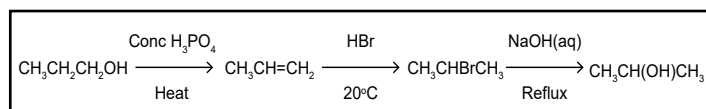


An alternative involving halogenoalkanes would preferentially select propan-2-ol due to the greater stability of the secondary carbocation intermediate. The major product is 2-bromopropane. Whilst the separation of the final product is required, this synthesis sequence has an improved atom economy.



Key Point:

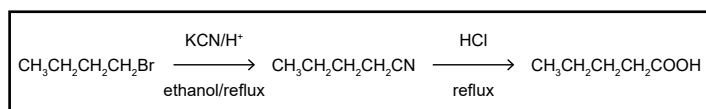
Markovnikov's rule states that the acid hydrogen bonds with carbon having the greater number of existing hydrogen substituents; the halide therefore bonds to carbon with more alkyl substituents.

Extending The Carbon-Chain

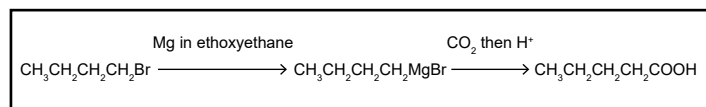
A synthesis may require extending the length of the carbon-chain. There are several possible reactions add a carbon to the original molecule. Selecting an appropriate method depends on the target product.

Example 4: The preparation of pentanoic acid made from 1-bromobutane

The length of the carbon-chain needs to be increased from 4 to 5 carbons. One means for increasing the carbon-chain is to react the halogenoalkane with potassium cyanide, the cyanide ion provides the additional carbon. This forms the nitrile intermediate (Figure 11a). The nitrile is then hydrolysed with dilute hydrochloric acid to form the carboxyl group (Figure 7).



An alternative means for extending the carbon-chain is via a Grignard reagent. Grignard reagents are made in situ, typically by adding magnesium filings to the required halogenoalkane in ether. The Grignard intermediate is then treated with carbon dioxide and the solution acidified (Figure 11a).



Synthesis Of Aromatic Compounds

The synthesis of aromatic compounds plays an important role in the chemical industry and in the commercial production of a wide range of products, including pharmaceuticals, polymers, dyes and fragrances. The simplest aromatic molecule is benzene, which can undergo different reactions in order to present different side-groups (Figure 8). The coupling of aromatic molecules with aliphatic groups involves alkylation or acylation (via the Friedel-Craft reaction).

The initial substituted group will affect the relative positions of subsequent substitutions.

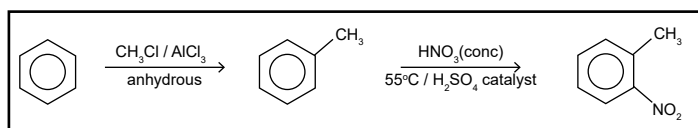
- Electron donating groups activate the π -electron ring system

and direct substitution at the 2-, 4-, and 6- positions. Activating groups include $-\text{OH}$, $-\text{NH}_2$, $-\text{CH}_3$ and $-\text{O}-\text{CH}_3$ groups.

- Electron withdrawing groups deactivate the π -electron ring system and direct substitution at the 3- and 5- positions. Deactivating groups include $-\text{NO}_2$, $-\text{CO}-\text{R}$, $-\text{SO}_3\text{H}$ and $-\text{CCl}_3$.
- Halogens weakly deactivate the ring, but direct substitution at the 2-, 4-, and 6- positions.

Example 5: The preparation of 2-nitromethylbenzene from benzene

This involves two substitution groups on benzene. The respective reactions are straightforward (Figure 8), but in order to obtain the correctly substituted product it is necessary to add the methyl group first, which will direct the subsequent nitro-group substitution at position 2- (and 6-). Substitution will also occur at 4-, requiring fractional distillation to separate the products.



$-\text{NO}_2$ is 3- and 5- directing, meaning if this is added first the methyl group will be substituted at position 3- (and 5-), forming 3-nitrotoluene.

Testing For Functional Groups

The success of a synthesis may be determined by testing the product obtained. Simple chemical tests can be applied to identify functional groups present. This can be used to confirm if the reaction mixture contains unreacted reagents or unwanted products. For example testing for an aldehyde following an oxidation of an alcohol, or for an alcohol after hydrolysing a halogenoalkane. Examination questions will often present observed evidence of chemical tests to identify different functional groups (Figures 12a, 12b and 12c).

Aliphatic Reaction Schematics

Figure 1 Reactions of alkanes

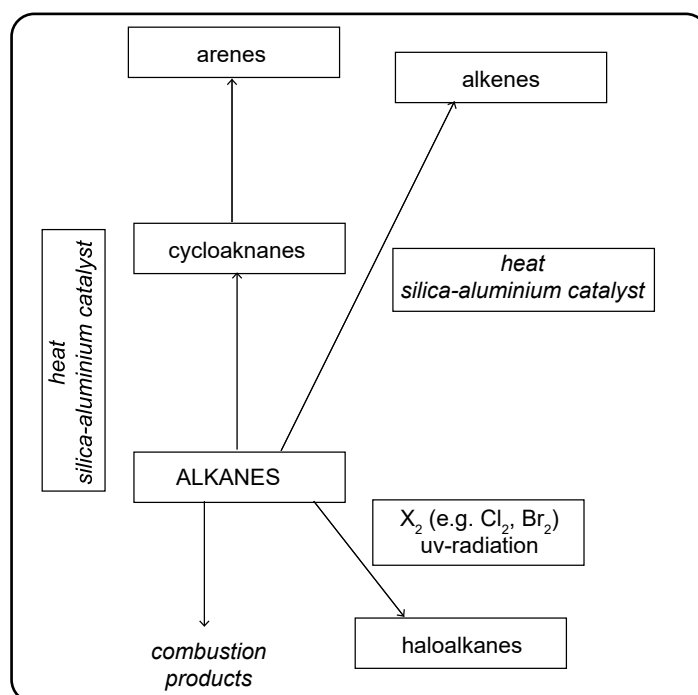


Figure 2 Reactions of alkenes

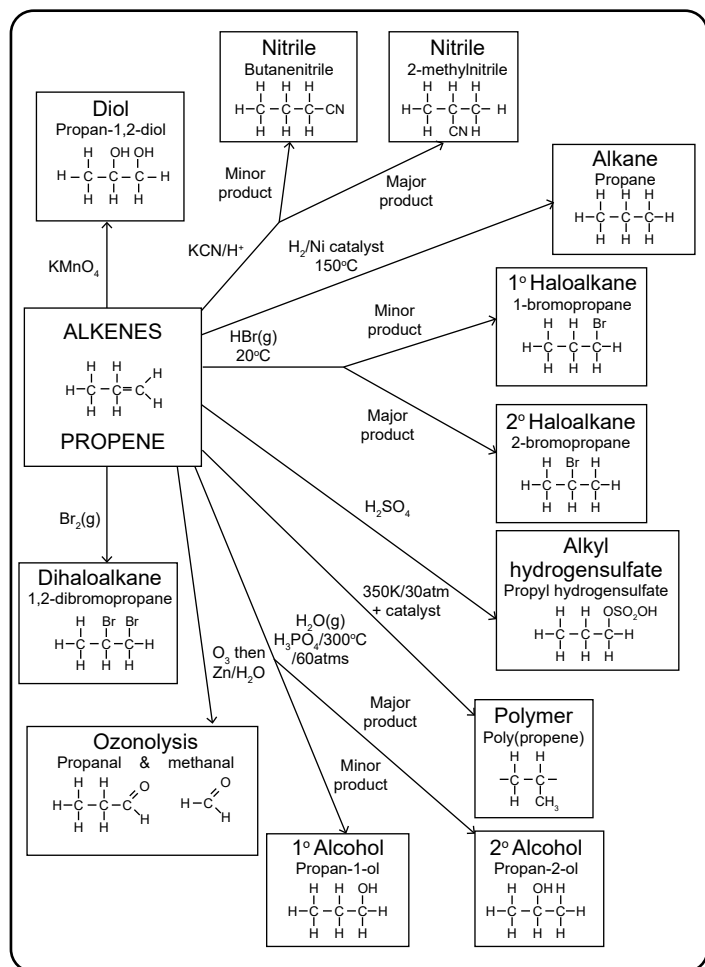


Figure 3 Reactions of halogenoalkanes

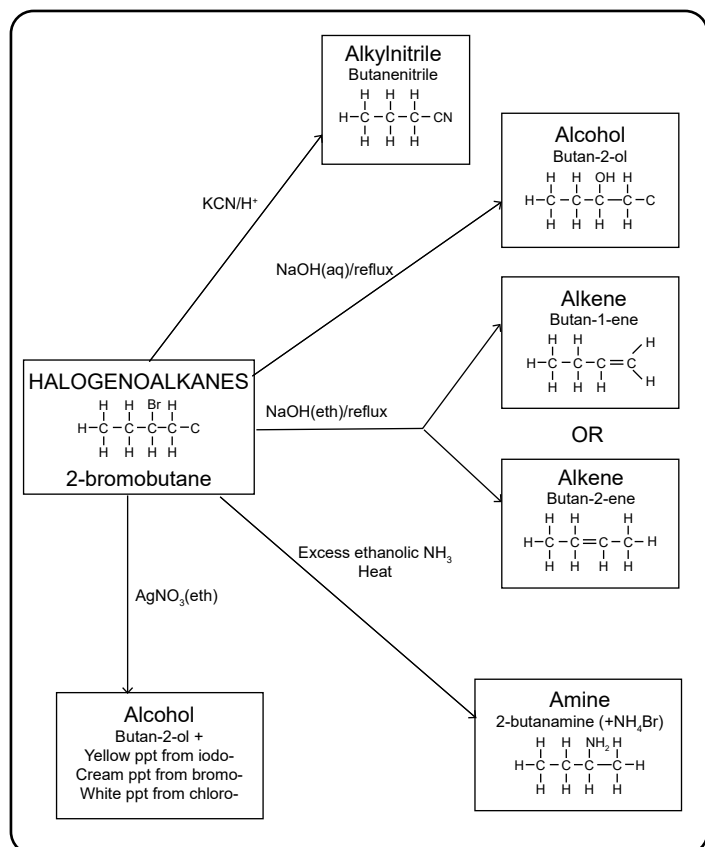


Figure 4a Reactions of primary alcohols

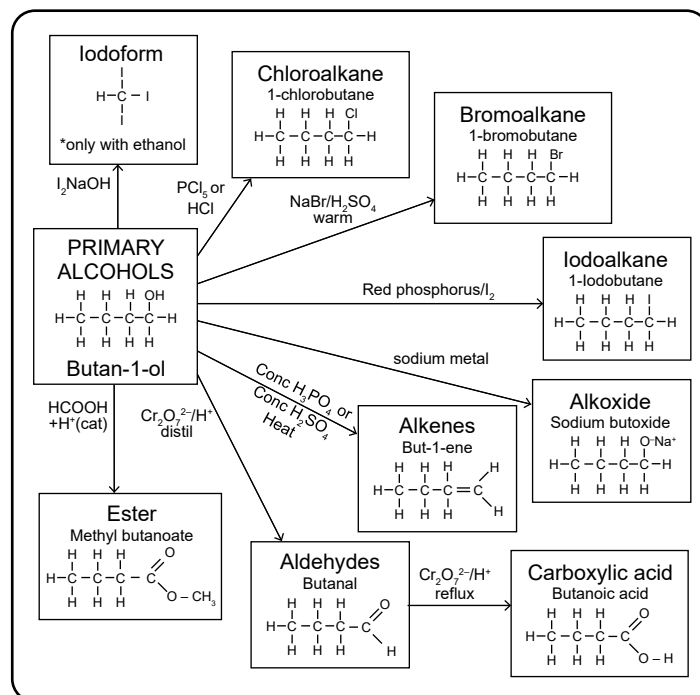


Figure 4b Reactions of secondary alcohols

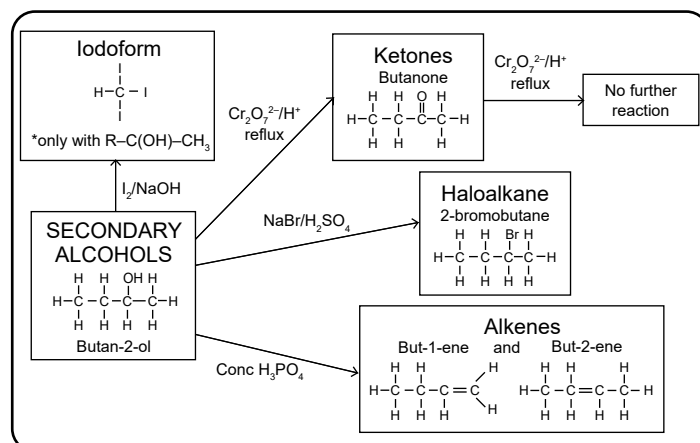


Figure 5a Reactions of aldehydes

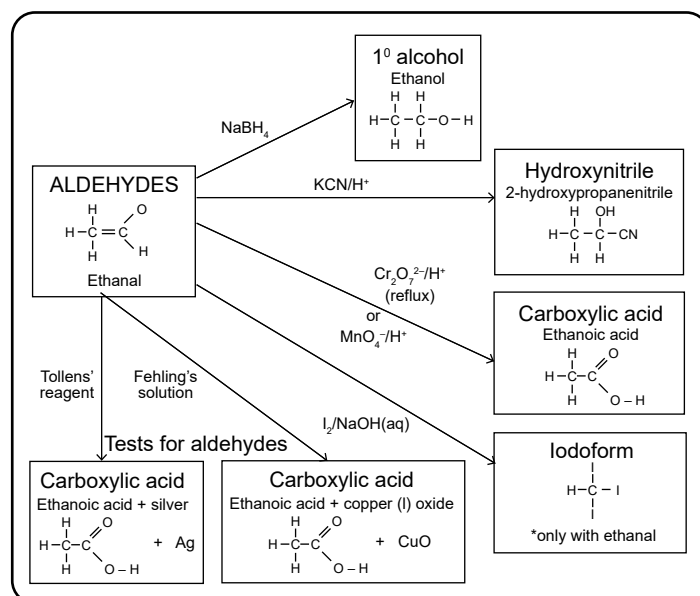


Figure 5b Reactions of ketones

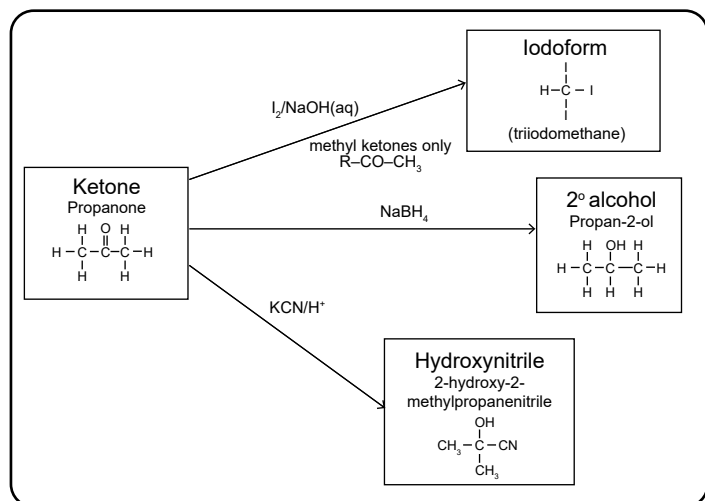


Figure 6 Reactions of carboxylic acids

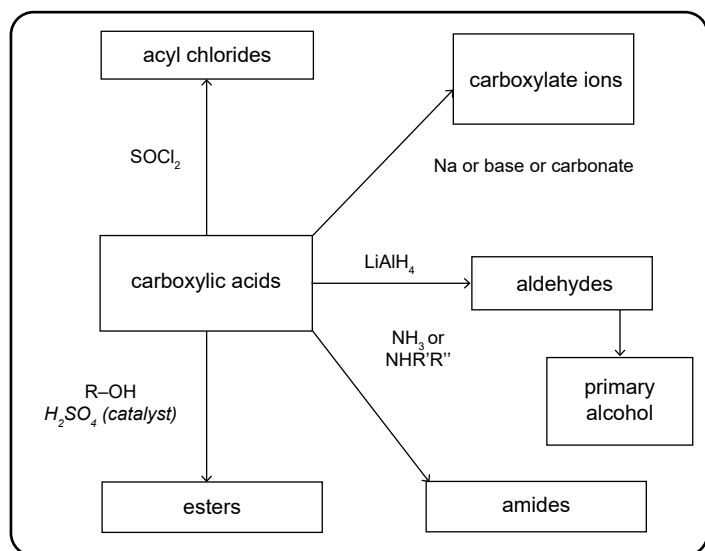
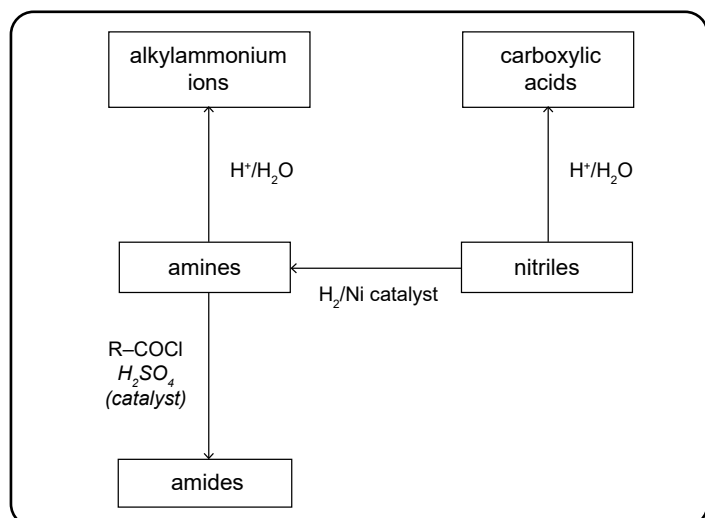


Figure 7 Reactions of amines and nitriles



Aromatic Reaction Schematics

Figure 8 Reactions of benzene

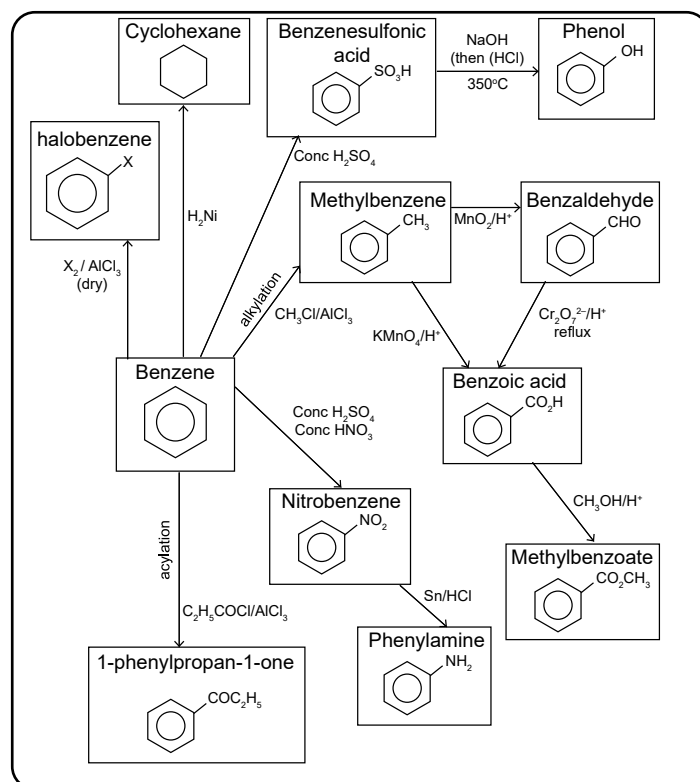


Figure 9 Reactions of phenylamine (alanine)

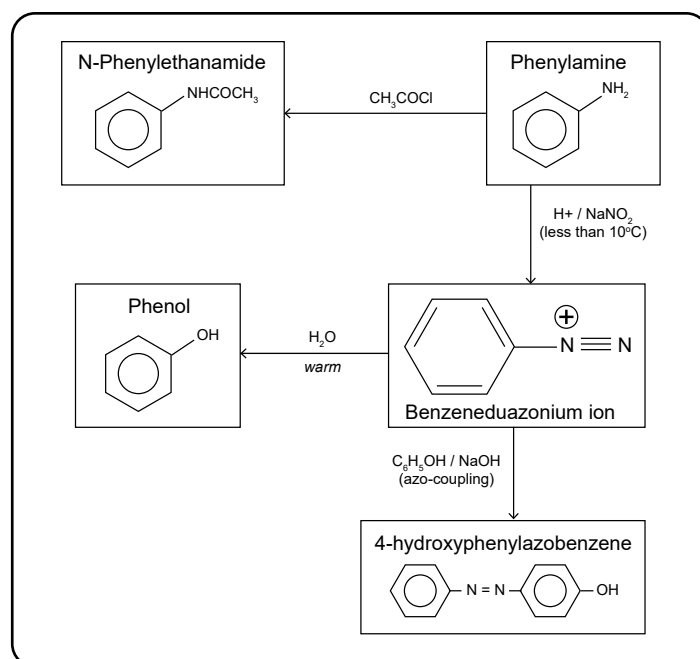
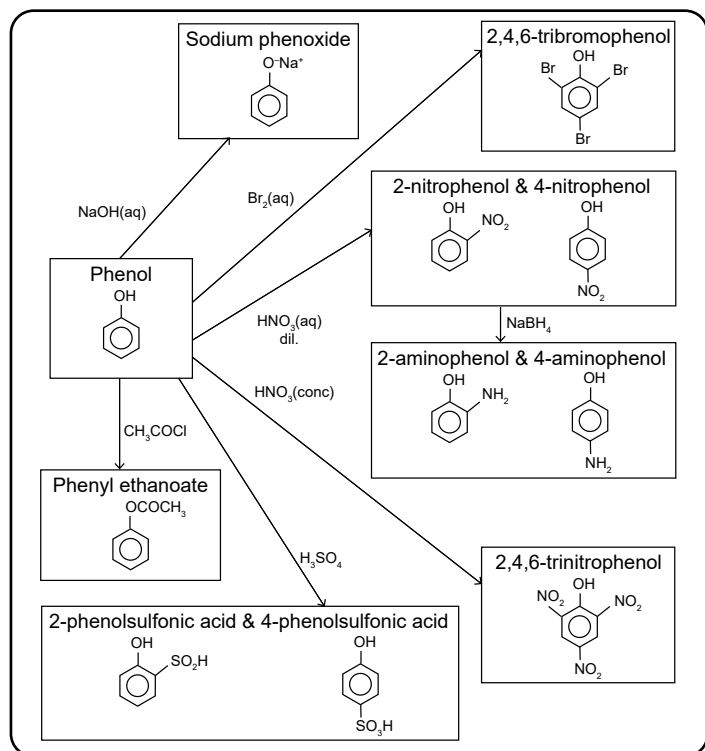


Figure 10 Reactions of phenol



Increasing the Carbon-chain

Figure 11a Increasing the carbon-chain (RX)

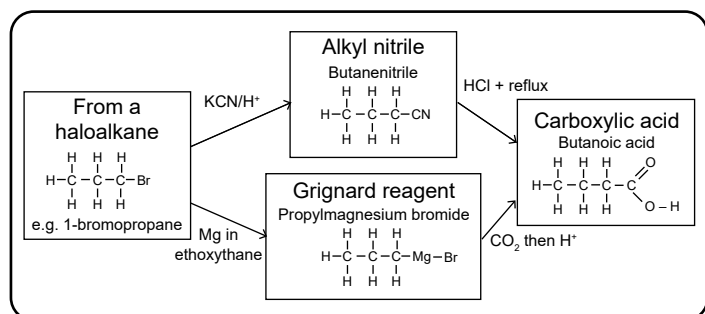
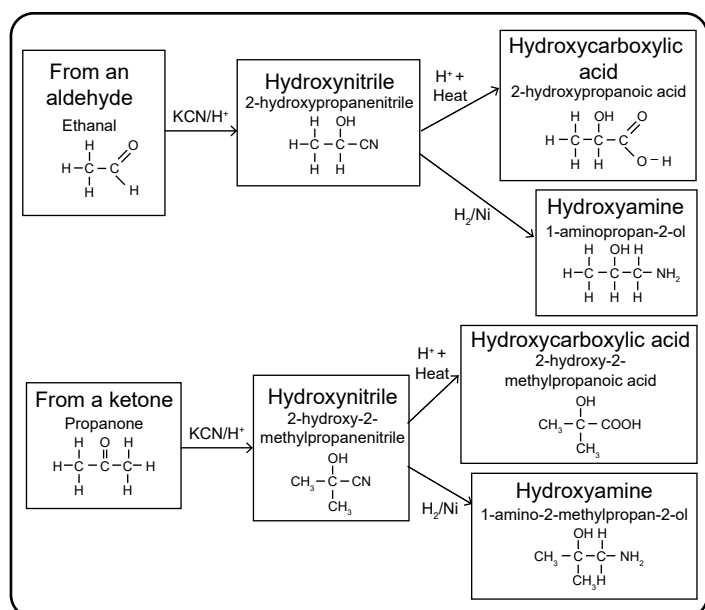


Figure 11b Increasing the carbon-chain (-CO-)



Testing for Functional Groups

Figure 12a Testing for alkenes halogenoalkanes alcohols and carboxylic acids

Functional Group	Test	Positive Outcome	
-C=C- (alkenes)	add to Br ₂ (aq)	orange/brown solution decolourises	
R-X (halogenoalkanes)	warm with NaOH(aq) and a water/ethanol solution containing AgNO ₃	white precipitate	chloroalkane
		cream precipitate	bromoalkane
		yellow precipitate	iodoalkane
R-OH (alcohols)	add acidified Cr ₂ O ₇ ²⁻ (aq) and warm gently	orange solution turns green	(quickly) primary alcohol (slowly) secondary alcohol
		orange solution unchanged	tertiary alcohol
-OH (hydroxyl- group)	add dry solid PCl ₅	white misty fumes formed (HCl)	
-COOH (carboxyl- group)	add drops NaHCO ₃ (aq) or Na ₂ CO ₃ (aq)	effervescences (CO ₂ liberated)	
	add damp blue litmus paper	litmus paper turns red	

Figure 12b Testing for carbonyls (aldehydes and ketones)

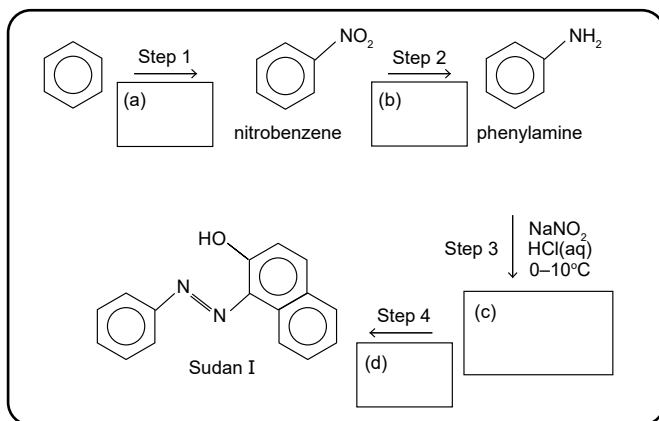
Functional Group	Test	Positive Outcome	
-CO- (carbonyl- group)	add drops of Brady's reagent (2,4-dinitrophenylhydrazine)	yellow or orange precipitate	
	add acidified Cr ₇ O ₇ ²⁻ (aq) and warm gently	orange solution turns green	aldehyde
R-CHO (aldehydes)	add Tollens' reagent (warm gently)	silver mirror (silver precipitate)	
	add Fehling's (blue) solution (warm gently)	(brick) red precipitate	
-CO-CH ₃ (ethanal and methyl ketones)	add iodine (in KI(aq)) then NaOH dropwise to remove colour of iodine (warm gently)	yellow precipitate (iodoform)	

Figure 12c Testing for amines amides phenols and nitro-group

Functional Group	Test	Positive Outcome	
-NRR' ¹ (amines)	add to Cu ²⁺ (aq) solution	forms dark blue solution (complex ion)	
	add to H ⁺ / NaNO ₂ (aq)	effervescences (N ₂ liberated)	primary amine
		yellow oil	secondary amine
-CONR- (amides)	add to NaOH(aq) and boil acidify cooled solution	colourless solution	tertiary amine
		NH ₃ liberated	aliphatic amine
Ar-OH (phenols)	add to NaOH(aq) and boil acidify cooled solution	white precipitate	aromatic amide
	test pH and Na ₂ CO ₃ (aq)	pH 4-6 but does not react with CO ₃ ²⁻ (aq)	
	add Br ₂ (aq)	bromine water decolourises White precipitate	
-NO ₂ (nitro group)	add Fe ³⁺ (aq) solution	solution turns purple	
	add Fe(OH) ₂ (aq)	red-brown precipitate	

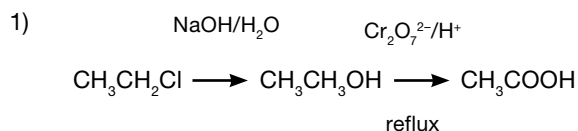
Questions

- 1) Draw out the synthesis for the preparation of ethanoic acid from chloroethane.
- 2) Complete the details on the multistep synthesis of the azo-dye **Sudan I** from benzene.
 - a) Give reagents and conditions.
 - b) Give reagents and conditions.
 - c) Name intermediate (c).
 - d) Draw the structure of the organic compound coupled to (c) in Step 4.



- 3) Identify compounds A, B and C given that all are organic compounds containing (i) **three** carbon atoms, and (ii) **one** functional group.
 - (a)
 - Steamy fumes observed on adding PCl₅.
 - No observable change on adding NaHCO₃(aq).
 - A pale-yellow precipitate forms on adding NaOH(aq) and then dropwise I₂(aq).
 - (b)
 - Steamy fumes observed on adding PCl₅.
 - Effervesces on adding NaHCO₃(aq).
 - (c)
 - Yellow-orange precipitate observed on adding Brady's reagent and warming.
 - A silver mirror is observed on adding Tollens' reagent and warming.

Answers



- 2) a) Concentrated H₂SO₄ and HNO₃ at 55 °C.
- b) Tin and concentrated HCl
- c) Benzenediazonium ion (chloride)
- d)

- 3) (a) Propan-2-ol (CH₃CH(OH)CH₃)
- (b) Propanoic acid (CH₃CH₂COOH)
- (c) Propanal (CH₃CH₂CHO)

Acknowledgements: This **Chemistry Factsheet** was researched and written by **David Willmot**, and published in **September 2020** by **Curriculum Press**. Chem Factsheets may be copied free of charge by teaching staff or students, provided that their school is a registered subscriber. No part of these Factsheets may be reproduced, stored in a retrieval system, or transmitted, in any other form or by any other means, without the prior permission of the publisher.