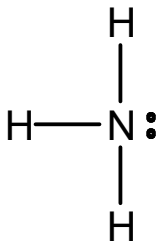
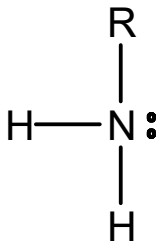
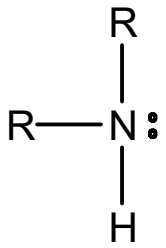
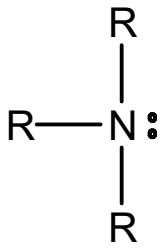
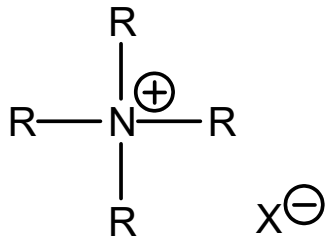
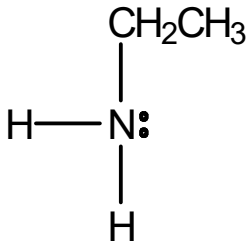
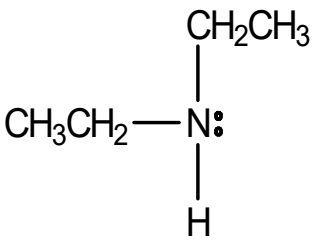
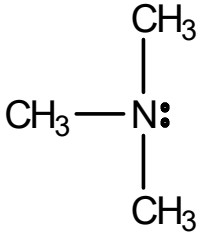
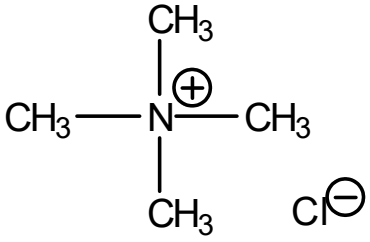
WWW.CHEMSHEETS.CO.UK

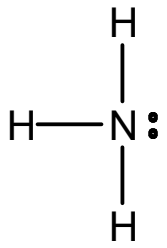
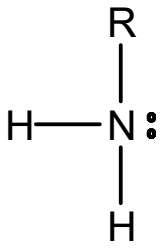
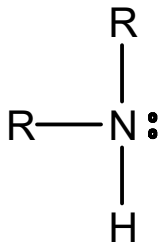
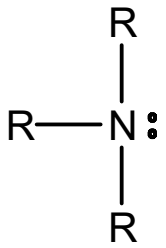
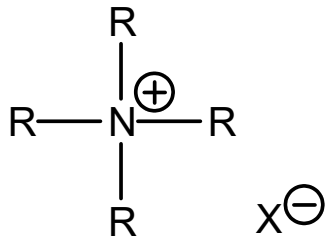
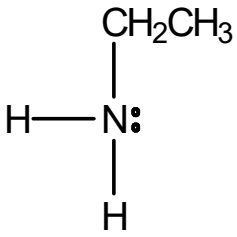
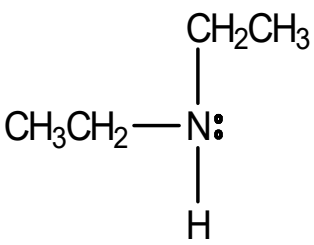
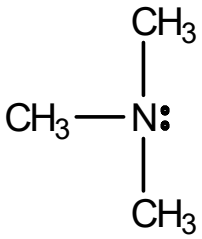
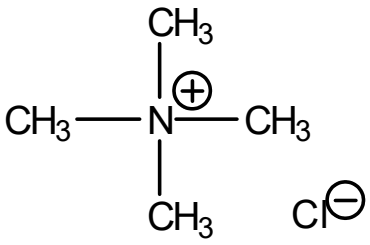
AMINES

TYPES OF AMINES

ammonia	1ʸ amine	2ʸ amine	3ʸ amine	4ʸ ammonium salts
				
				

NOT AMINES

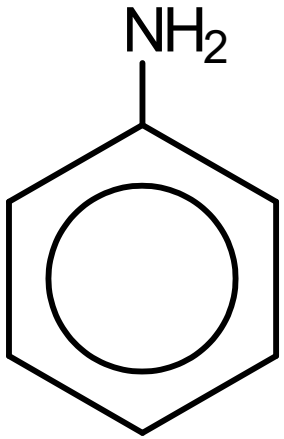
TYPES OF AMINES

ammonia	1ʸ amine	2ʸ amine	3ʸ amine	4ʸ ammonium salts
				
				
	ethylamine (ethanamine)	**diethylamine (N-ethyl ethanamine)**	**Trimethylamine (N,N-dimethyl methanamine)**	**tetramethylammonium chloride**

NOT AMINES

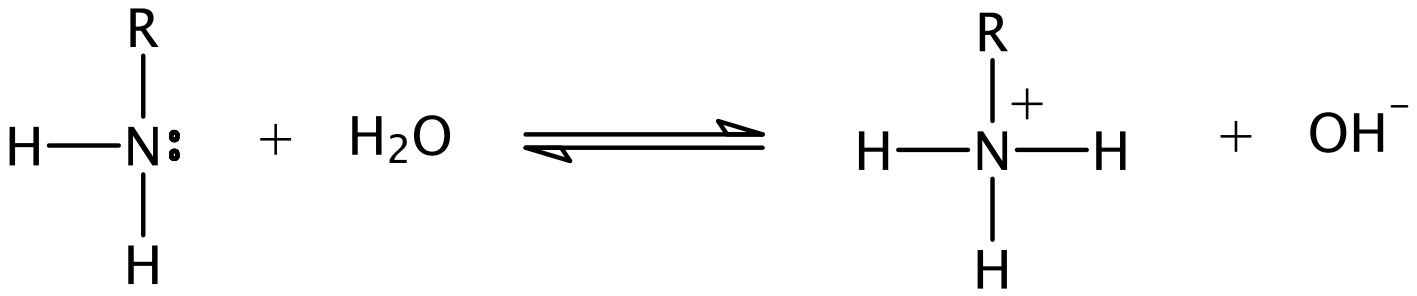
TYPES OF AMINES

- **There is some H-bonding between 1^{y} and 2^{y} amines.**
- **Quaternary ammonium salts are not amines.**
- **Aromatic amines have the N joined to the benzene ring, e.g. phenylamine.**



BASE STRENGTH OF AMINES

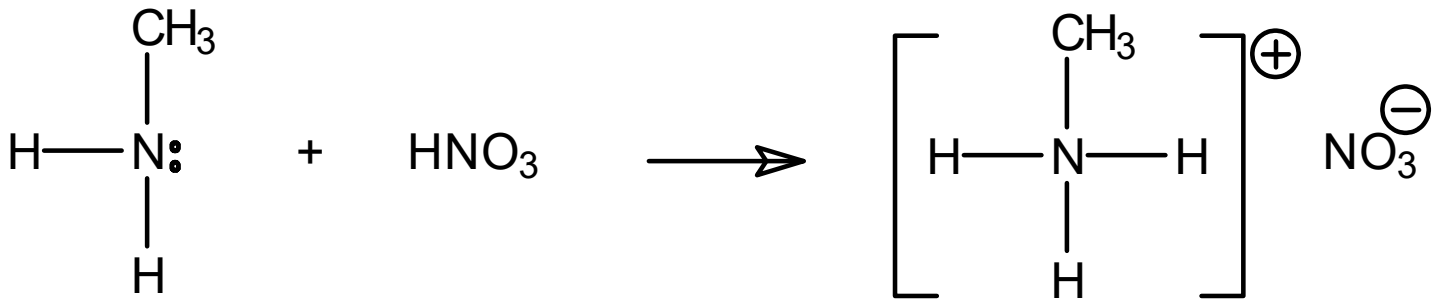
- **Amines are weak bases.**
- **Lone pair on N can accept a proton.**



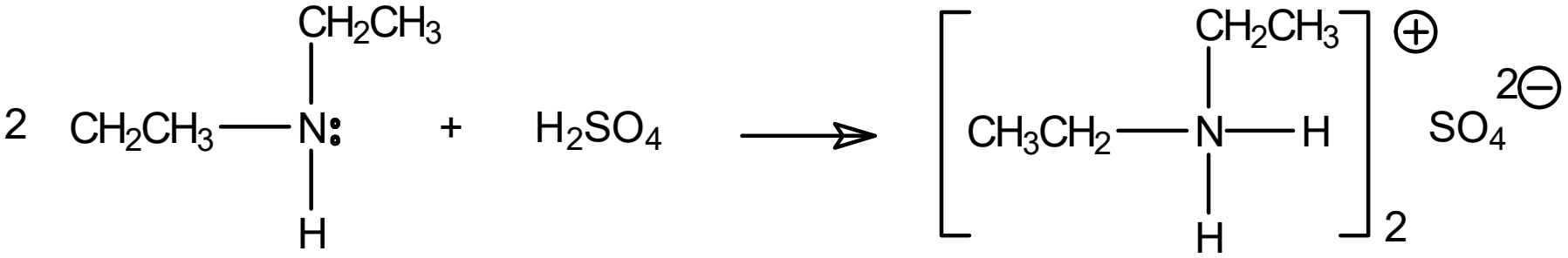
BASE STRENGTH OF AMINES

TASK 1

methylamine + nitric acid



diethylamine + sulfuric acid



BASE STRENGTH OF AMINES

- **Amines are weak bases.**
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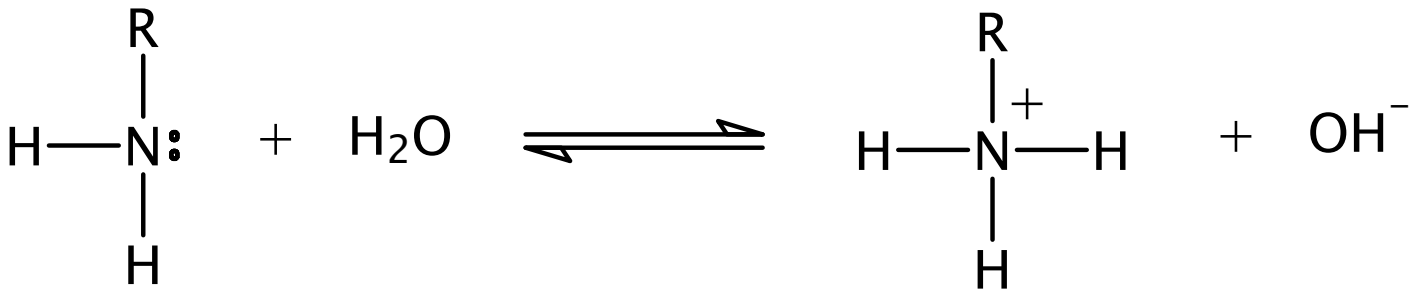
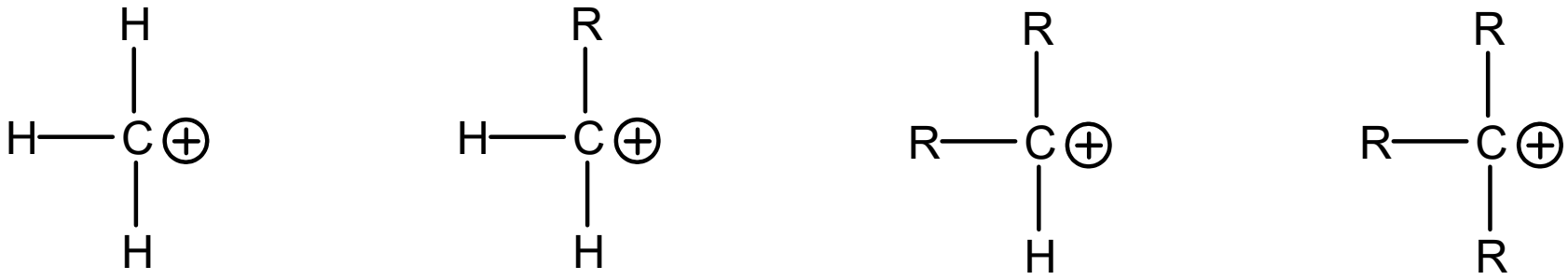


- **Base strength depends on how well N lone pair can accept H^+.**
- **The higher the electron density of the N lone pair, the stronger the base.**

BASE STRENGTH OF AMINES

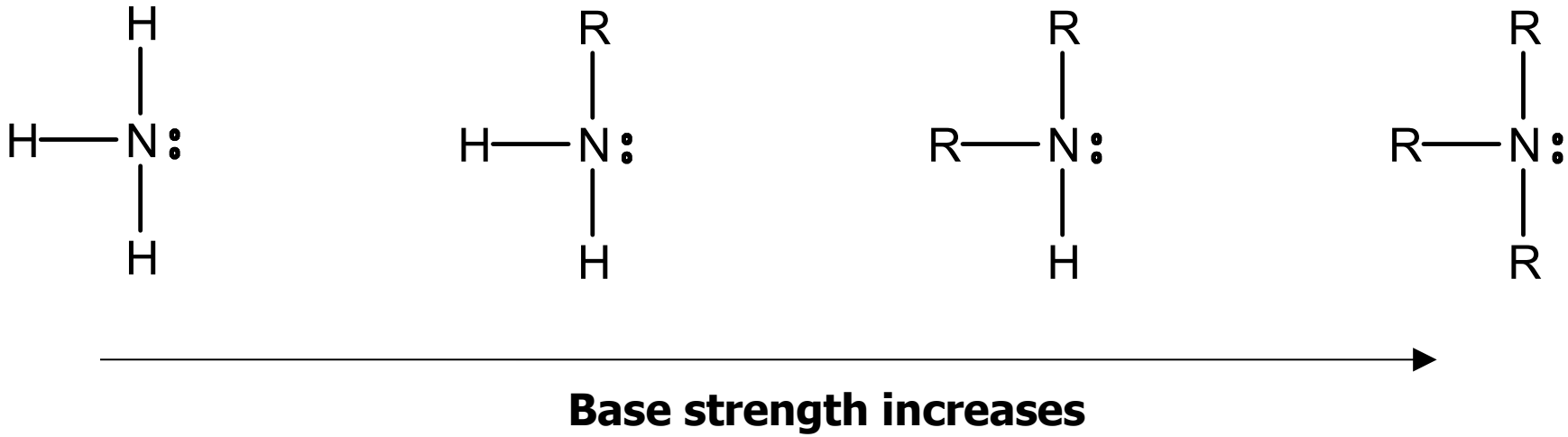
- **Alkyl groups push electrons towards the N better than H (remember carbocation stability).**



- **INDUCTIVE EFFECT of alkyl groups pushing away electron density more than H atoms**

BASE STRENGTH OF AMINES

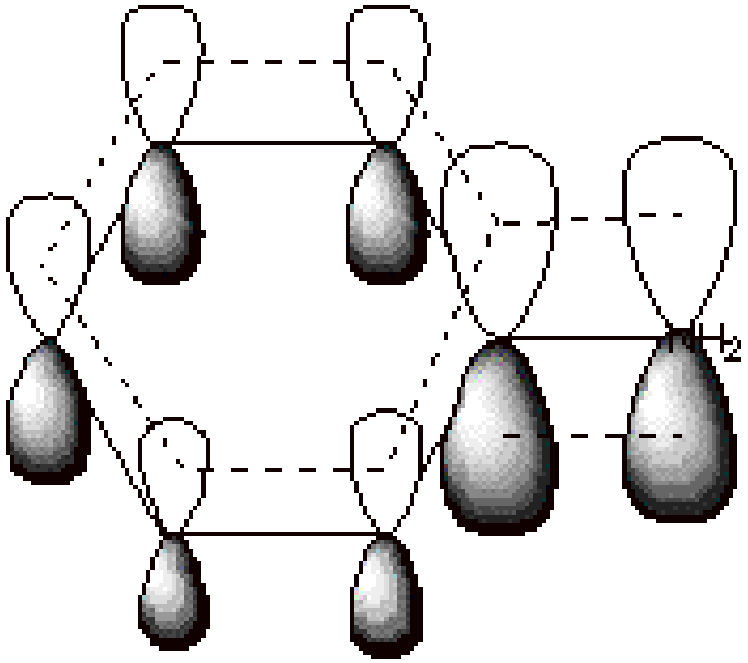
- **The more alkyl groups, the greater the inductive effect pushing electron density onto the N lone pair**



$3^y > 2^y > 1^y > NH_3$

BASE STRENGTH OF AMINES

- **In aromatic amines, the N lone pair is partially delocalised into the benzene ring, lowering the electron density on N lone pair, lowering the base strength.**

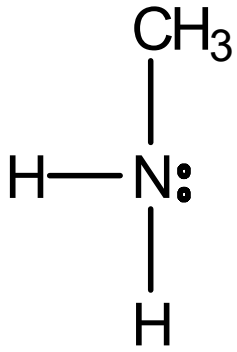


$3^y > 2^y > 1^y > NH_3 >$ aromatic

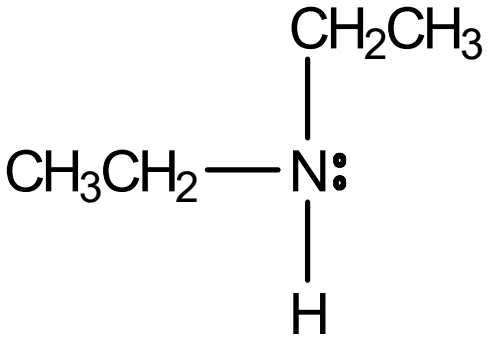
BASE STRENGTH OF AMINES

TASK 2

methylamine



diethylamine



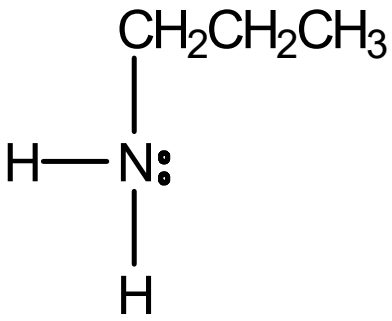
Stronger base = diethylamine

- 2^{Y} compared to 1^{Y}
- Extra inductive effect of two alkyl groups compared to one
- Diethylamine has greater electron density on N lone pair
- Diethylamine has greater ability to accept H^{+}

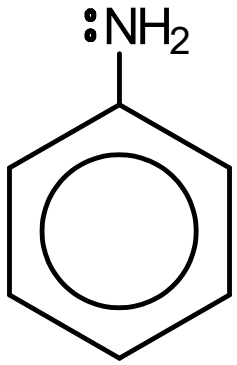
BASE STRENGTH OF AMINES

TASK 2

propylamine



phenylamine



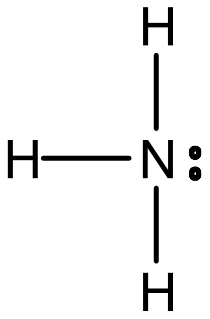
Stronger base = propylamine

- Lone pair on phenylamine N is partially delocalised into benzene ring
- Propylamine has greater electron density on N lone pair
- Propylamine has greater ability to accept H^+

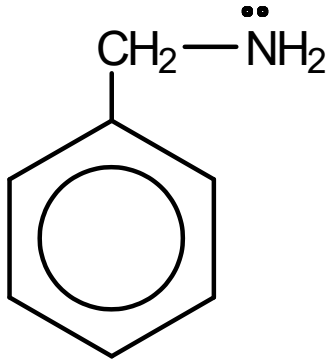
BASE STRENGTH OF AMINES

TASK 2

ammonia



phenylmethylamine



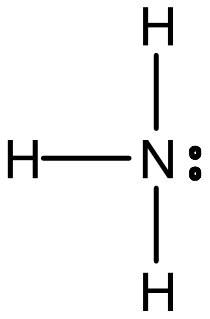
Stronger base = phenylmethylamine

- 1^{Y} compared to ammonia
- Inductive effect of an alkyl group compared to H
- Phenylmethylamine has greater electron density on N lone pair
- Phenylmethylamine has greater ability to accept H^{+}

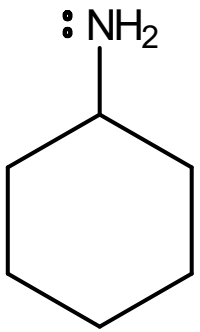
BASE STRENGTH OF AMINES

TASK 2

ammonia



cyclohexylamine

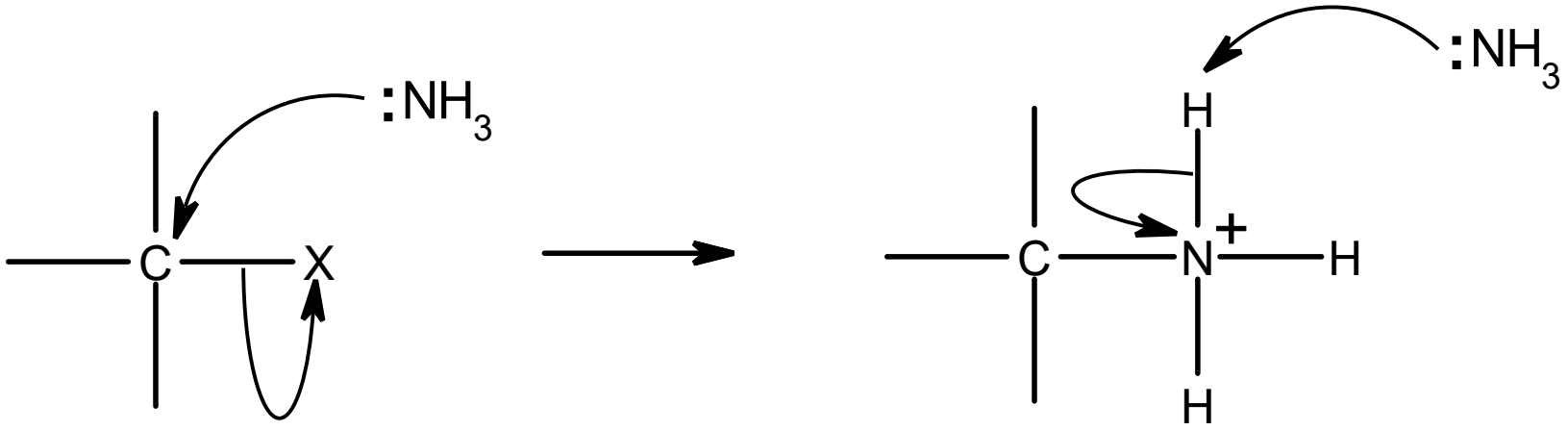


Stronger base = cyclohexylamine

- 1^{Y} compared to ammonia
- Inductive effect of an alkyl group compared to H
- Cyclohexylamine has greater electron density on N lone pair
- Cyclohexylamine has greater ability to accept H^{+}

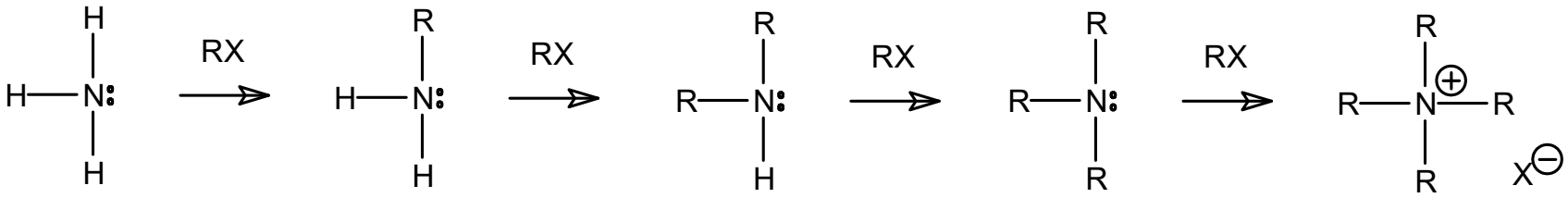
NUCLEOPHILIC SUBSTITUTION

- **Lone pair on N can attack δ+ C of haloalkane.**



NUCLEOPHILIC SUBSTITUTION

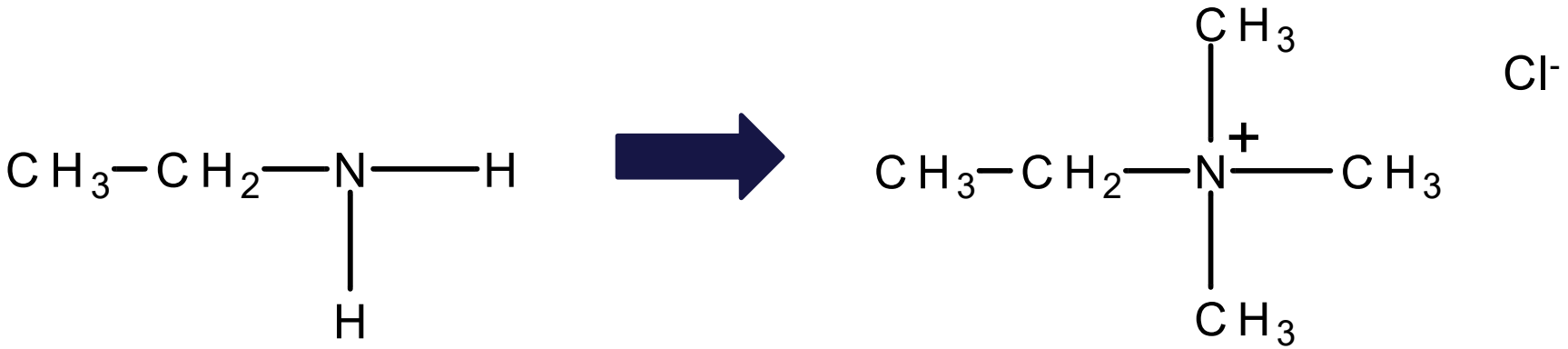
- **H on N is swapped by R from haloalkane.**
- **Product also has lone pair on N so product reacts further.**



- **To get mainly 1^{y} amine use XS NH_3.**
- **To get mainly 4^{y} ammonium salt use XS RX.**

NUCLEOPHILIC SUBSTITUTION

ethylamine + XS chloromethane

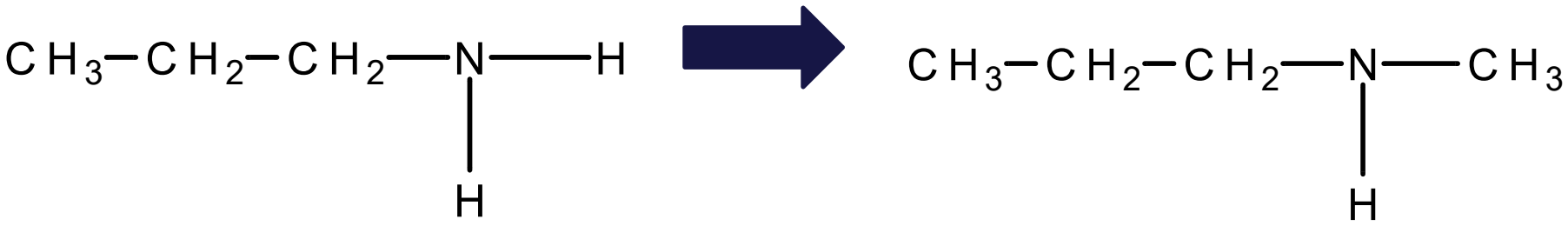


ethyltrimethylammonium chloride

TASK 3 Q1

NUCLEOPHILIC SUBSTITUTION

XS propylamine + chloromethane

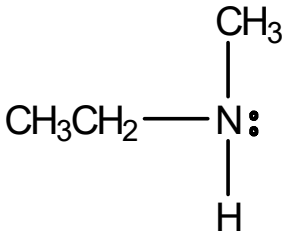


N-methylpropylamine
OR
(N-methyl propan-1-amine)

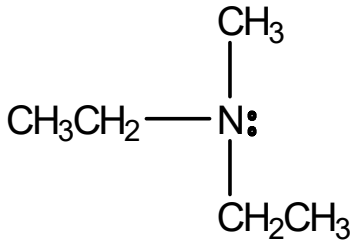
TASK 3
Q2

NUCLEOPHILIC SUBSTITUTION

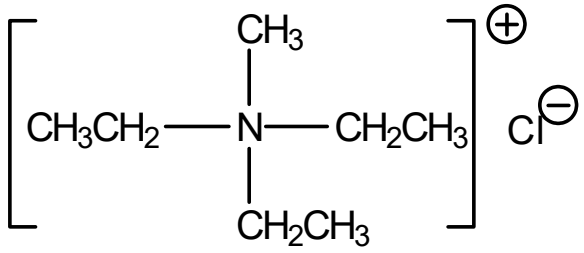
methylamine + chloroethane (products & 1st mechanism)



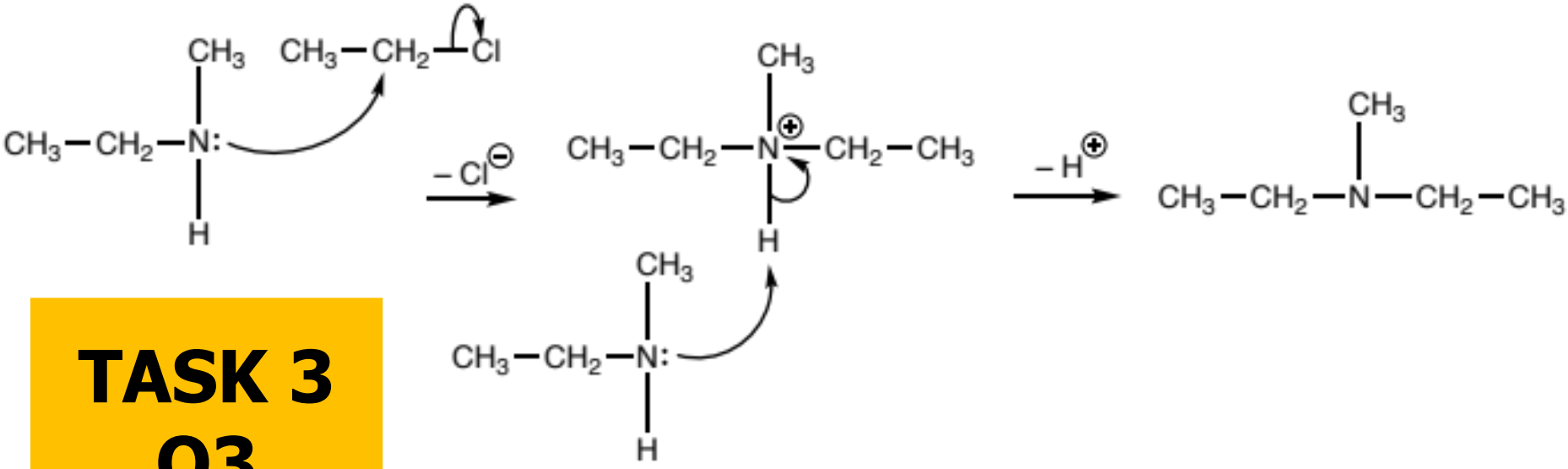
N-methyethylamine
or
N-methyl ethanamide



N-methydiethylamine
or
N-ethyl N-methyl ethanamide



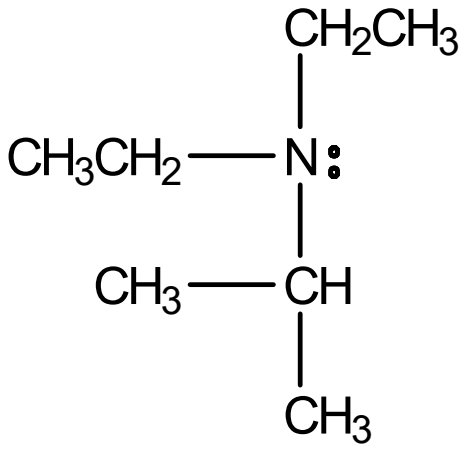
N-methytriethylammonium chloride

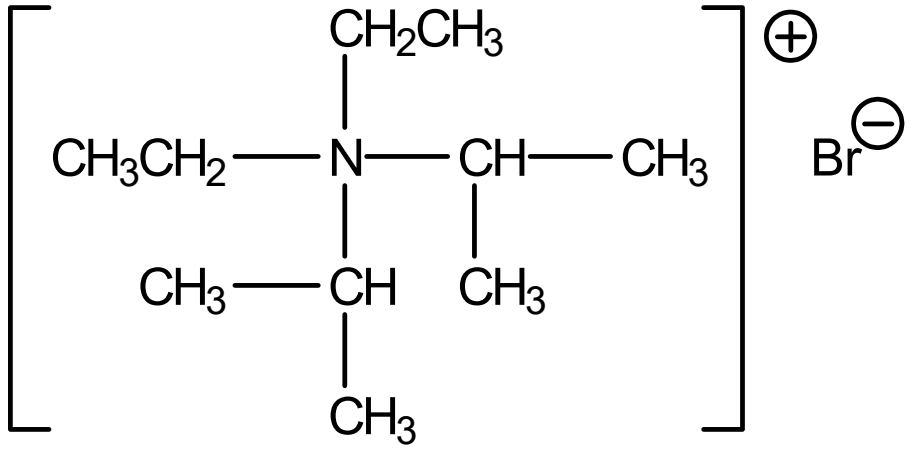


TASK 3 Q3

NUCLEOPHILIC SUBSTITUTION

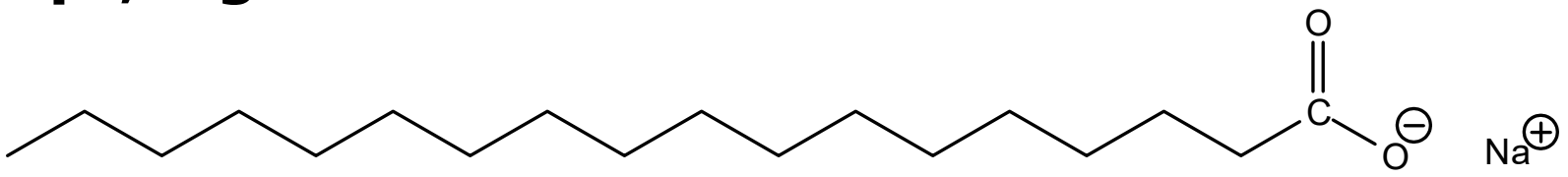
diethylamine + 2-bromopropane **(products)**





TASK 3
Q4

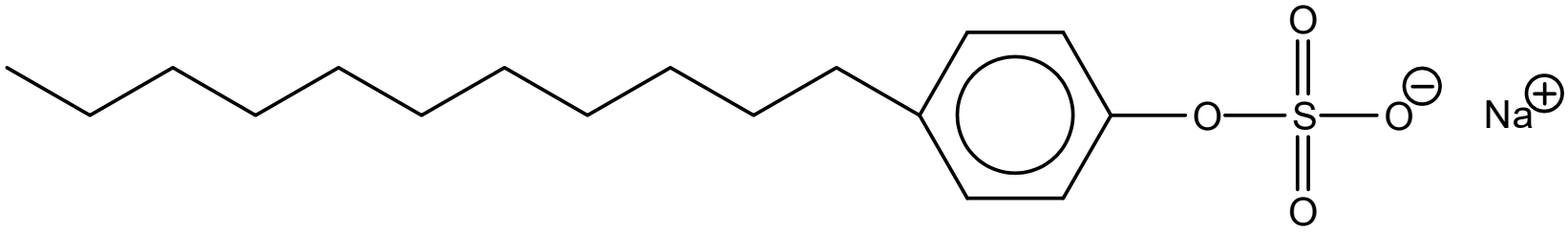
Soaps, e.g.



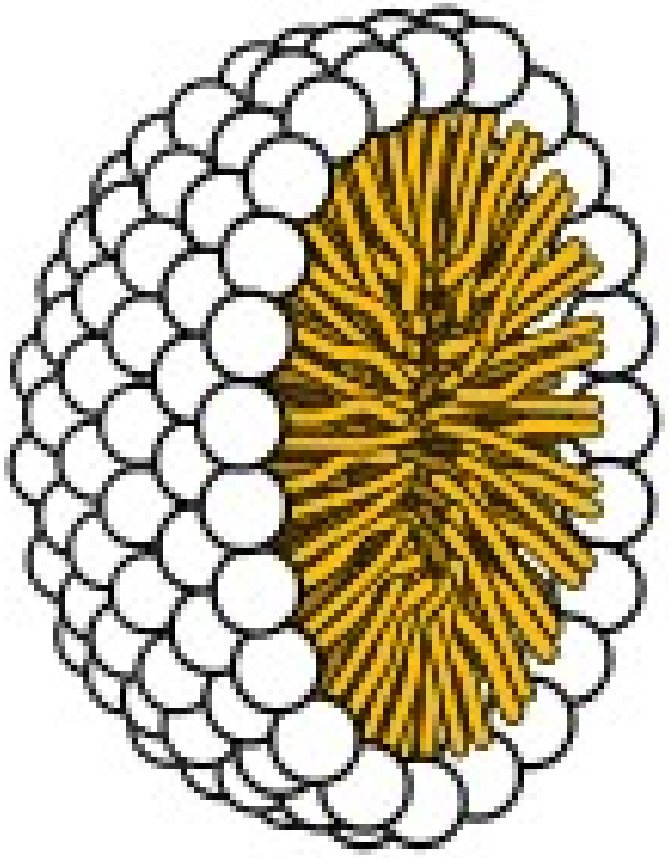
long alkyl tail
(hydrophobic)
dissolves grease

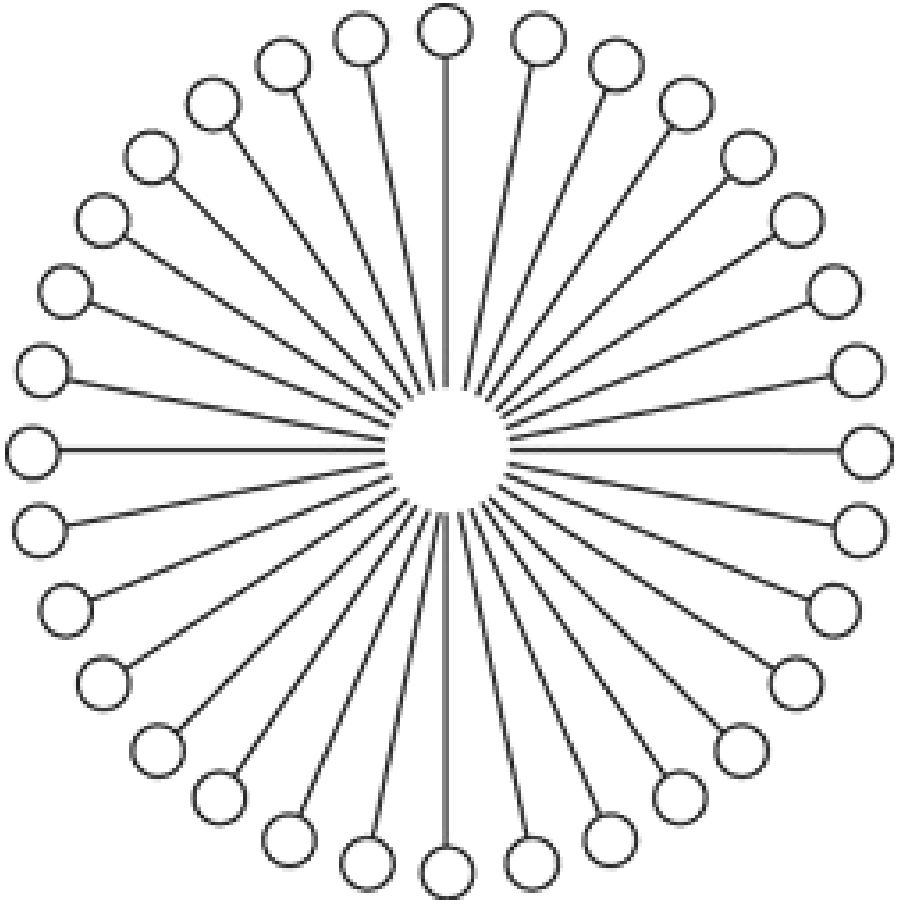
ionic head
(hydrophylic)
dissolves in water

Detergents, e.g.



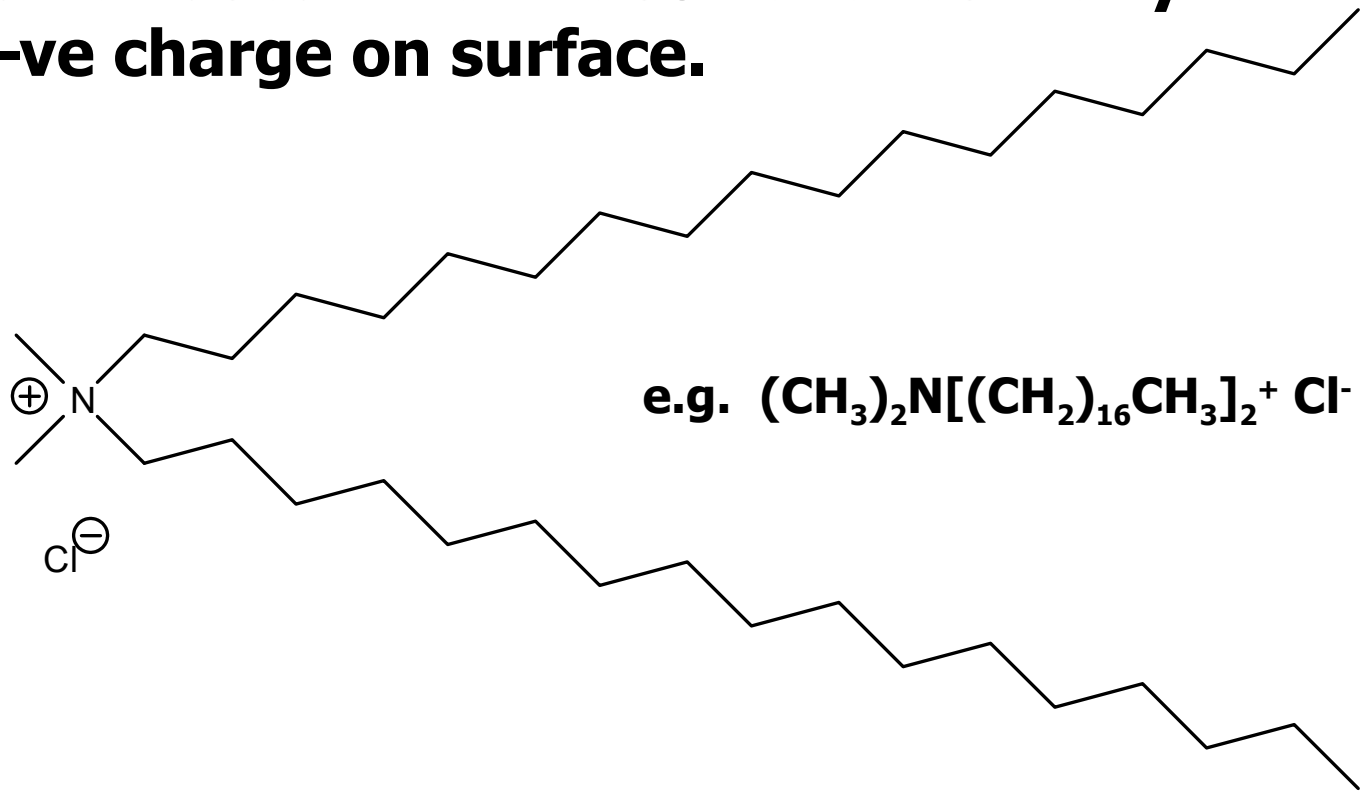
Micelle





4ʸ ammonium salts

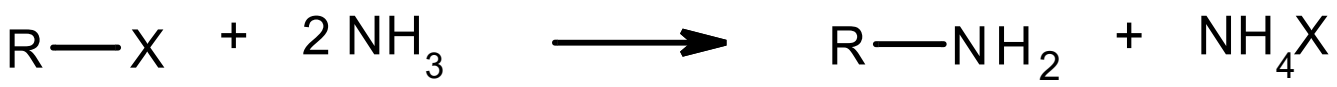
- **Ones with some long chain alkyl groups can be used as cationic surfactants.**
- **Often used in fabric softener as many fabrics have –ve charge on surface.**



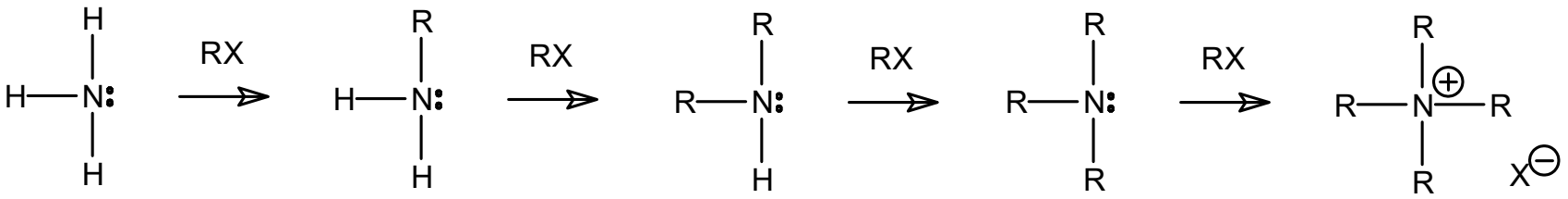
e.g. $(CH_3)_2N[(CH_2)_{16}CH_3]_2^+ Cl^-$

MAKING ALIPHATIC 1^{y} AMINES

1 – Reaction of NH_3 with halogenoalkanes

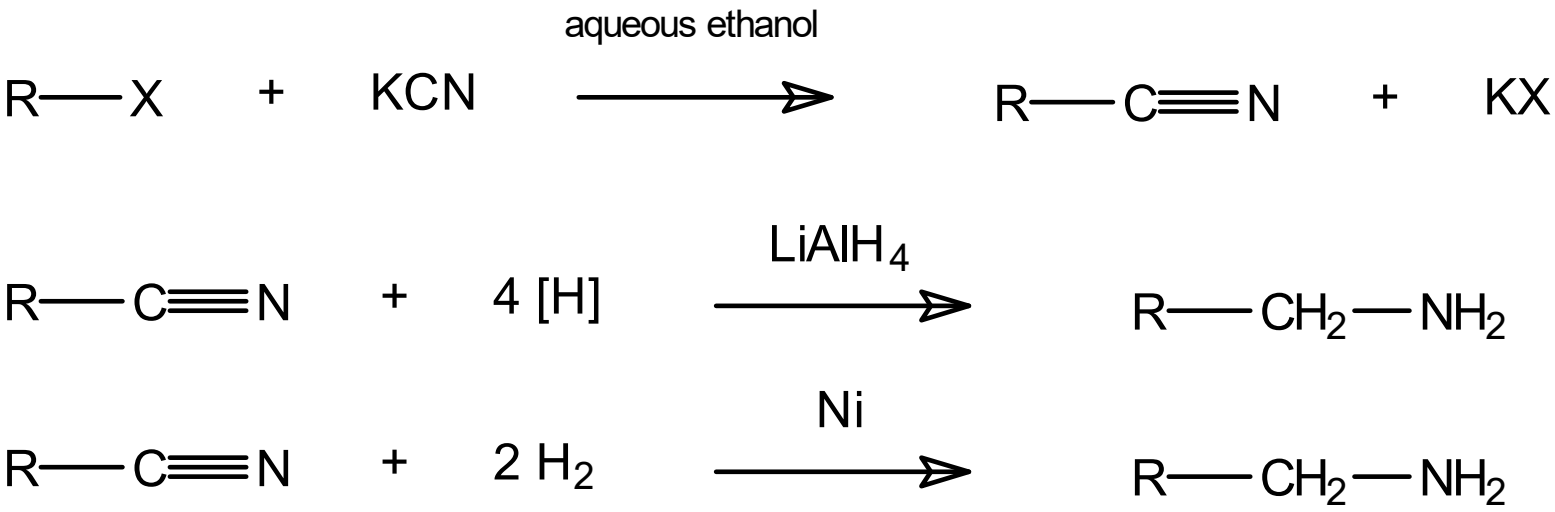


- **Products under further substitution**
- **Get a mixture of products so method rarely used**



MAKING ALIPHATIC 1^{y} AMINES

2 – Reduction of nitrile compounds

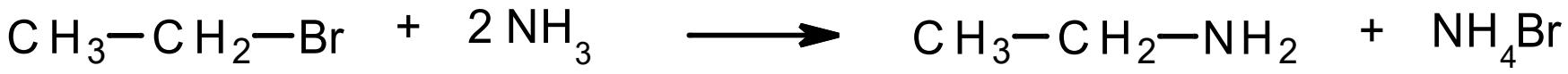


- **Preferred method – only one amine formed**

MAKING ALIPHATIC 1^{y} AMINES

e.g. ethylamine

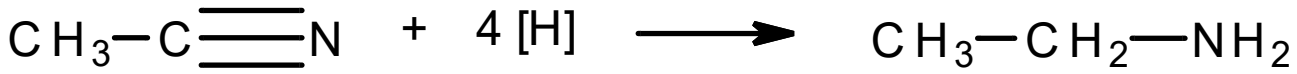
route 1



route 2

step 1

step 2

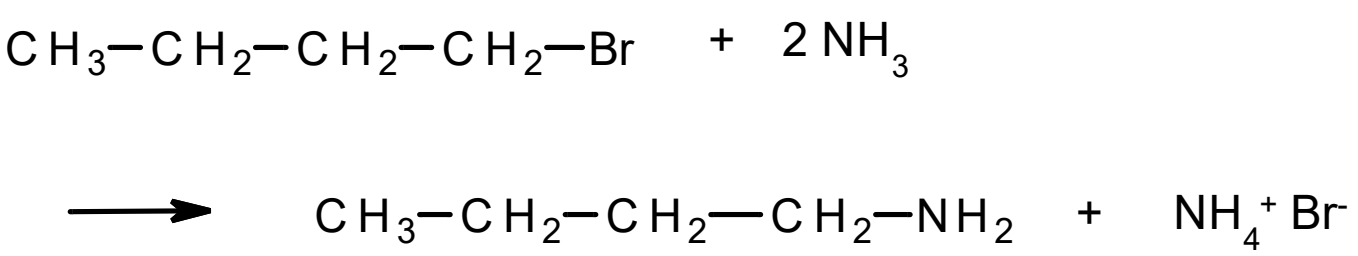


MAKING ALIPHATIC 1^{y} AMINES

TASK 4

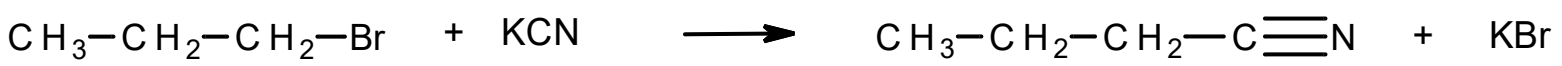
e.g. buylamine

route 1

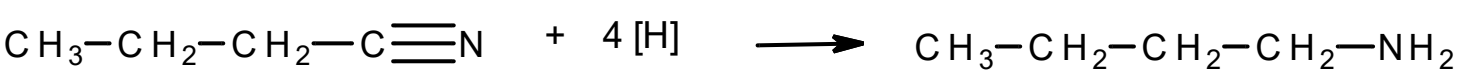


route 2

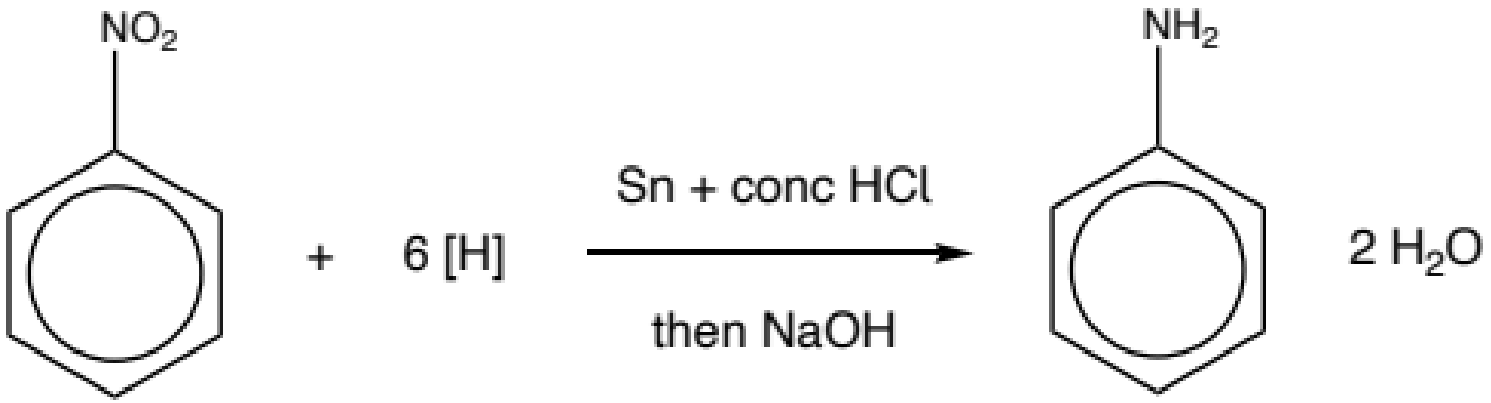
step 1



step 2

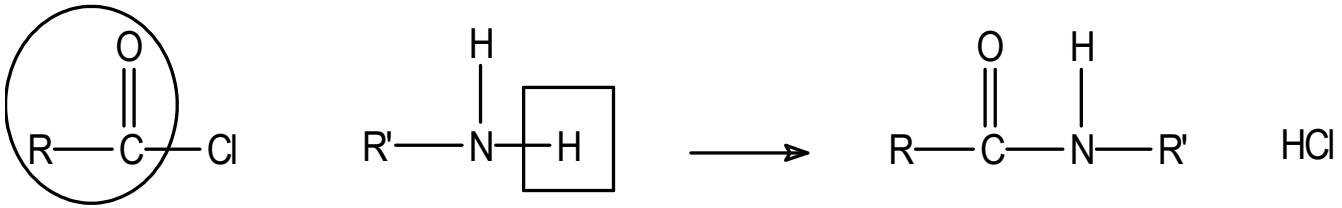


MAKING AROMATIC AMINES

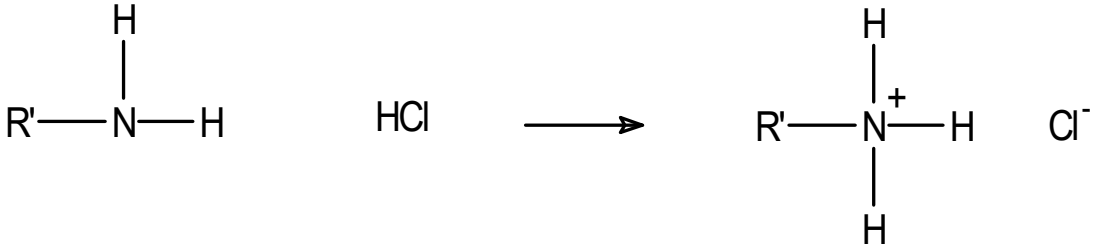


ACYLATION

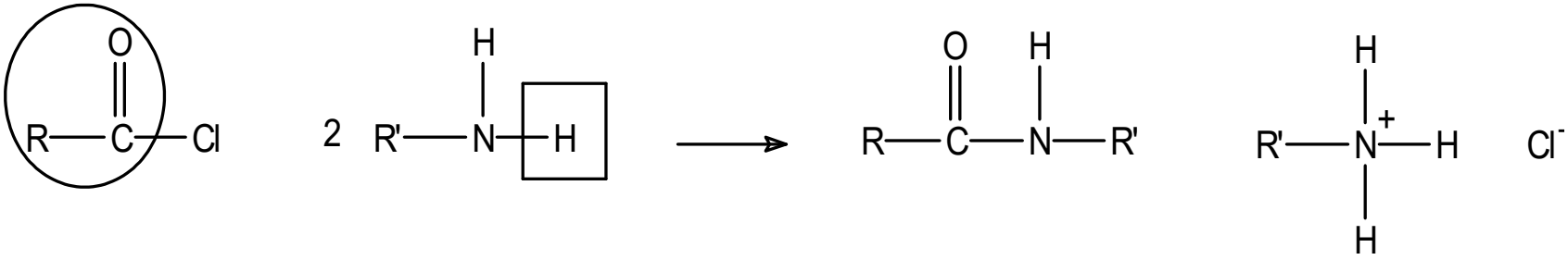
Acylation = replacing an H with an acyl group



then



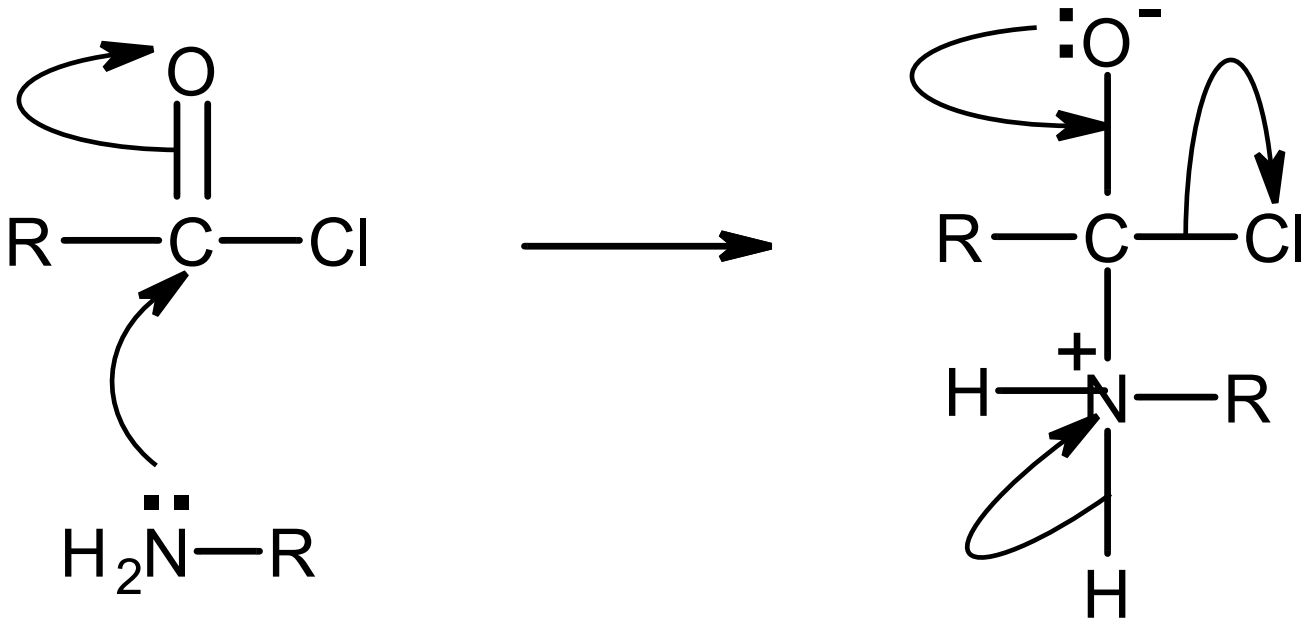
overall



ACYLATION

Nucleophilic addition-elimination

amines & ammonia



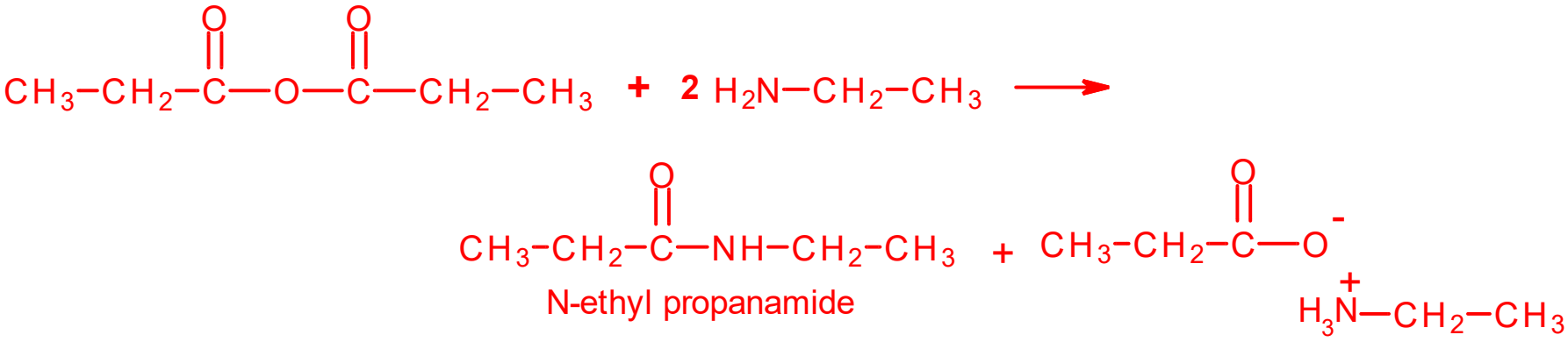
then

$$H^+ + RNH_2 \longrightarrow RNH_3^+$$

ACYLATION

Acylation = replacing an H with an acyl group

e.g. ethylamine + propanoic anhydride

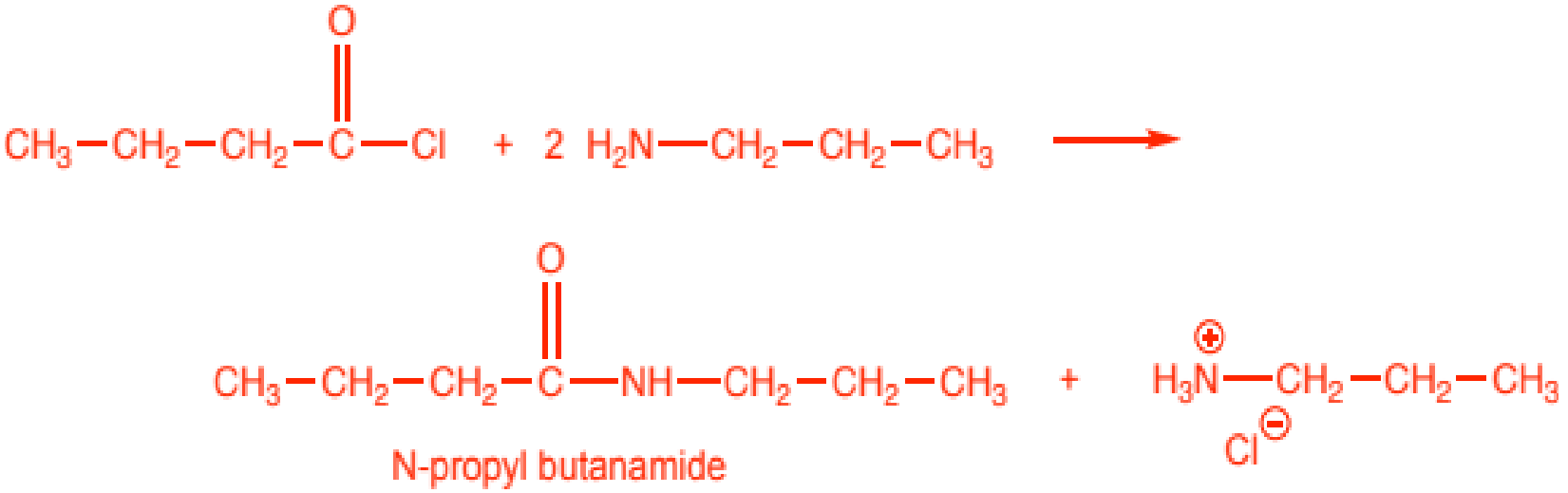


N-ethyl propanamide

ACYLATION

Acylation = replacing an H with an acyl group

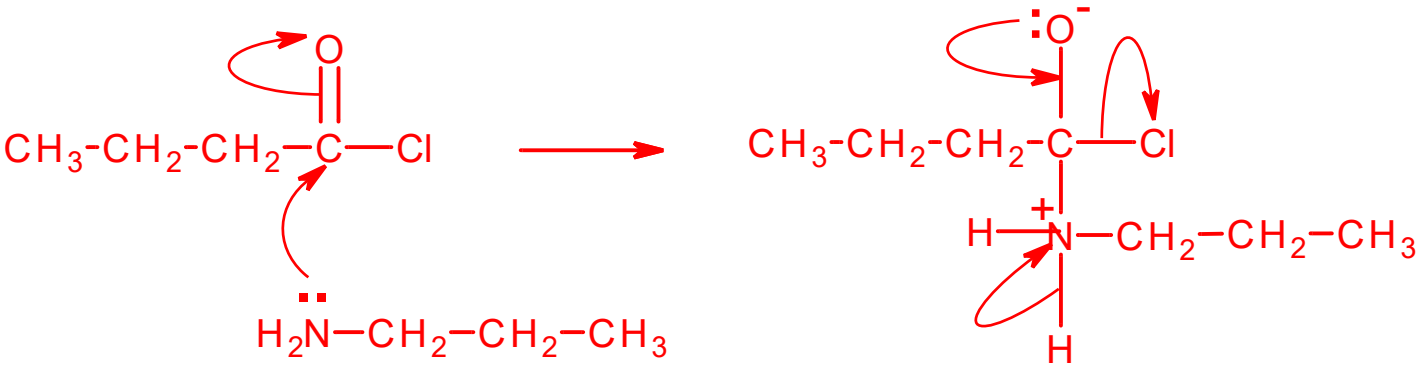
e.g. propylamine + butanoyl chloride



ACYLATION

Nucleophilic addition-elimination

e.g. propylamine + butanoyl chloride



then