

Preparatory chemistry course

Organic Chemistry

Day 5

29 May 2020

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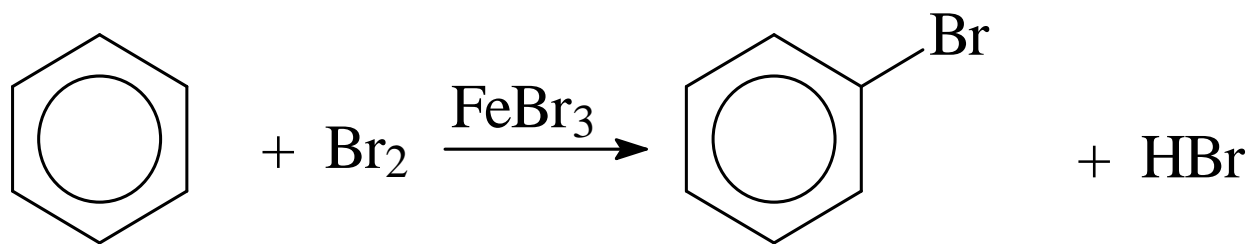
PART C – TRUE OR FALSE SECTION

1. For aromatic hydrocarbons more characteristic are substitution reactions Addition reactions are possible but they are more difficult.

True

Benzene prefers to undergo **substitution reactions** in spite of the high degree of unsaturation. This is due to high stabilisation of benzene ring by resonance (or by delocalization of π electrons). The substitution reactions in benzene are initiated by electrophilies. Thus, characteristic reactions of benzene are electrophilic substitution reactions.

Some example
Halogenation



Chlorine or bromine react with benzene in the presence of Lewis acids like ferric or aluminium salts of the corresponding halogen, which act as catalysts.

Substitution reaction, any of a class of chemical reactions in which an atom, ion, or group of atoms or ions in a molecule is replaced by another atom, ion, or group.

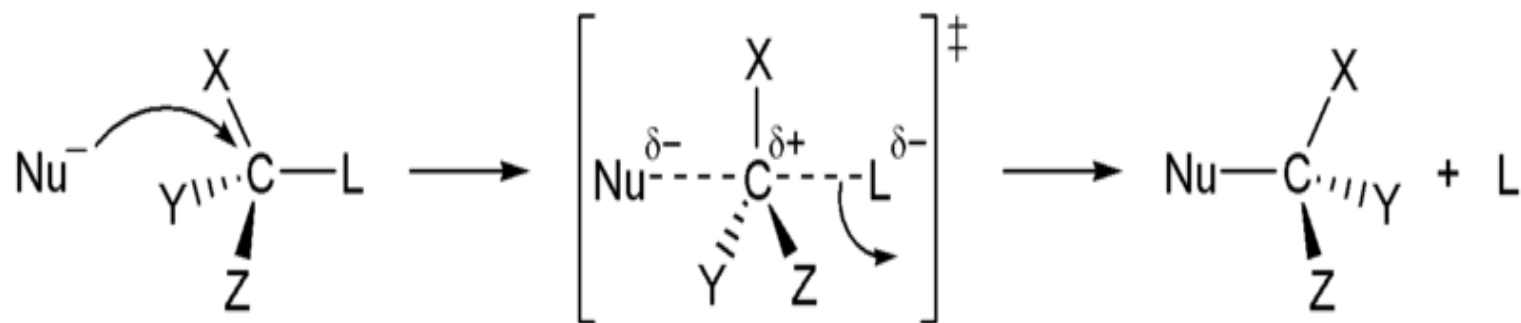
Substitution reaction is a major class in organic reaction. It can be of two types, namely **electrophilic substitution** reaction and **nucleophilic substitution** reaction. Depending upon the reagent used in the organic reaction it can be either an electrophilic or nucleophilic substitution reaction. Starting material either can be an aliphatic or an aromatic compound. This type of reaction proceeds through an intermediate which is a carbocation, carbanion or a free radical.

Nucleophilic substitution reaction

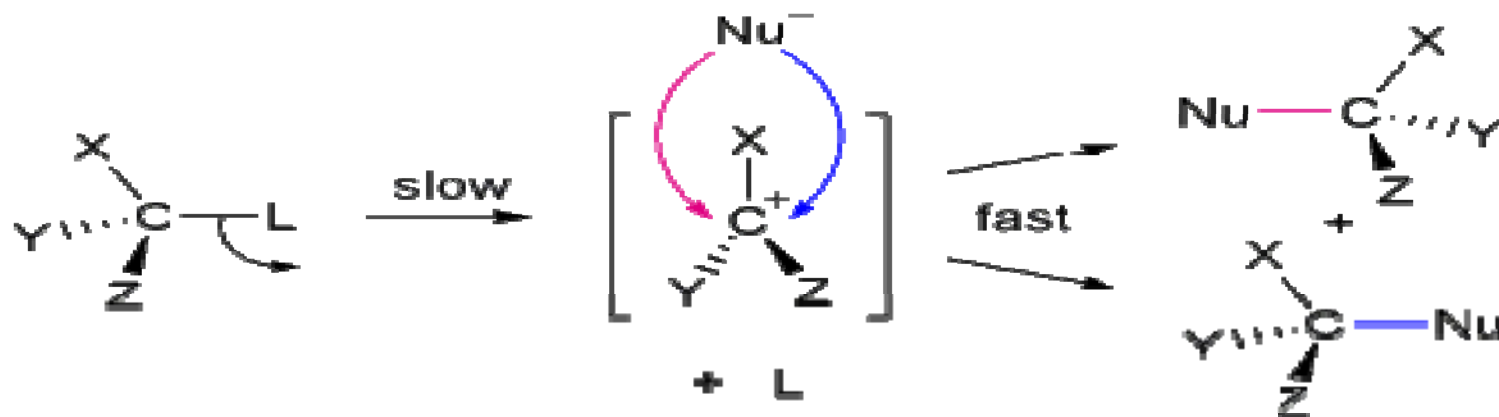
Nucleophilic substitution reaction can be SN1 or SN2 type. SN1 describes nucleophilic substitution unimolecular reactions and SN2 describes nucleophilic substitution bimolecular reactions. In a SN1 reaction, the leaving group is detached from the starting material first forming a carbocation and then nucleophile is attacked the carbocation. Generally tertiary compounds which are sterically hindered undergoes in a SN1 reaction. This reaction is unimolecular because the slowest, that is, rate determining step is the first step which is dependent on the substrate only.

Nucleophilic substitution at carbon

SN2 Mechanism



SN1 Mechanism

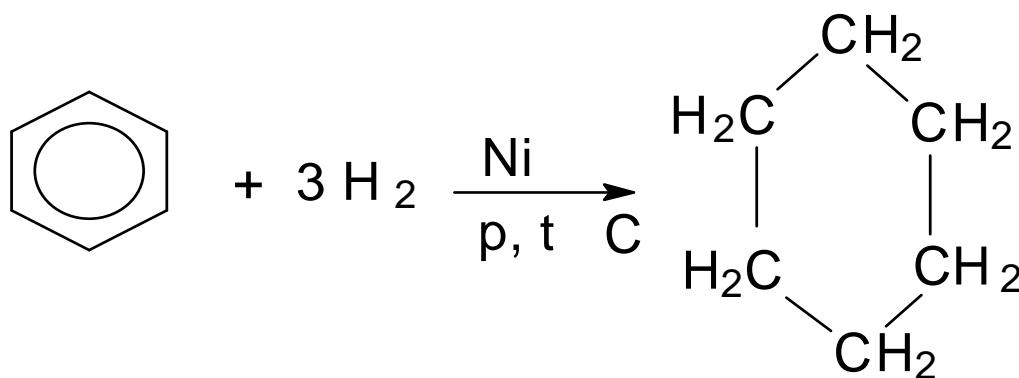


Electrophilic substitution reaction

In an **electrophilic substitution** reaction, electronically richer substrate attacks the electronically deficient electrophile forming a carbocation then it undergoes to protonation.

Benzene and its homologues undergo some **addition** reactions characteristic of alkenes and alkynes, but under more drastic conditions (like higher temperature and pressure). This is due to the fact that these compounds are relatively more stable and behave like saturated hydrocarbons.

Benzene reacts with hydrogen in the presence of catalyst, nickel or platinum at high temperature and produce cyclohexane.



PART C – TRUE OR FALSE SECTION

2. Arenes halogenation rings through mechanism of nucleophilic substitution.

False

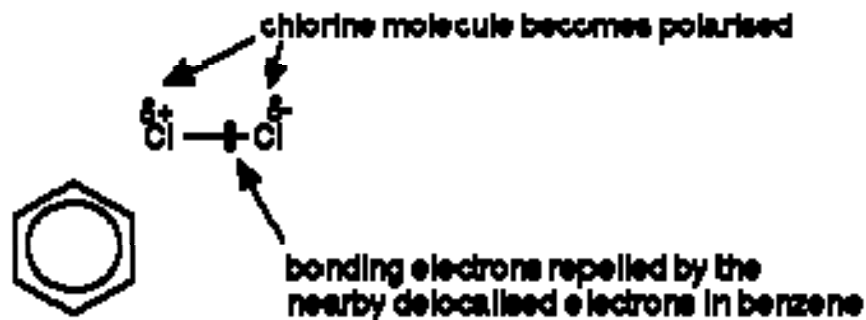
THE HALOGENATION OF BENZENE

Benzene reacts with chlorine or bromine in an **electrophilic substitution** reaction, but only in the presence of a catalyst. The catalyst is either aluminium chloride (or aluminium bromide if you are reacting benzene with bromine) or iron.

As a chlorine molecule approaches the benzene ring, the delocalised electrons in the ring repel electrons in the chlorine-chlorine bond.

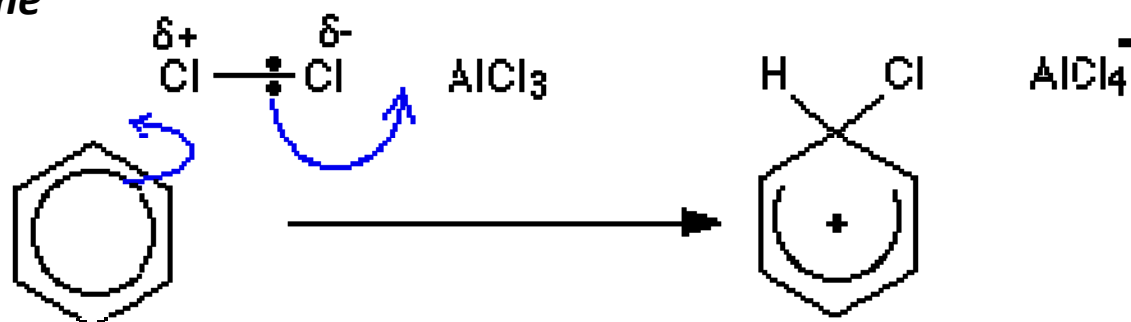
It is the slightly positive end of the chlorine molecule which acts as the electrophile.

The presence of the aluminium chloride helps this polarisation.

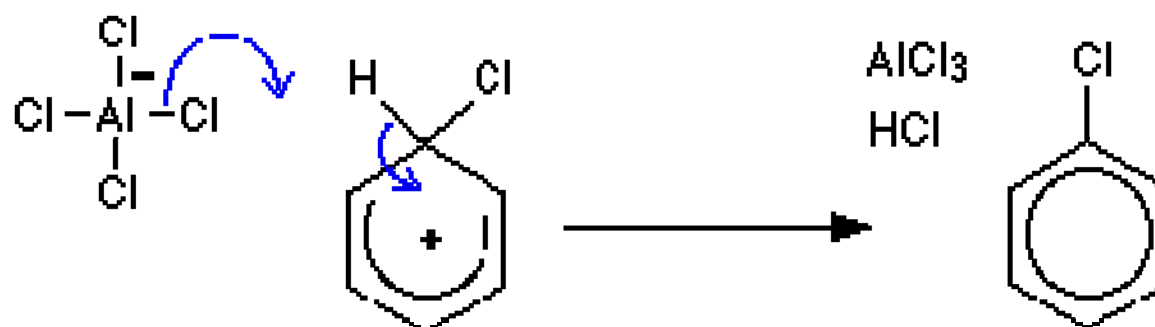


The electrophilic substitution mechanism

Stage one



Stage two



The hydrogen is removed by the AlCl_4^- ion which was formed in the first stage. The aluminium chloride catalyst is re-generated in this second stage.

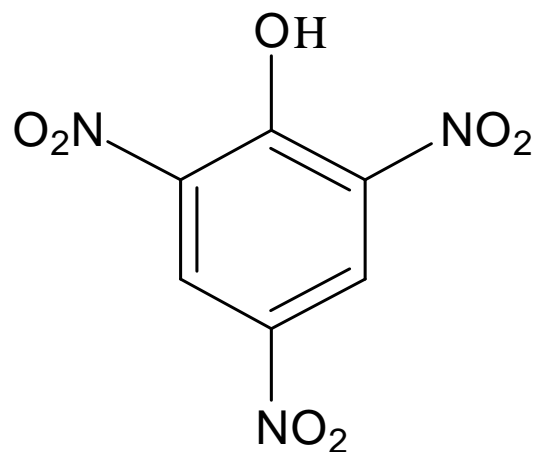
A **nucleophile** is a reactant that provides a pair of electrons to form a new covalent bond.

An **electrophile** is a species that accepts a pair of electrons to form a new covalent bond.

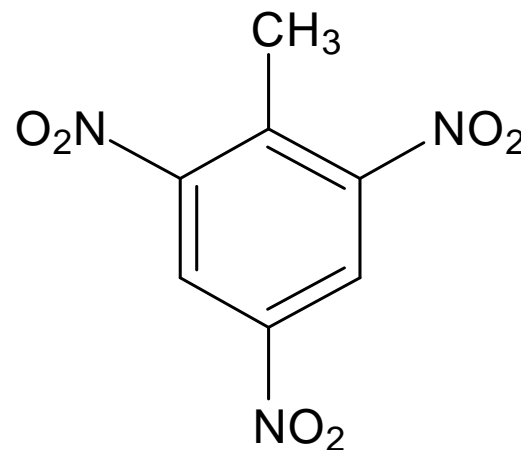
PART C – TRUE OR FALSE SECTION

3. The other name of picric acid is 2,4,6-trinitrotoluene.

False



picric acid – 2,4,6-trinitrophenol



2,4,6-trinitrotoluene

PART C – TRUE OR FALSE SECTION

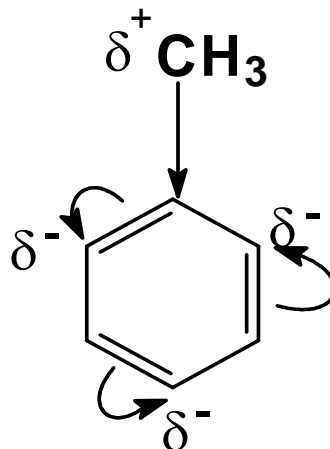
4. Upon electrophilic substitution in the aromatic nucleus of the benzene homologues, the alkyl groups are ortho- and para-orientating.

True

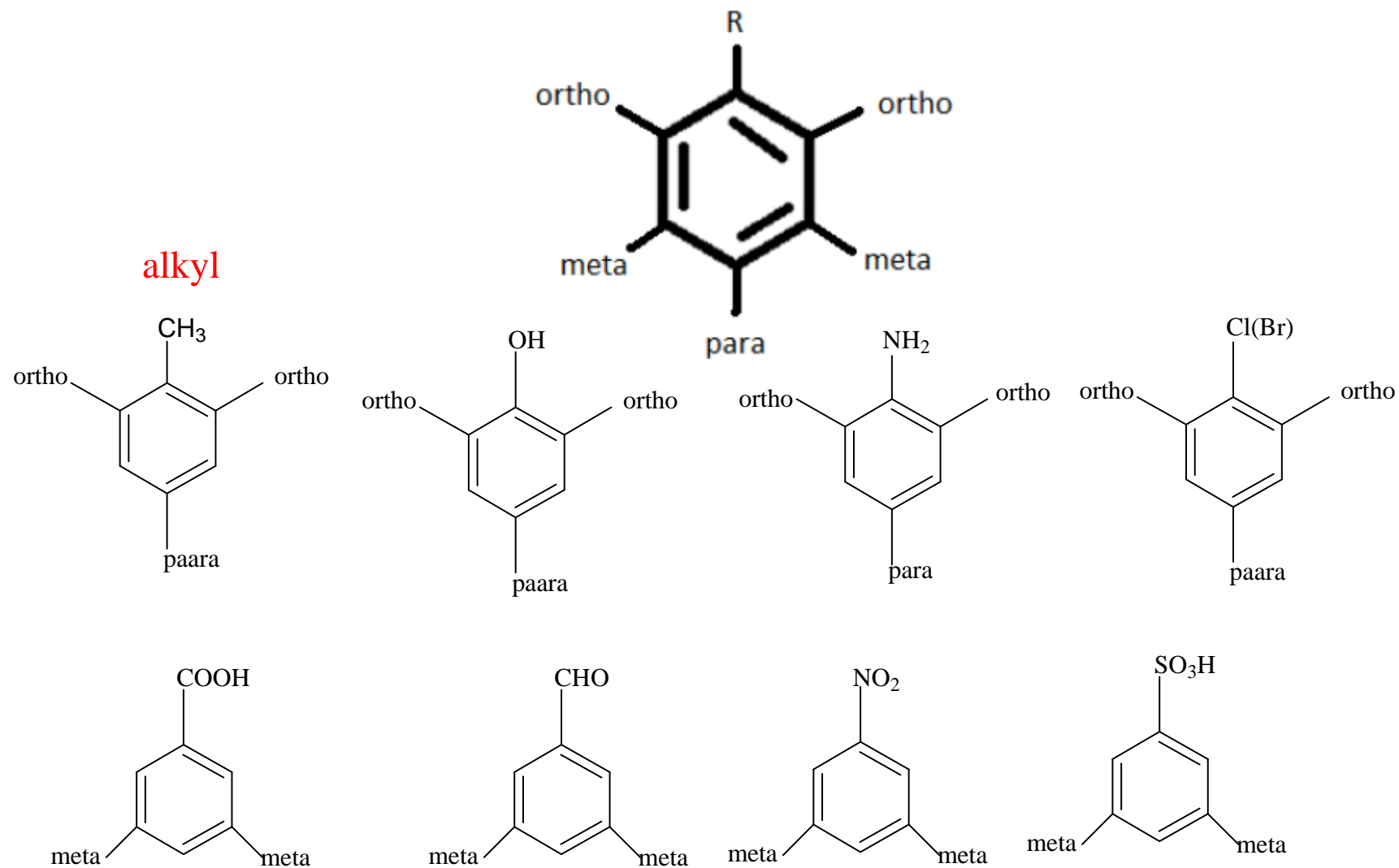
For example

Alkyl groups, for example the methyl group, have a positive inductive effect. They give electronic density to the benzene core, which is partially negative. The electron density of the ortho- and para-positions relative to the alkyl group is increased.

$$I_{\text{CH}_3} > 0 ; I_{\text{R}} > 0 ; [\delta^+] = 3[\delta^-]$$



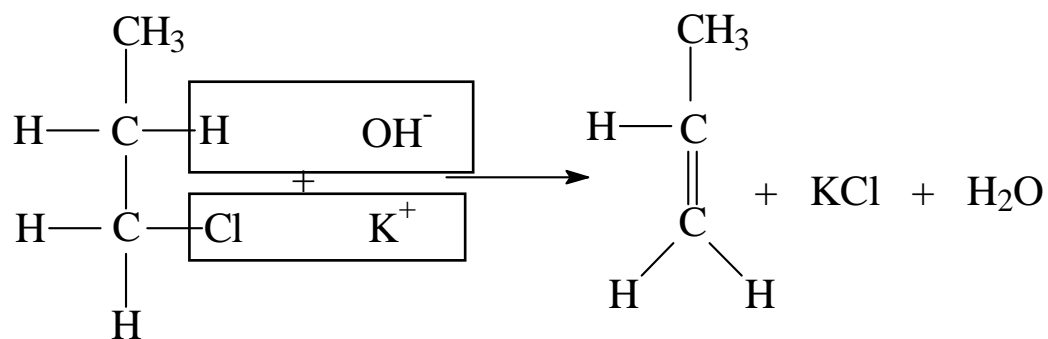
The **alkyl** groups are ortho- and para-orientating.



PART C – TRUE OR FALSE SECTION

5. The dehydrohalogenation reactions (elimination) in the presence of an alcoholic solution of potassium hydroxide of halogen derivatives of alkanes give unsaturated hydrocarbons.

True



PART C – TRUE OR FALSE SECTION

9. The esterification of phenol is done with anhydride or acid chloride.

True

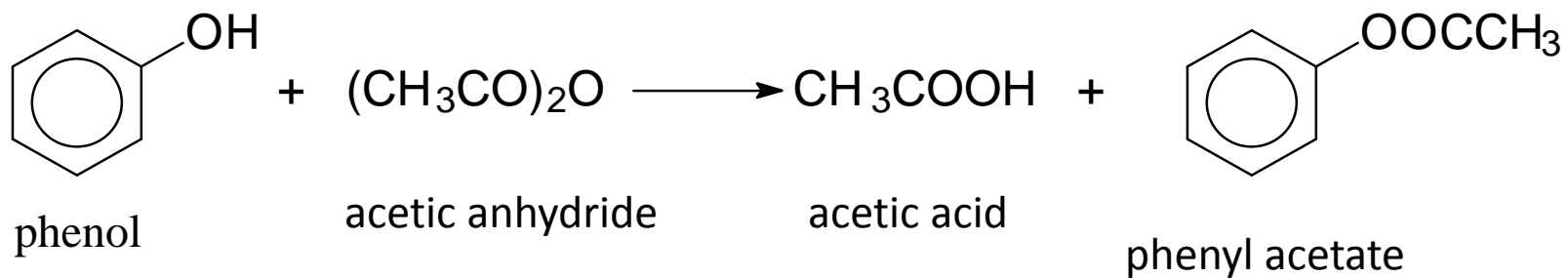
Why do acid chlorides and anhydrides react very well with phenol and carboxylic acids don't?

The reason is in the different reactivity of the carbonyl-compound.

Acid chlorides and acid anhydrides are the most reactive carbonyl compounds.

Whereas carboxylic acids are rather weak in comparison.

Esterification of phenol



PART C – TRUE OR FALSE SECTION

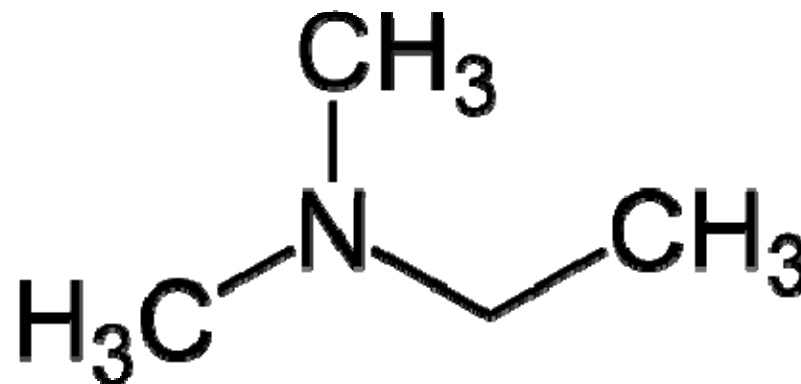
10. The chemical name of the compound presented below is N,N-methylaminoethane.

False

N,N-dimethylethan-1-amine

N,N-dimethylethylamine

ethyl(dimethyl)amine



PART B MATCHING TYPE QUESTIONS

Match each item in column 1, marked with letter with those given in column 2, marked with number. In the table enter the digits below the appropriate letter.

1.

A	B	C	D
4	6	2	1

3.

A	B	C	D
3	5	2	4

2.

A	B	C	D
7	5	3	6

4.

A	B	C	D
6	1	5	2

5.

A	B	C	D
4	3	5	6

8.

A	B	C	D
6	5	6	5

6.

A	B	C	D
4	2	6	3

9.

A	B	C	D
2	4	6	5

7.

A	B	C	D
4	2	5	3

10.

A	B	C	D
2	1	3	5

11.

A	B	C	D
2	4	4	4

14.

A	B	C	D
4	3	6	2

12.

A	B	C	D
1	3	5	6

15.

A	B	C	D
6	3	1	4

13.

A	B	C	D
2	3	4	6

16.

A	B	C	D
2	1	5	3

17.

A	B	C	D
1	5	6	4

PART D - FILL IN THE BLANKS SECTION

Read the text and fill in the blanks with proper terms.

3. In benzene there are 6- σ bonds between carbon atoms and 6- σ bonds between carbon and hydrogen atoms. And 3 – π bonds between carbon atoms.

Therefore 12- σ bonds and 3- π bonds are present in benzene molecule.

4. electrophilic aromatic substitution

5. alkenes.

10. hydroxyl

15. hydrogen.