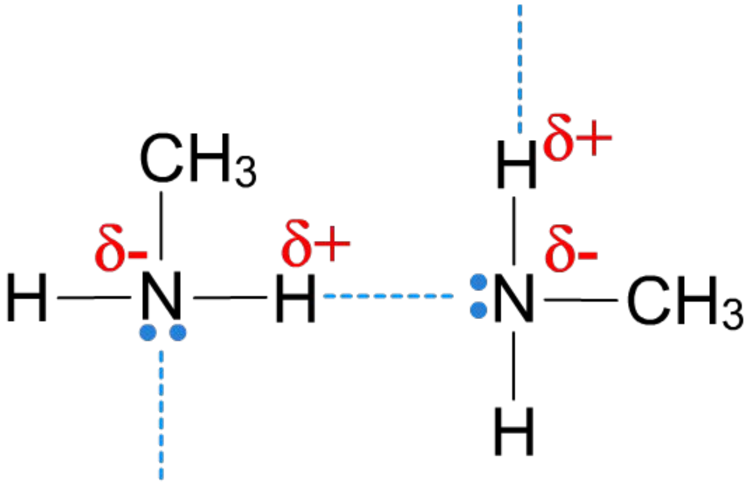
It is useful to compare the boiling point of methylamine (CH_3NH_2) with that of ethane (CH_3CH_3) because both molecules contain the same number of electrons and have roughly the same shape.

Boiling point (°C)			
alkane		**primary amine**	
CH_3CH_3	**-88.6**	CH_3NH_2	**-6.3**
$CH_3CH_2CH_3$	-42.0	$CH_3CH_2NH_2$	16.6
$CH_3(CH_2)_2CH_3$	-0.5	$CH_3(CH_2)_2NH_2$	48.6

The main reason the boiling points of the primary amines are higher is that they can form hydrogen bonds with each other.

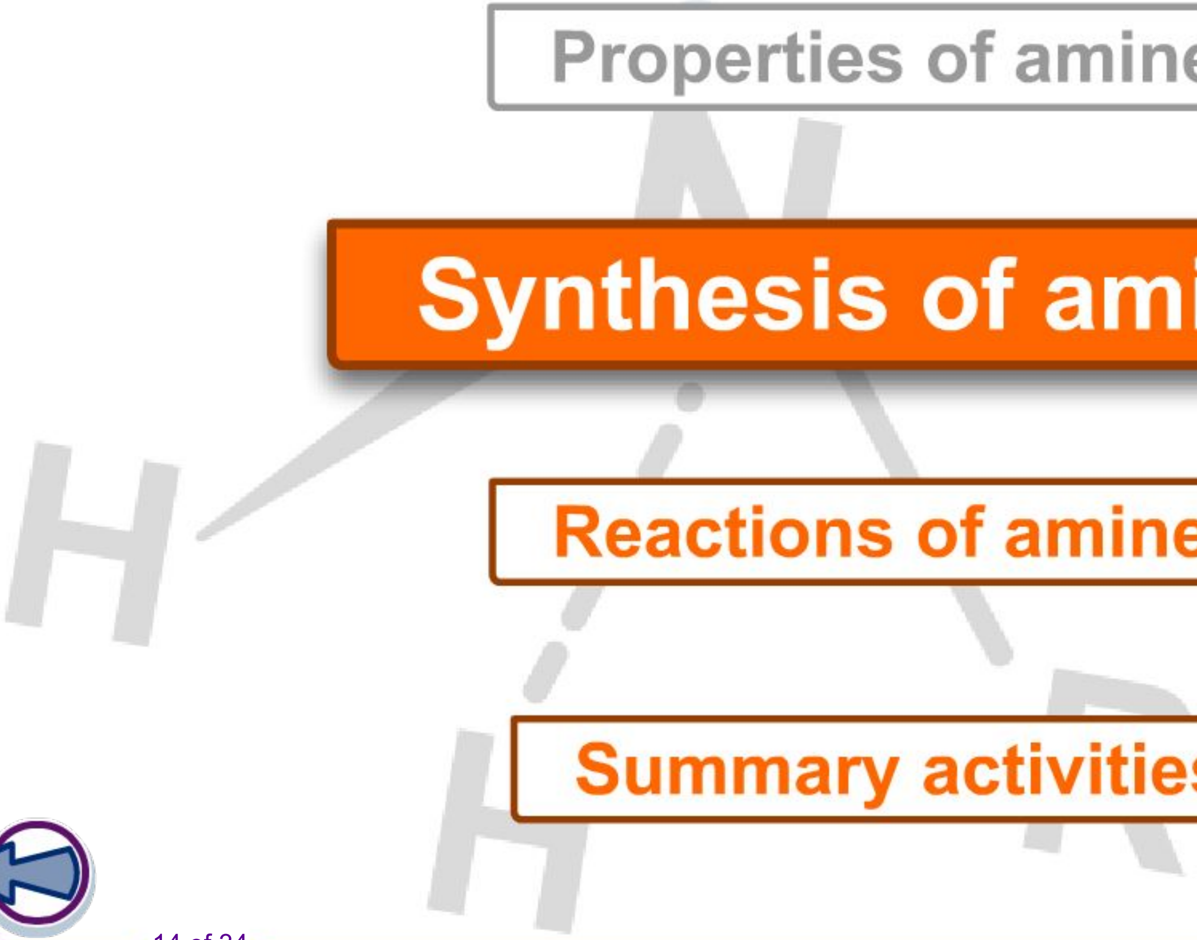
Boiling points of isomeric amines

Secondary amines also form hydrogen bonds, but as the nitrogen atom is in the middle of the hydrocarbon chain the strength of the dipole is slightly less. This decreases the strength of dipole–dipole attractions.



amine type	formula	boiling point (°C)
1°	$CH_3(CH_2)_2NH_2$	48
2°	$CH_3CH_2NHCH_3$	37
3°	$(CH_3)_3N$	3

In tertiary amines, there are no hydrogens attached directly to the nitrogen, so hydrogen bonding between molecules is impossible.



Properties of amines

Synthesis of amines

Reactions of amines

Summary activities

Ammonia and halogenoalkanes

Halogenoalkanes will undergo **nucleophilic substitution** reactions with **ethanolic ammonia** to form a primary amine:

$$RX + NH_3 \rightarrow RNH_2 + HX$$

The primary amine may then nucleophillically attack another molecule of halogenoalkane, to form a secondary amine:

$$RX + RNH_2 \rightarrow R_2NH + HX$$

A tertiary amine can be formed by nucleophilic attack of a halogenoalkane by a secondary amine:

$$RX + R_2NH \rightarrow R_3N + HX$$

In reality, a mixture of the above products is usually formed, which must be separated by distillation.

Reduction of nitriles

Nitriles can be reduced to primary amines using hydrogen in the presence of a nickel catalyst:

$$\boxed{RCN + 2H_2 \rightarrow RCH_2NH_2}$$

E.g: $CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2$

ethanenitrile **ethylamine**

Nitriles can also be reduced to primary amines using strong reducing agents such as lithium tetrahydridoaluminate ($LiAlH_4$), which can be represented as [H]:

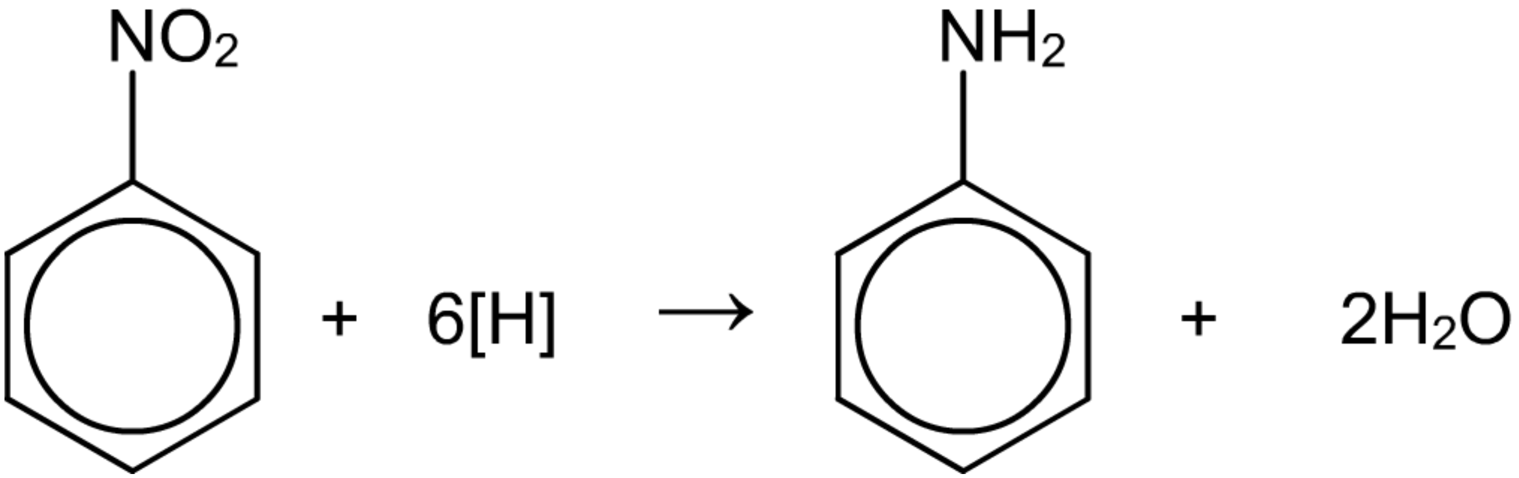
$$\boxed{RCN + 4[H] \rightarrow RCH_2NH_2}$$

E.g: $CH_3CH_2CN + 4[H] \rightarrow CH_3CH_2CH_2NH_2$

propanenitrile **propylamine**

Preparation of phenylamine

Aromatic amines can be prepared by the reduction of nitrated arenes using a mixture of tin metal and concentrated hydrochloric acid:

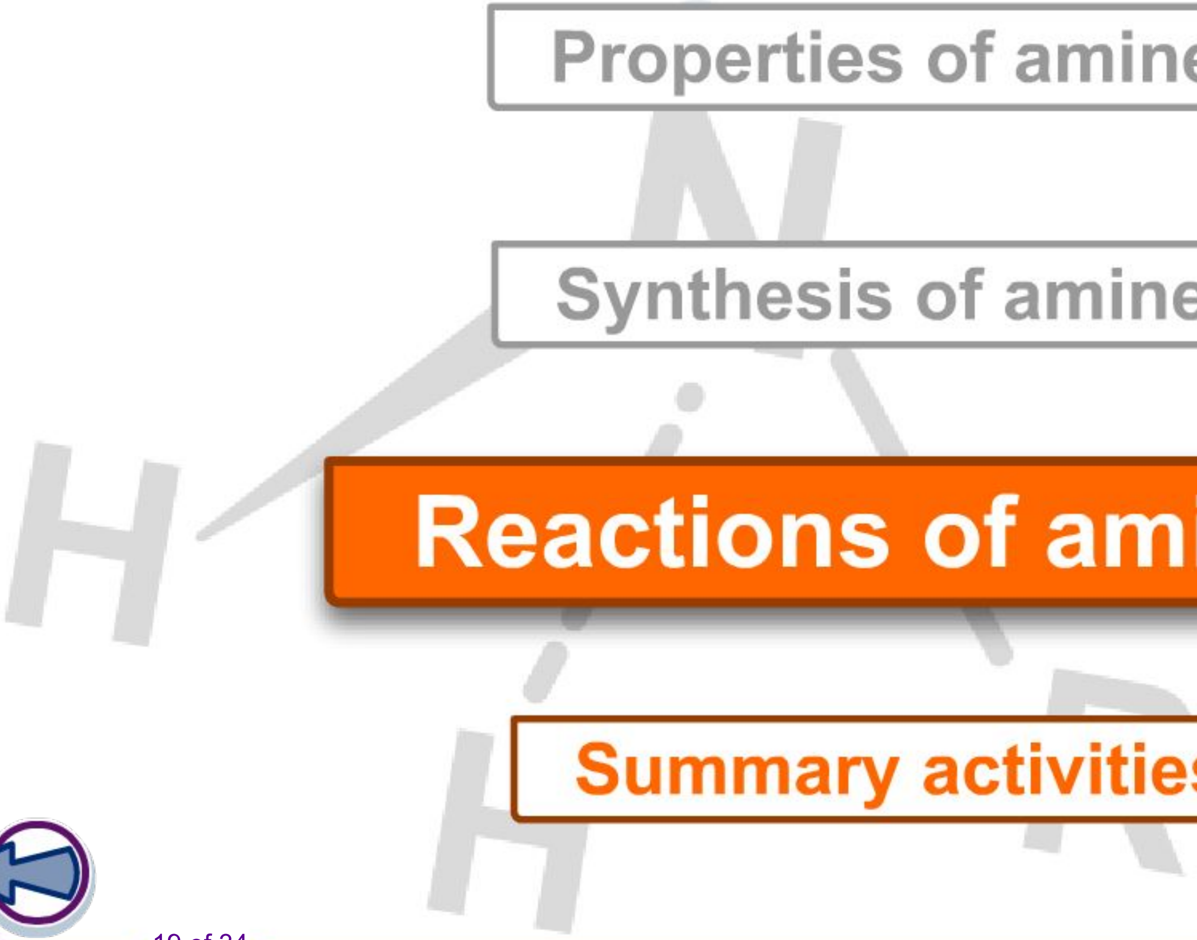


phenylamine

This method is commonly used to prepare aromatic amines in the lab. A similar method, using iron instead of tin, is used to prepare phenylamine industrially.

Which conditions?

Amines



Properties of amines

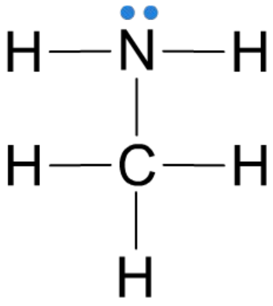
Synthesis of amines

Reactions of amines

Summary activities

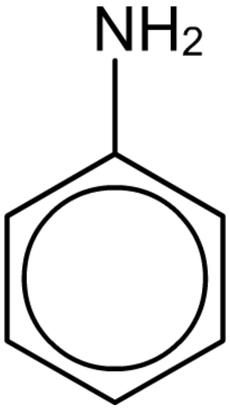
Aliphatic and aromatic amines

Aliphatic amines have at least one alkyl group bonded to the nitrogen. The lone pair of electrons on the nitrogen means that aliphatic amines behave similarly to ammonia:



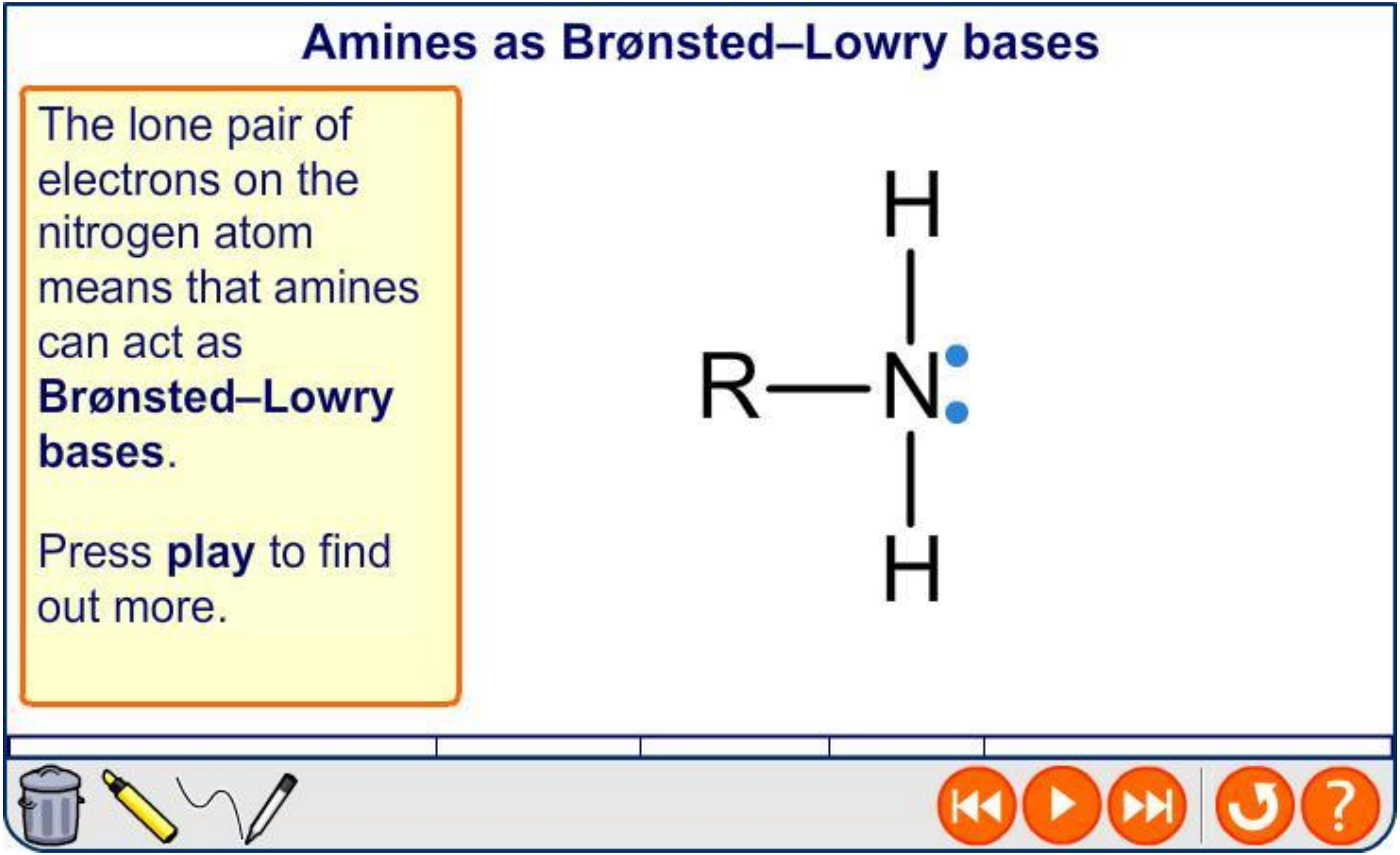
- they act as **nucleophiles** and take part in reactions involving donation of the lone pair
- they act as **Brønsted–Lowry bases** (H^+ acceptors).

Aromatic amines contain a benzene ring directly attached to the NH_2 group.



The delocalized system of the benzene group is able to incorporate the lone pair of electrons from the nitrogen atom, meaning that aromatic amines have different properties to aliphatic amines.

Amines as Brønsted–Lowry bases



Amines as Brønsted–Lowry bases

The lone pair of electrons on the nitrogen atom means that amines can act as **Brønsted–Lowry bases**.

Press **play** to find out more.

Relative base strength

Aliphatic amines are stronger bases (lower pK_b) than ammonia.

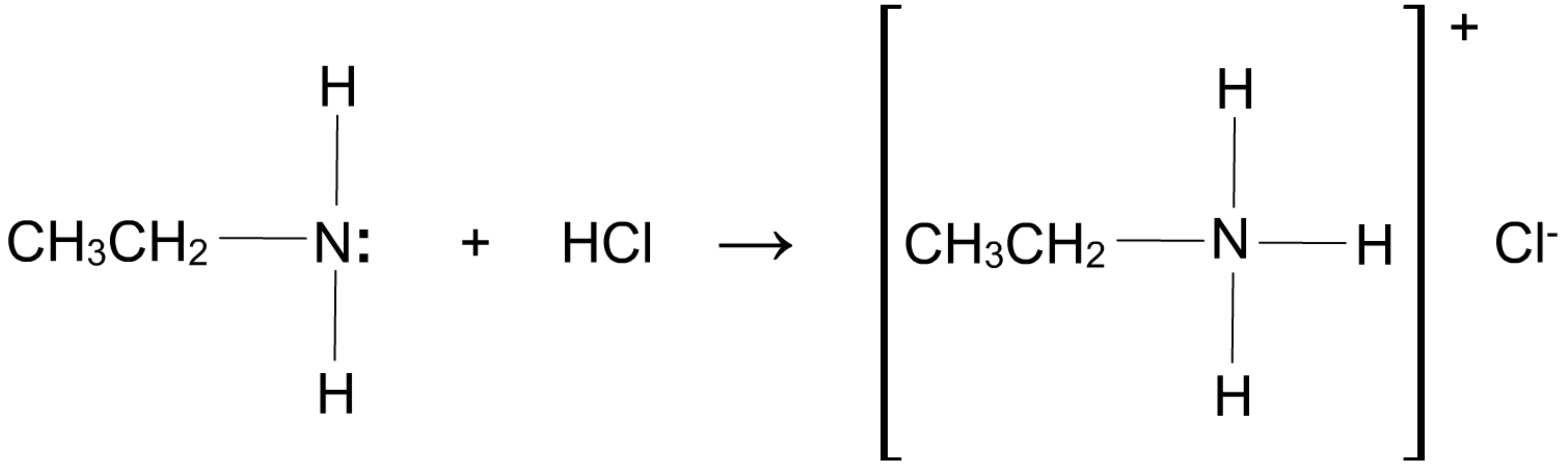
This is because alkyl groups repel electrons, leading to an increase in negative charge around the nitrogen so that it more readily attracts and accepts an H^+ ion. This means, 2° amines are more basic than 1° amines, and 3° amines are more basic still.

Compound	**pK_b**
NH_3	4.75
CH_3NH_2	3.36
$(CH_3)_2NH$	3.27
$C_6H_5NH_2$	9.38

Phenylamine is less basic than ammonia because the phenyl ring is an **electron-withdrawing** group. The lone pair of electrons interact with the delocalized electrons in the ring, and so are less readily donated to an H^+ ion.

Reactions of amines as bases

Amines accept protons (H^+) from acids to form salts:



$$CH_3CH_2NH_2 + HCl \rightarrow [CH_3CH_2NH_3]^+ Cl^-$$

ethylamine

ethylammonium chloride

If the reaction is carried out in solution, the amine accepts an H^+ from a hydroxonium ion to form an ionic salt and water (a neutralization reaction):

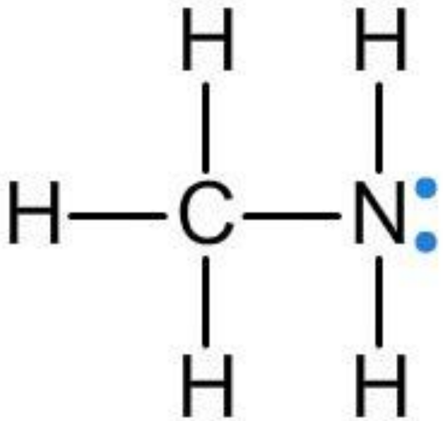
$$\mathbf{CH_3CH_2NH_{2(aq)} + H_3O^+_{(aq)} + Cl^-_{(aq)} \rightarrow CH_3CH_2NH_3^+Cl^-_{(aq)} + H_2O_{(l)}}$$

Reaction with halogenoalkanes

Amines as nucleophiles

Aliphatic amines act as **nucleophiles**, attacking and substituting the halogen atom in a halogenoalkane.

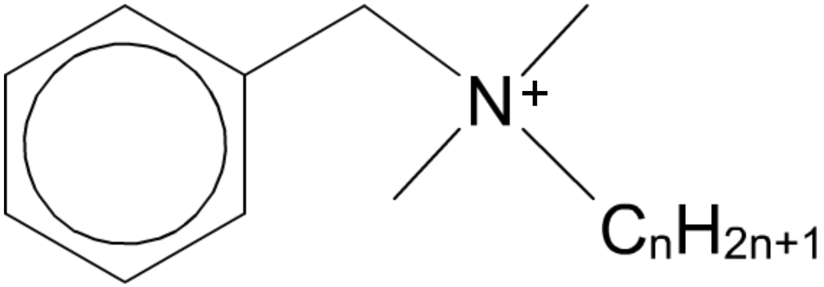
Press **play** to find out how this occurs.



Uses of quaternary ammonium salts

Quaternary ammonium salts are salts of a quaternary ammonium cation (NR_4^+) and an anion.

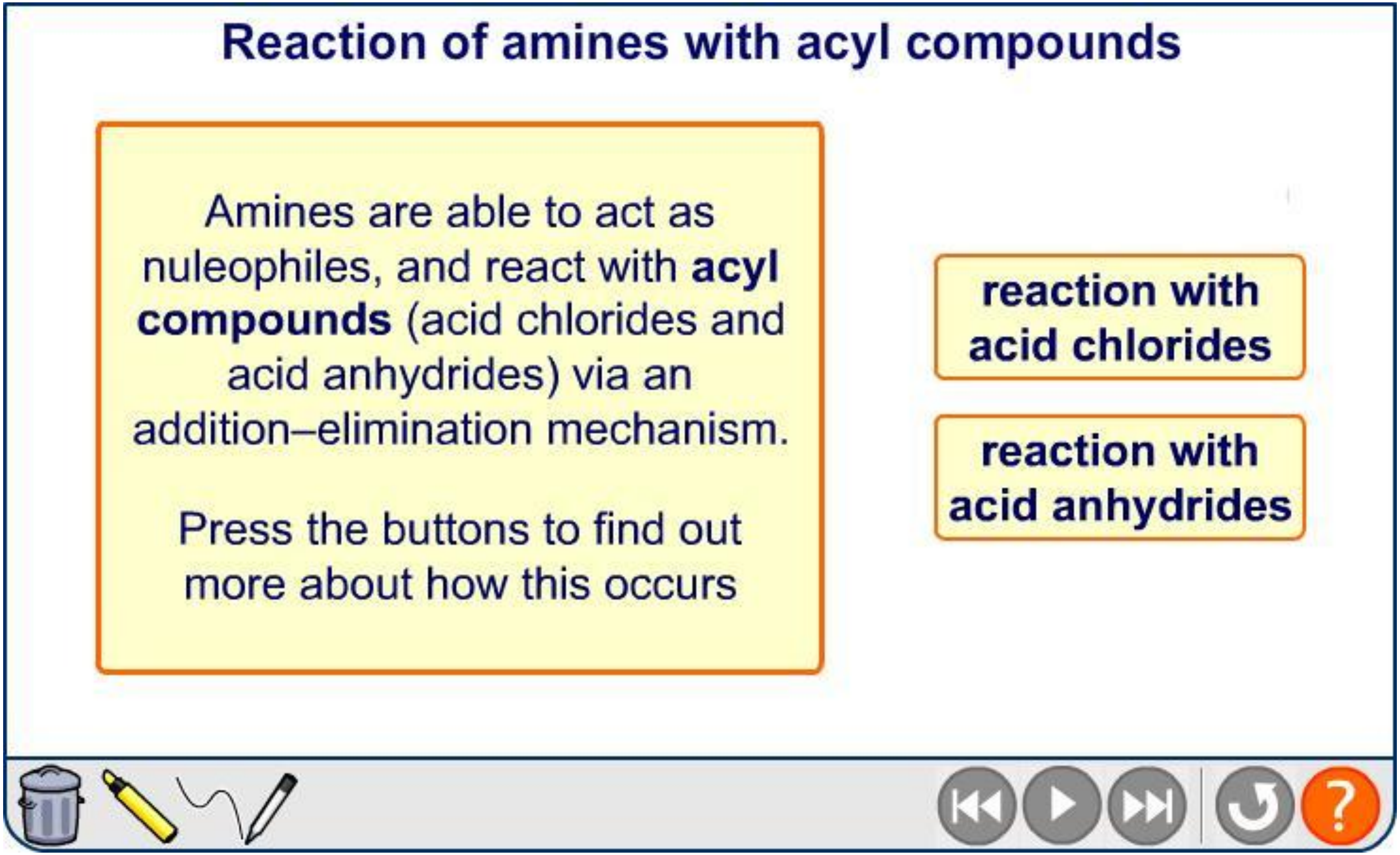
They are used as **cationic surfactants** in products such as fabric conditioner and shampoo. Their purpose is to smooth fabric or hair, making them softer, by reducing surface tension.



n = 8, 10, 12, 14, 16, 18

Other quaternary ammonium salts, similar to those shown *left*, are used as **antiseptics** in products such as wet wipes.

Reaction with acyl compounds



Reaction of amines with acyl compounds

Amines are able to act as nuleophiles, and react with **acyl compounds** (acid chlorides and acid anhydrides) via an addition–elimination mechanism.

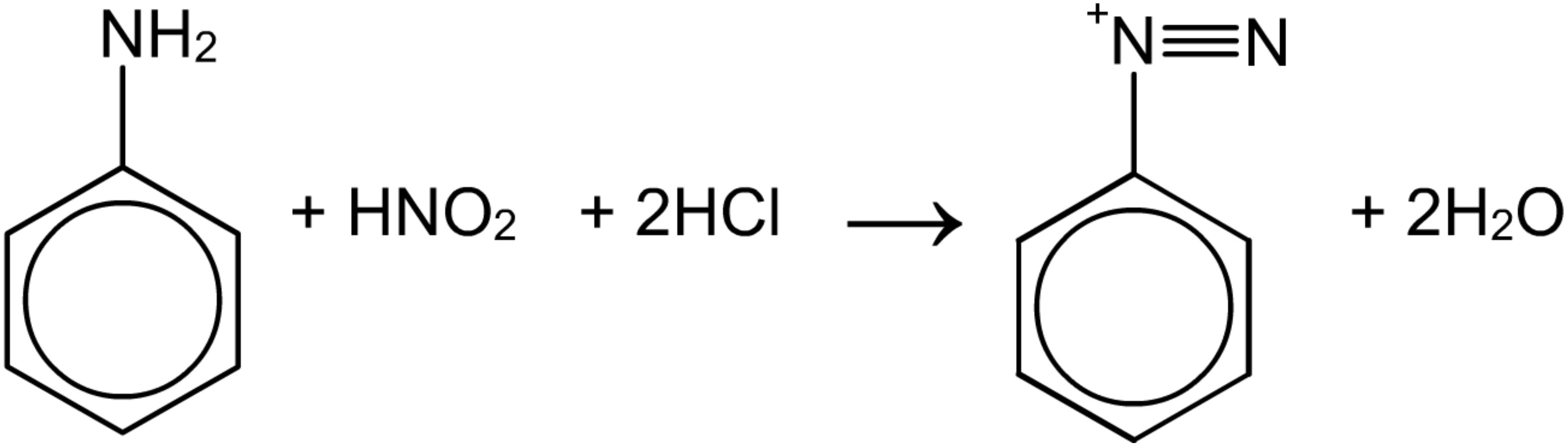
Press the buttons to find out more about how this occurs

reaction with acid chlorides

reaction with acid anhydrides

Synthesis of diazonium salts

An aromatic amine can be reacted with nitrous acid (HNO_2) to produce a diazonium ion:

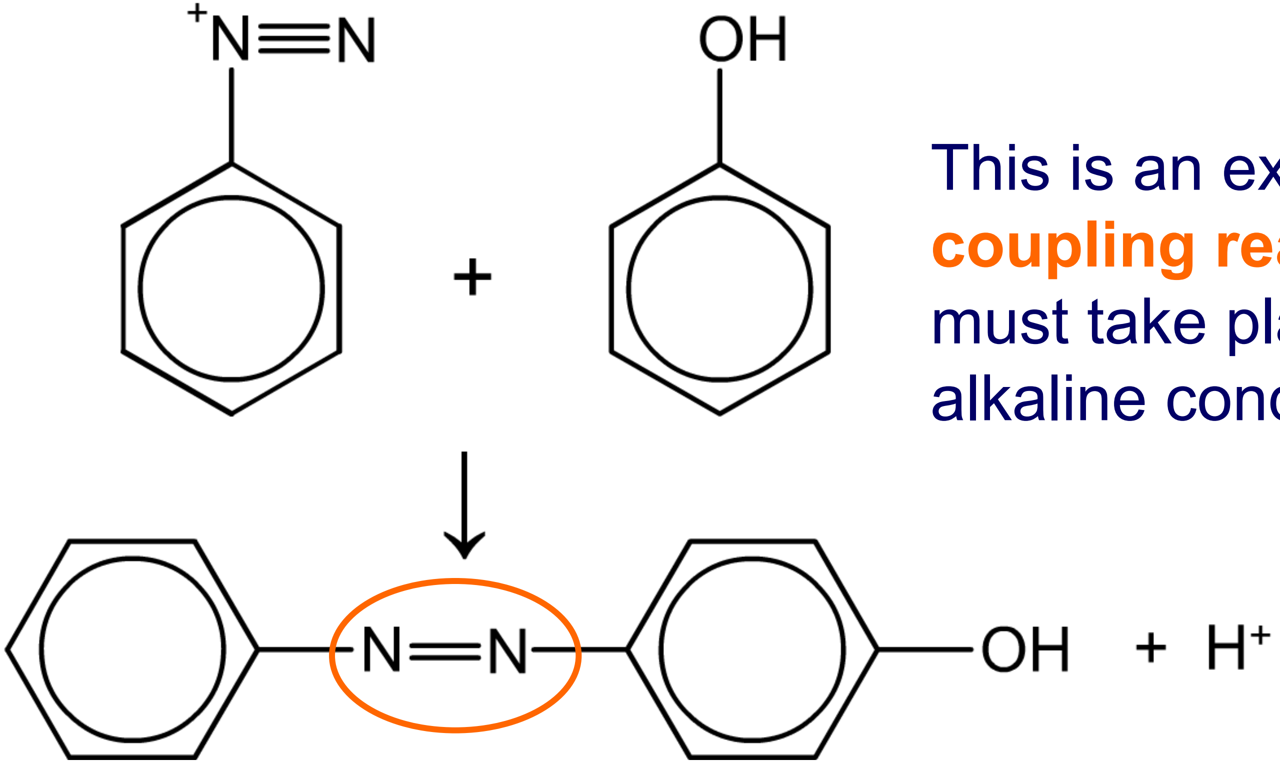


benzenediazonium chloride

The diazonium ion is very unstable, so the temperature of the reaction mixture must be kept below 10 °C in order to prevent the ion from decomposing.

Coupling reactions

The positive charge of the nitrogen makes the diazonium ion an electrophile, which is able to undergo electrophilic substitution with a benzene ring.



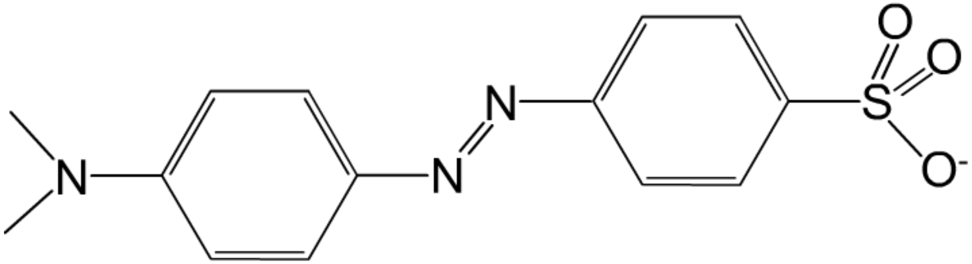
This is an example of a **coupling reaction**. It must take place under alkaline conditions.

The product is an **azo compound**.

Uses of azo compounds

Azo compounds are highly coloured. They are also stable and resistant to fading, and so are important in the **dye** industry.

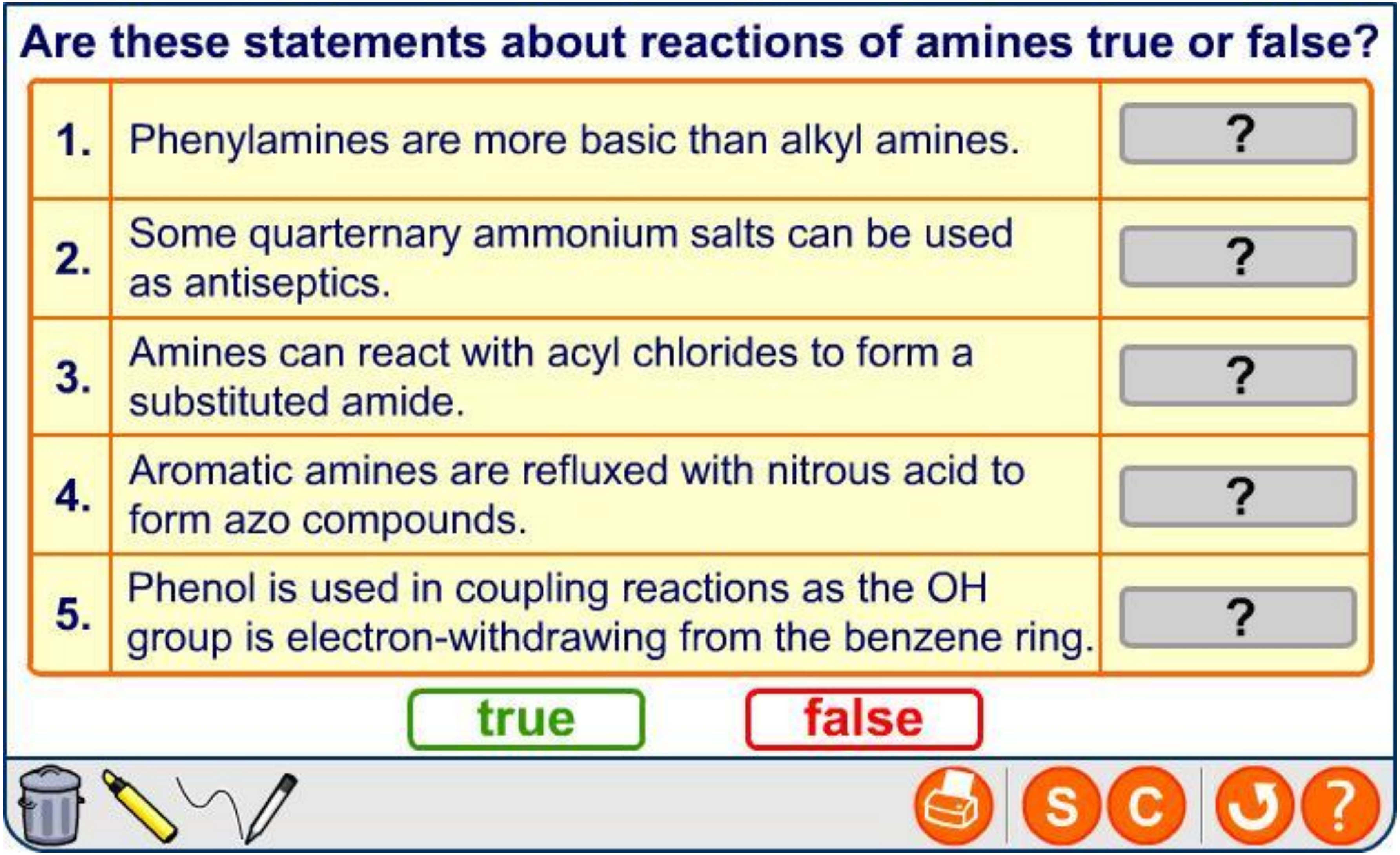
The colour results from the joining of the two delocalized electron systems via the N=N group. Colour can be altered by changing the number and type of functional groups attached.



methyl orange

Methyl orange indicator is an azo compound. The colour of the molecule changes when H^+ ions are added across the N=N bond.

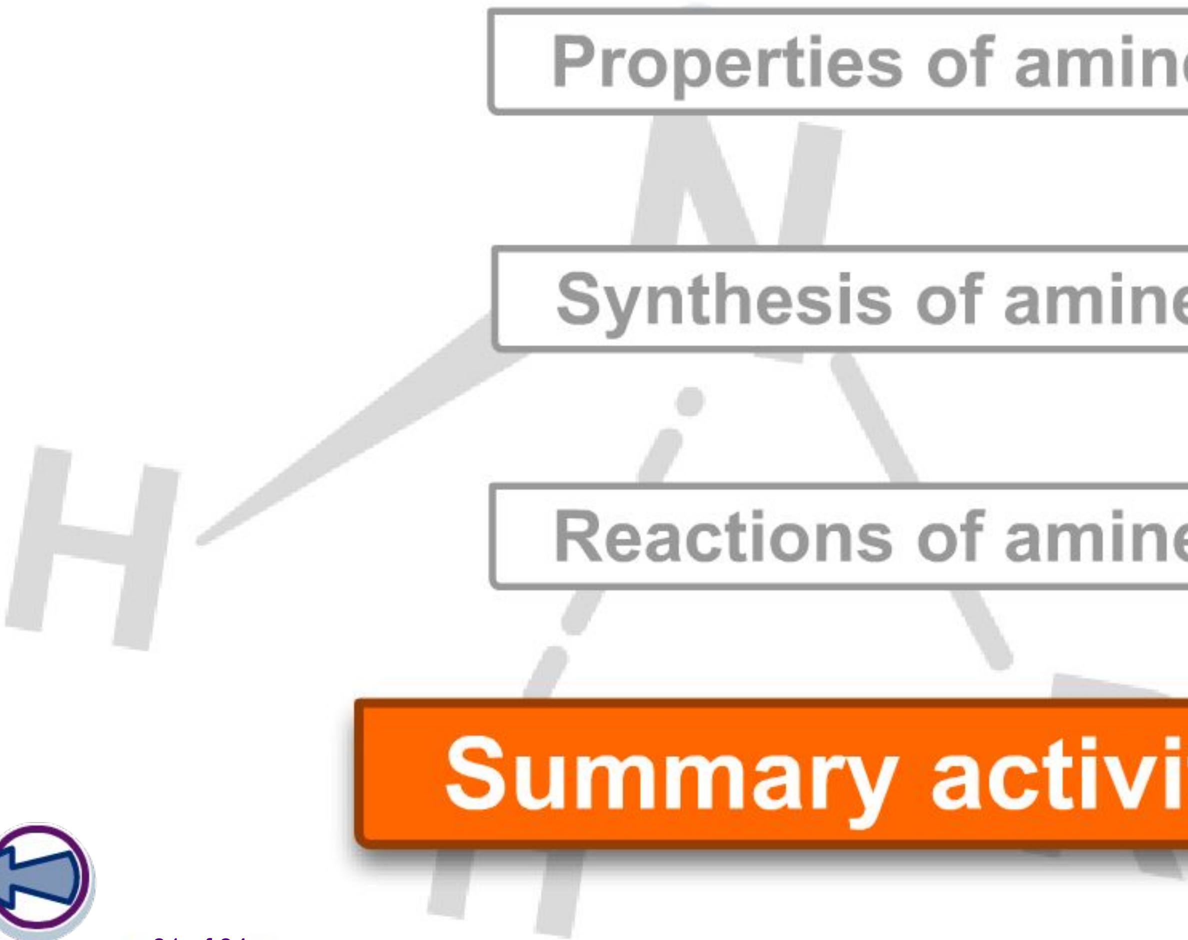
Reactions of amines: true or false?



Are these statements about reactions of amines true or false?

1.	Phenylamines are more basic than alkyl amines.	?
2.	Some quarternary ammonium salts can be used as antiseptics.	?
3.	Amines can react with acyl chlorides to form a substituted amide.	?
4.	Aromatic amines are refluxed with nitrous acid to form azo compounds.	?
5.	Phenol is used in coupling reactions as the OH group is electron-withdrawing from the benzene ring.	?

Amines



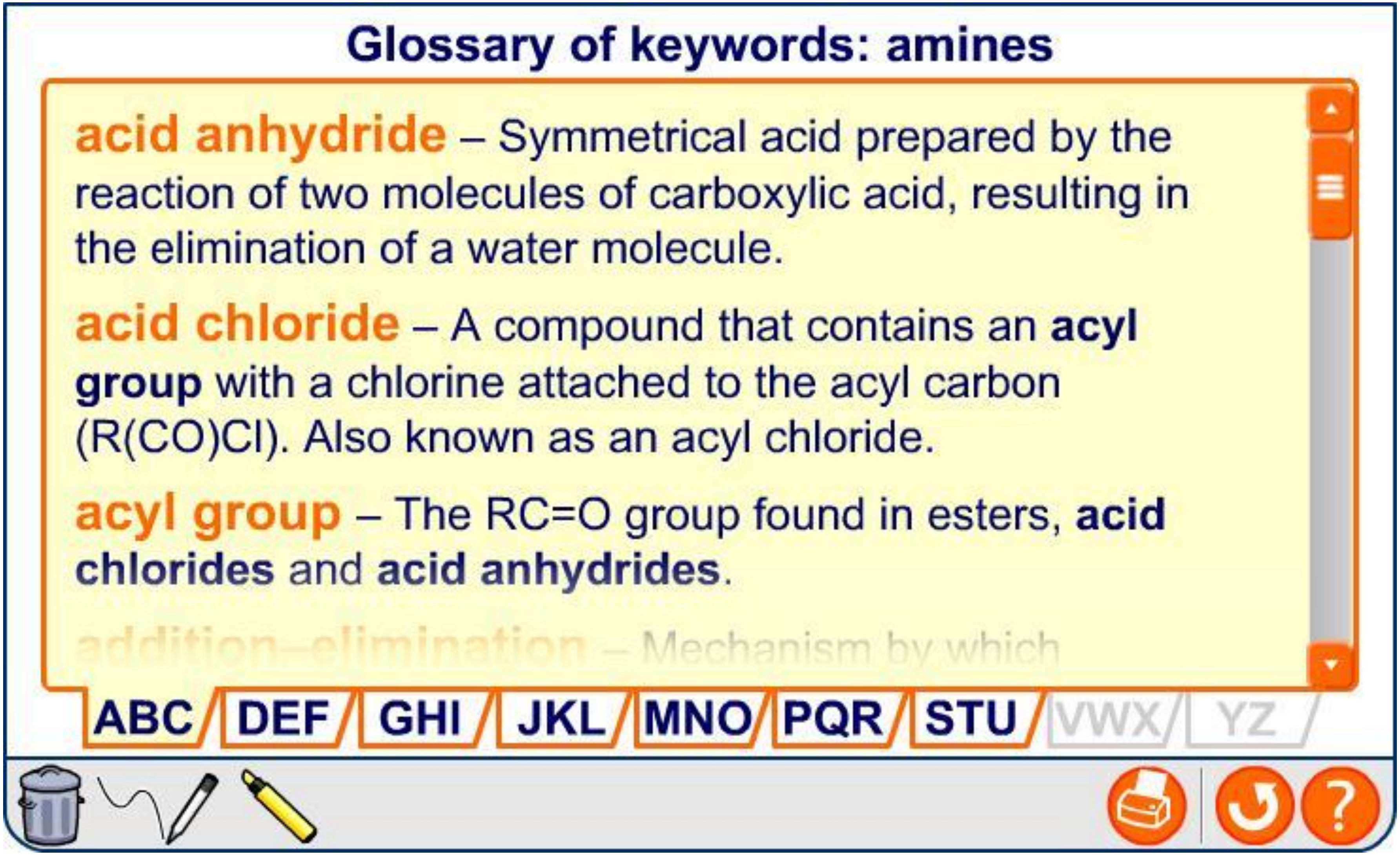
Properties of amines

Synthesis of amines

Reactions of amines

Summary activities

Glossary



Glossary of keywords: amines

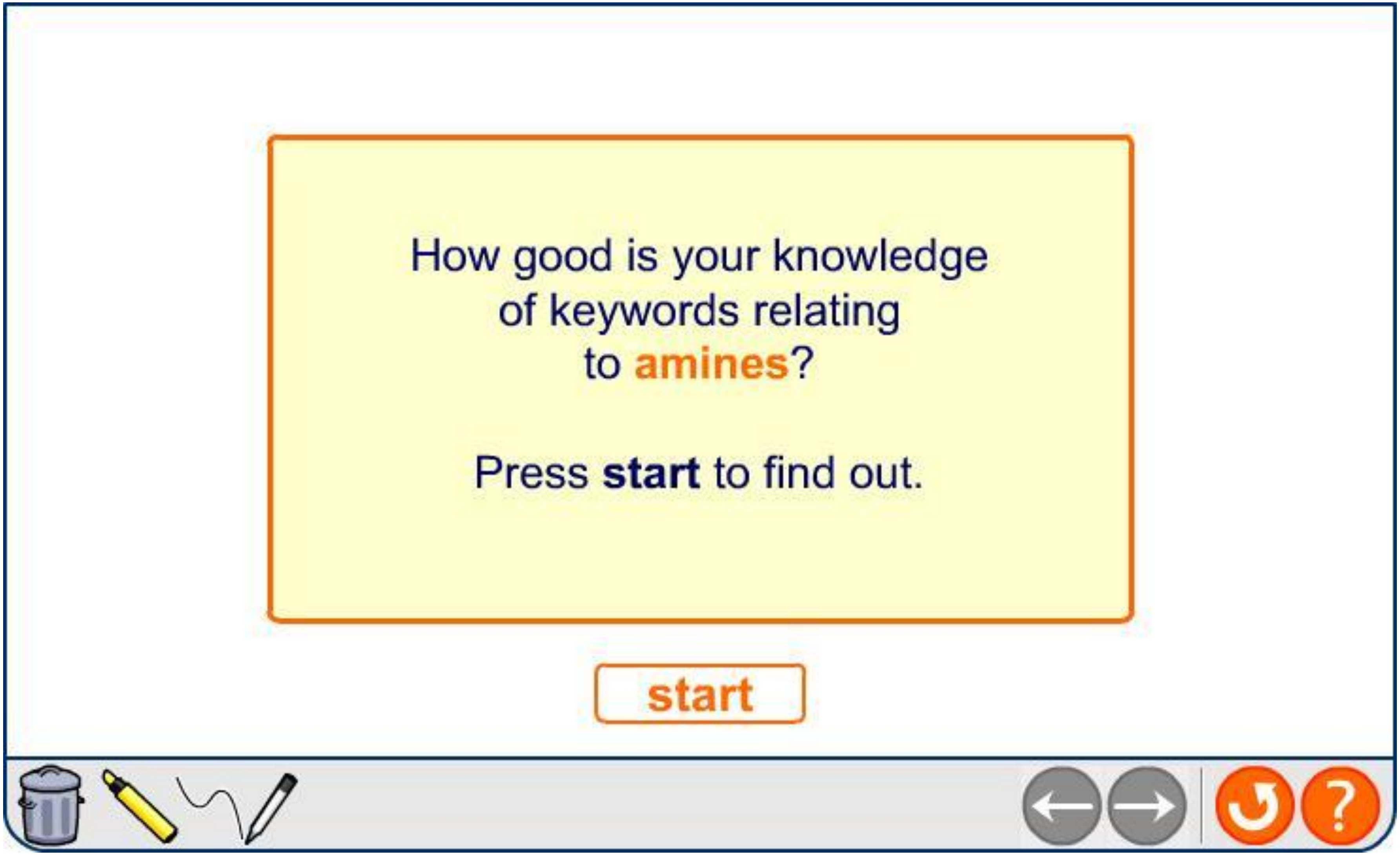
acid anhydride – Symmetrical acid prepared by the reaction of two molecules of carboxylic acid, resulting in the elimination of a water molecule.

acid chloride – A compound that contains an **acyl group** with a chlorine attached to the acyl carbon (R(CO)Cl). Also known as an acyl chloride.

acyl group – The RC=O group found in esters, **acid chlorides** and **acid anhydrides**.

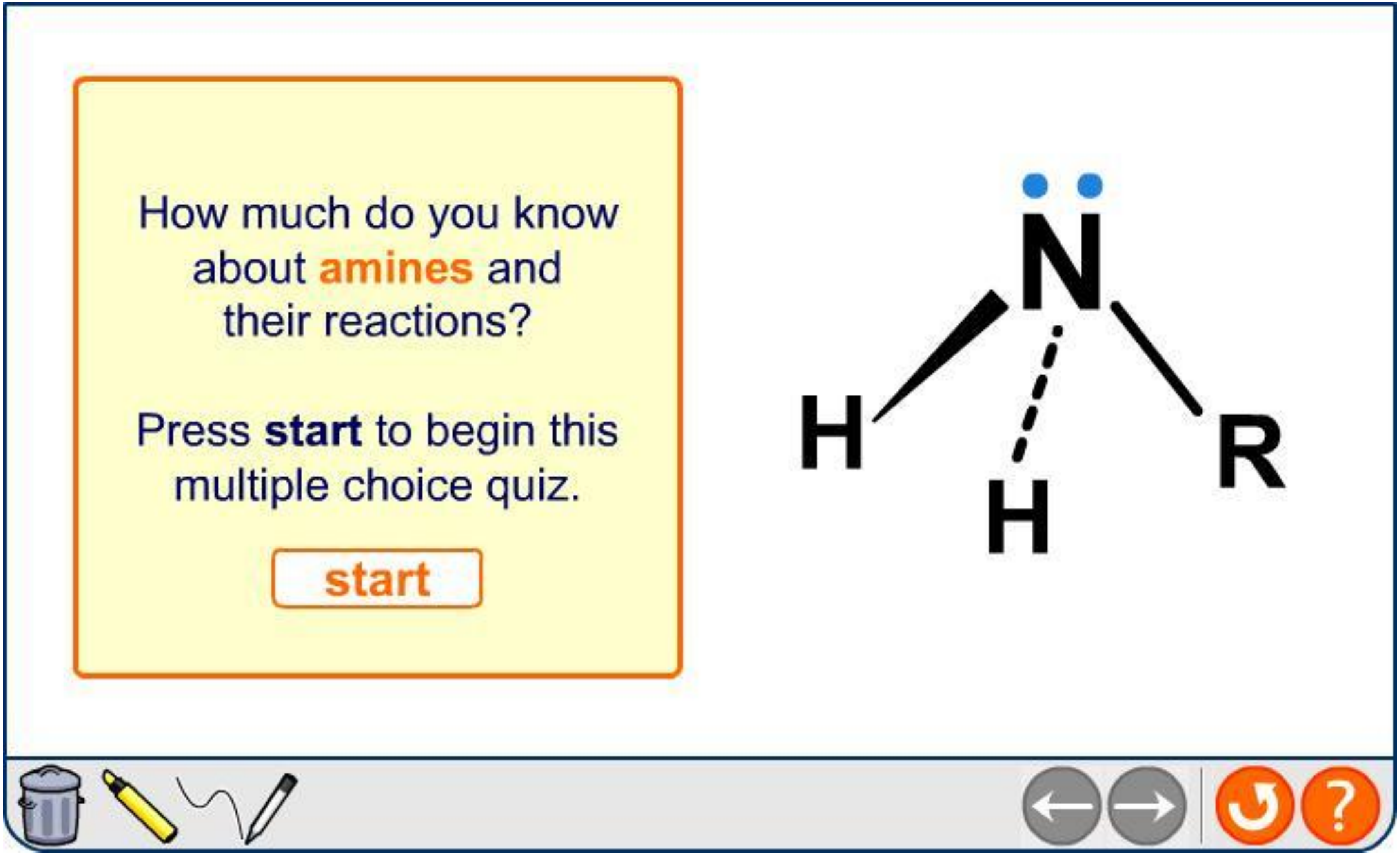
addition–elimination – Mechanism by which

What’s the keyword?


How good is your knowledge
of keywords relating
to **amines**?

Press **start** to find out.

Multiple-choice quiz



How much do you know about **amines** and their reactions?

Press **start** to begin this multiple choice quiz.