وزارة التعليم العالي و البحث العلمي

Ministry of Higher Education and Scientific Research

جامعة قاصدي مرباح ورقلة

University of Kasdi Merbah Ouargla

كلية الرياضيات و علوم المادة

Faculty of Mathematics and Matter Sciences

قسم الكيمياء

Department of Chemistry

Masters Dissertation

To obtain the master academy in chemistry

Specialization: Applied organic chemistry

Presented by: Korichi Selsabil

Title:

Nitration of Aromatic Compounds:

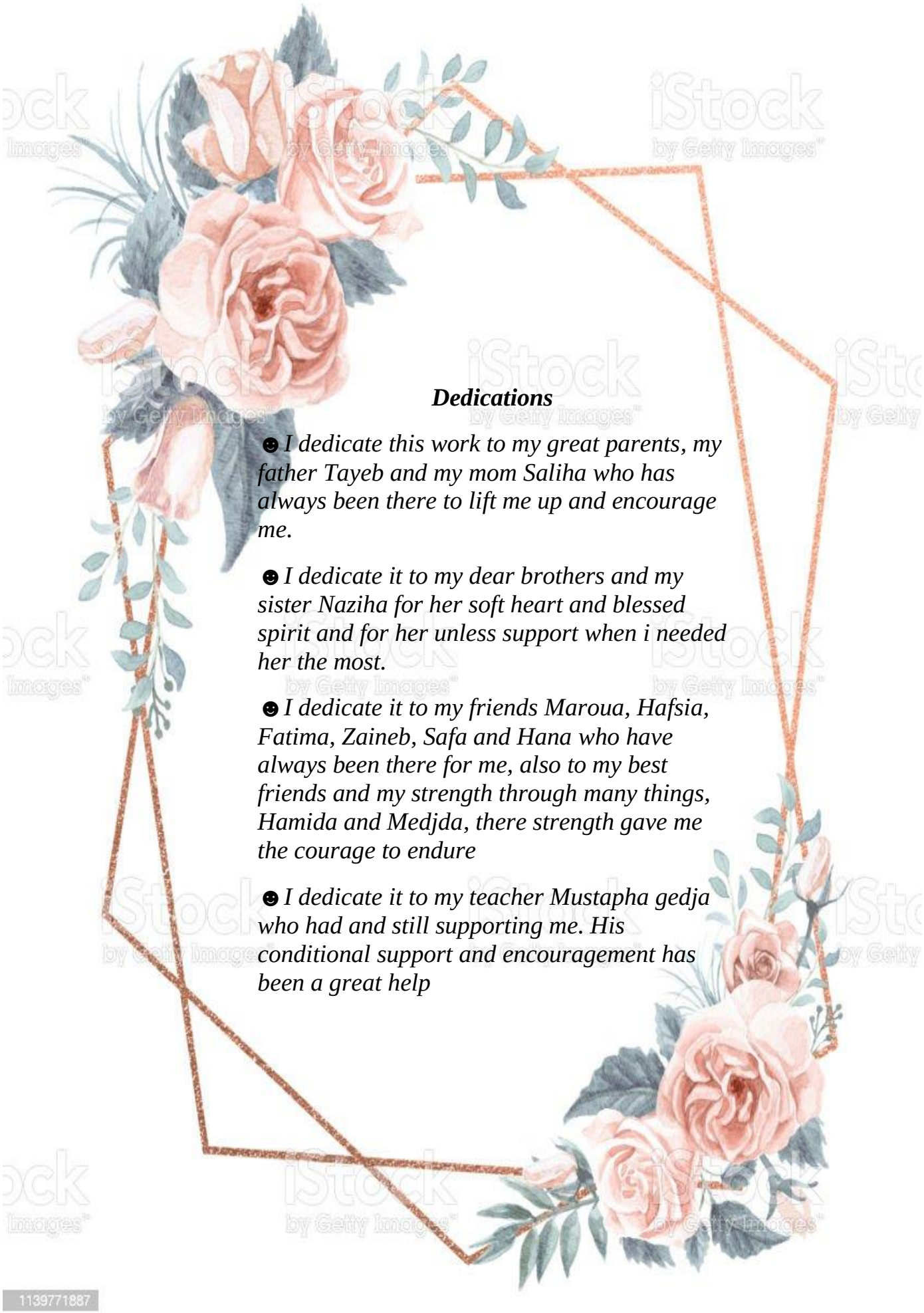
Preparation of methyl-m-nitrobenzoate

Defended on: June 9. 2022

In front of the jury composed of:

Saidi Mokhtar	Professor, Univ.K.M. Ouargla	President
Hadjadj Mohamed	Professor, Univ.K.M. Ouargla	Examiner
Zeghdi Saad	Doctor, Univ.K.M. Ouargla	Promoter

Year: 2021/2022



Dedications

☻ *I dedicate this work to my great parents, my father Tayeb and my mom Saliha who has always been there to lift me up and encourage me.*

☻ *I dedicate it to my dear brothers and my sister Naziha for her soft heart and blessed spirit and for her unless support when i needed her the most.*

☻ *I dedicate it to my friends Maroua, Hafsia, Fatima, Zaineb, Safa and Hana who have always been there for me, also to my best friends and my strength through many things, Hamida and Medjda, there strength gave me the courage to endure*

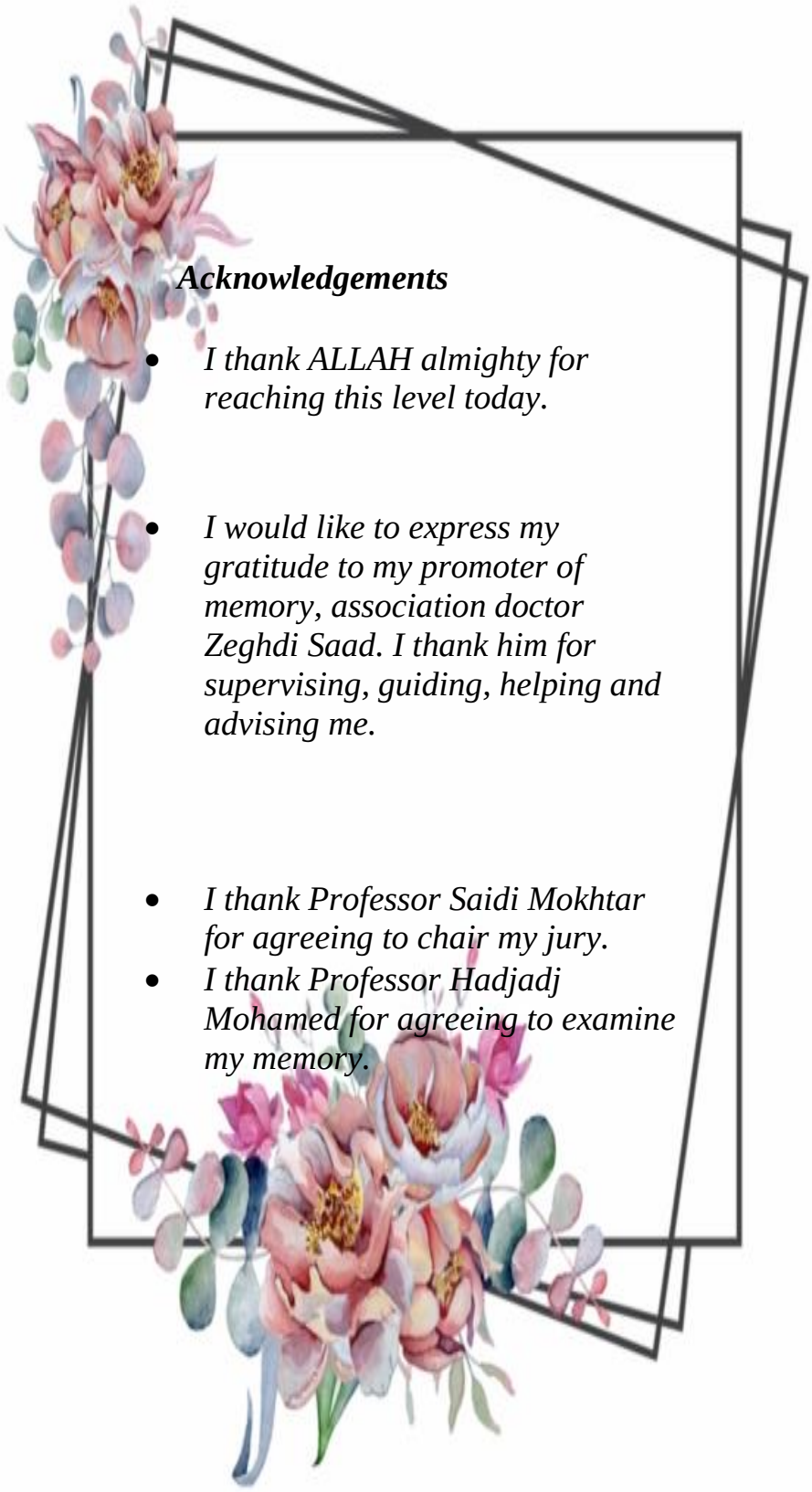
☻ *I dedicate it to my teacher Mustapha gedja who had and still supporting me. His conditional support and encouragement has been a great help*

Acknowledgements

- *I thank ALLAH almighty for reaching this level today.*

- *I would like to express my gratitude to my promoter of memory, association doctor Zeghdi Saad. I thank him for supervising, guiding, helping and advising me.*

- *I thank Professor Saidi Mokhtar for agreeing to chair my jury.*
- *I thank Professor Hadjadj Mohamed for agreeing to examine my memory.*



Abbreviations list

A

$AlCl_3$	Aluminium chloride

C

$Ca(NO_3)_2$	Calcium nitrate
$C_8H_8O_2$	Methyl benzoate
CH_3CH_2COCl	Propanoyl chloride
$(C_2H_3)_3CCl$	Tert-butyl chloride
CH_3COOH	Acetic acid

D

DNS	Dinitro salicylic acid

H

H_2SO_4	Sulphuric acid
HNO_3	Nitric acid

N

NO_2	Nitrogen Dioxide

P

PPm	Parts per million

R

R	Alkyl

S

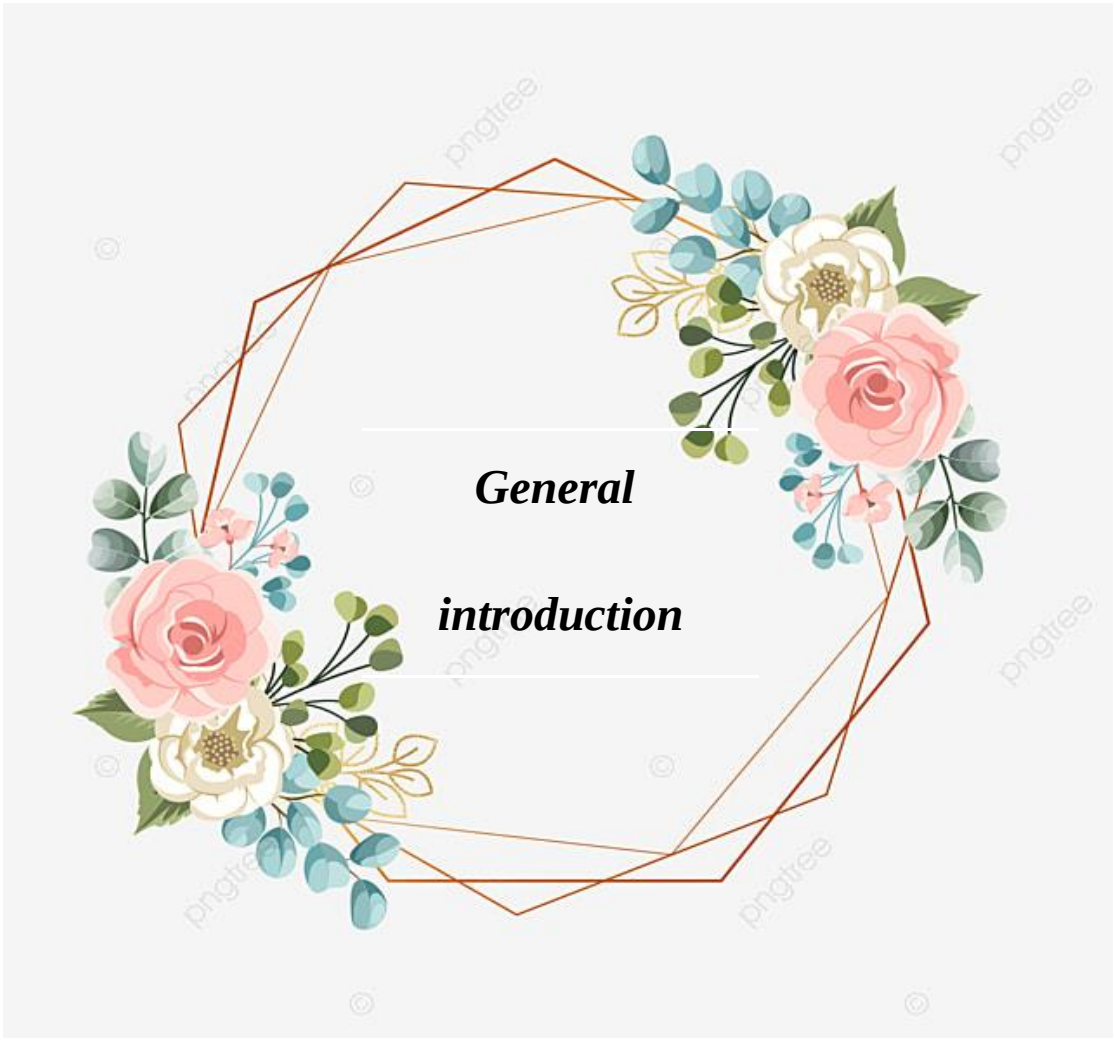
SO_3	Sulfur trioxide
SO_3H	Sulfonic acid

List of Figures

List of pictures

List of tables

Summary



General

introduction

Introduction:

The meaning of the word aromaticity has evolved as understanding of the special properties of benzene and other aromatic molecules has deepened. Originally, aromaticity was associated with a specific chemical reactivity. The aromatic hydrocarbons undergo substitution reactions in preference to addition. Later, the idea of special stability became more important. Benzene can be shown to be much lower in enthalpy than predicted by summation of the normal bond energies for the C=C, C−C, and C−H bonds in the Kekule representation of benzene. Aromaticity is now generally associated with this property of special stability of certain completely conjugated cyclic molecules. A major contribution to the stability of aromatic systems comes from the delocalization of electrons in these molecules, which also imparts other properties that are characteristic of aromaticity [1].

Aromatic compounds are those chemical compounds (most commonly organic) that contain one or more rings with π electrons delocalized all the way around them In contrast to compounds that exhibit aromaticity, aliphatic compounds lack this delocalization.

The term "aromatic" was assigned before the physical mechanism determining aromaticity was discovered, and referred simply to the fact that many such compounds have a sweet or pleasant odor; however today, the classification of aromatic compounds is no longer based on odor because many compounds containing a benzene ring are not fragrant. Many aromatic compounds are solids that have little or no odor so not all aromatic compounds have a sweet odor, and not all compounds with a sweet odor are aromatic compounds [2].

These compounds contain many properties and characteristics and constitute a large part of our lives, and most of these compounds contain a benzene ring linked to substituents, and the last is considered to be the first and most famous of these compounds. and it is component of many important natural products and useful organic compounds, also the ability to put substitutions on the benzene ring in Specific positions relative to each other, this is a very important factor in the synthesis of organic compounds and the most used and preferred type of reaction is electrophilic aromatic substitution.

So this is what we want to improve or to explain by this research: the importance of these compounds and so on, as well as knowing the changes that will occur in benzene when it goes through one of the Electrophilic aromatic substitution reactions, all that is represented by "Nitration of Aromatic Compounds: Preparation of methyl-m-nitrobenzoate", so:

-What is the importance of these compounds?
-what is the most common reaction for them?
-How is "methyl-m-nitrobenzoate" formed?

We will review the answer of all these questions through:
Chapter one: "Aromatic compounds "
Chapter two: "Electrophilic substitution"
Part one:" Nitration"
Part two: "Methyl-m-nitrobenzoate"
Chapter three: "practical study"

The theoretical part

Chapter one:

Aromatic compounds

I-Chapter one: Aromatic compounds

I-1-Difinition:

In organic chemistry we frequently refer to certain compounds as being aromatic, this terminology came about in a time when we noticed pleasant odors emanating from certain compounds isolated from natural oils produced by plants, it wasn't until much leter that we understood that this property is actually due to the presence of a fully conjugated unsaturated ring systems, so now we are referring to the molecular structure. So aromatic compounds are a larg class of unsaturated chemical compounds characterized by one or more planar rings of atoms joined by covalent bonds, the unique stability of these compounds is referred to as aromacity, this result from electron delocalization within a ring system that typically contains several conjugated binary bonds.

I-2-History:

Aromatic compounds are currently defined as cyclic hydrocarbons in which the carbon skeleton is linked by a specified number of conjugated n-bonds in addition to a-bonds (Hückel's rule). During the early days of industrial aromatic chemistry in the mid-19th century, the structure of aromatic compounds had not yet been elucidated. The name of this class of compounds is historically-based since the first members were obtained from aromatic, pleasant-smelling resins, balsams and oils; examples of this are benzoic acid, which was obtained from gum benzoin, toluene from tolu balsam and benzaldehyde from oil of bitter almonds.

The history of aromatic compounds was, at the outset, closely linked to the development of coal carbonization to produce coke, gas and tar.

The parent compound of the aromatics is benzene; it was first discovered by Michael Faraday in 1825 in the condensed part of a lighting gas derived from whale oil and obtained some years later by Eilhard Mitscherlich by decarboxylation of benzoic acid (as calcium benzoate). The occurrence of benzene in coal tar was first described by August Wilhelm v. Hofmann in 1845. John Leigh had already demonstrated to the British Natural Research Conference in 1842, that benzene is present in coal tar; this claim was not immediately published, however. Even before the discovery of benzene, Ferdinand Runge had found aniline and phenol in coal tar in 1834. The composition of the aromatic mixture, coal tar, was still largely unknown up to the middle of the 19th century. As tar production grew, so analytical investigations increased; August Wilhelm v. Hofmann, a disciple of Justus v. Liebig, was particularly active in this field.

In 1845, Hofmann went to London as Principal of the newly-founded Royal College of Chemistry, to continue his investigations at the original source of coal tar. Hofmann gathered a number of young chemists around him, who concentrated on

investigating the reactions of tar components. London thus became the Mecca of aromatic chemistry.

Concurrent with the rather haphazard discovery of the first coal-tar dyes, important scientific knowledge was being accumulated, which significantly advanced the understanding of the chemical reactions involved in the production of dyestuffs. After Friedrich August Kekule, a Professor at Bonn University, had postulated the tetravalent bonding of carbon in 1857, he proposed, in 1865, the ring formula for benzene, which provided the basis for understanding the essentials of aromatic chemistry.

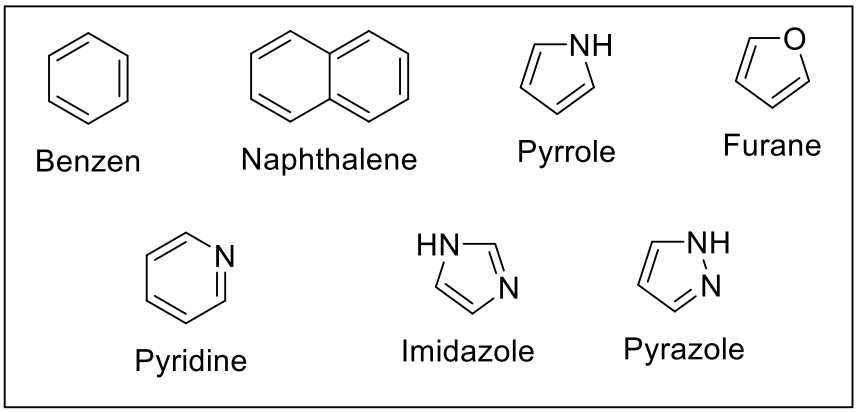
Initially, coal-derived raw materials were the almost exclusive source of aromatics. However, beginning in the 1930's, the growth of the automobile industry brought petroleum to the fore in ever-increasing quantities as a source of raw materials for monocyclic aromatics.

Alongside pyrolytic processes for the production of aromatics, this new development was accompanied by the introduction of catalysis; even today, catalytic and purely thermal processes still complement each other in the production of aromatics [3].

I-3-Structure of aromatic compounds:

Aromatic compounds are cyclic structures in which each ring atom is a participant in a π bond, resulting in delocalized π electron density on both sides of the ring. Due to this connected network of pi bonds, the rings are planar.

I-4-Some examples of aromatic compounds:



Figure(I-1-) : Aromatic compounds

I-5-Aromatic property:

There are ubiquitous properties of each of the aromatic compounds, which are as follows:

1-The aromatic compound contains a ring shape containing a cloud in a circular path of non-positional pi electrons above and below the ring level resulting from interference between the electrons present in adjacent p orbits. In other words, to get

an electronic cloud in a circular path, the atoms in the ring must not be separated by a saturated carbon atom.

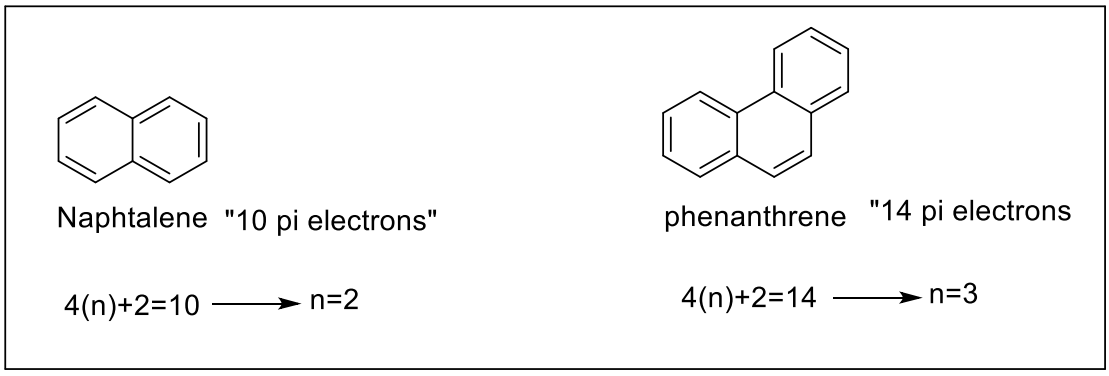
2-For maximum interference between π orbits, the atoms of the aromatic compound must be located at one level.

3-This cloud of non-positional π electrons leads to the stability of the aromatic ring so the ring prefers substitution reaction rather than addition reactions, which destroys the aromatic character.

4-The electronic cloud must contain a sum (4n + 2) From π electrons, where n is equal to a positive or zero integer, so it must contain special numbers of these electrons such as 2, 6, 10 and so on, so that the compound is aromatic, and this is what we call "Huckel rule" relative to its finder.

In the case of a benzene molecule, for example, n=1, so the law becomes 4(1)+2=6 and this applies to the number of Pi electrons in the benzen ring, since there are 6 π electrons. This rule can be applied to aromatic compounds involving more than one benzene ring, such as Naphthalene (10 π electrons) and phenantherene (14 π electrons). Heteroatomes compounds such as pyrrole, indole, etc[4].

Example:



Figure(I-2-) :Hückel's rule

I-6-Physical properties of aromatic compounds:

In general, arenes resemble other hydrocarbons in their physical properties. They are nonpolar, insoluble in water, and less dense than water. In the absence of polar substituents, intermolecular forces are weak and limited to van der Waals attractions of the induced-dipole/induced-dipole type.

At one time, benzene was widely used as a solvent. This use virtually disappeared when statistical studies revealed an increased incidence of leukemia among workers exposed to atmospheric levels of benzene as low as 1 ppm. Toluene has replaced benzene as an inexpensive organic solvent, because it has similar solvent properties

but has not been determined to be carcinogenic in the cell systems and at the dose levels that benzene is[5].

I-7-The future of aromatic chemistry:

The rise of industrial organic chemistry in the mid-19th century was initiated by pioneering innovations in the field of aromatic chemistry. It has since undergone continuous further development. Plastics and pesticides followed dyes and pharmaceuticals as the main areas of innovation.

The innovative impetus of industrial aromatic chemistry is likely to be maintained in the future, characterized by a qualitative growth.

The main sources of feedstock for the production of aromatics will continue to be the pyrolysis products of naphtha cracking and coal carbonization, and the catalyticre forming of gasoline fractions. These raw materials will be complemented by catalytic processes to provide aromatics from small aliphatic building blocks.

The raw material base for aromatic chemistry is sufficiently large to cope with wider future applications, since aromatics are used in vast quantities to produce fuels and industrial oils; in comparison the raw material requirement for the industrial aromatic chemistry is relatively small.

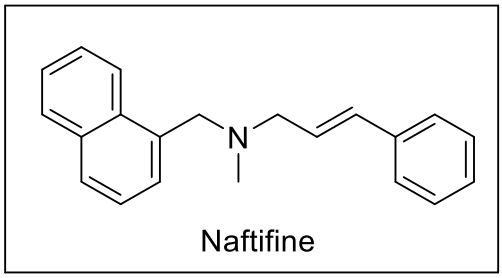
Among the methods used to recover pure aromatics, crystallization processes will gain further ground, since they generally are distinguished by lower energy consumption than distillative processes.

In future, catalytic processes will become increasingly important in the development of aromatic conversion processes. The prime objectives will include the highly selective production of pure grades of the desired product and an improvement in environmental protection. Catalysts with corrosive properties will be replaced by less corrosive ones, such as the zeolites.

The range of processes to further upgrade aromatics will be extended by the inclusion of biotechnical processes. Aromatic molecules are often more difficult toconvert by micro-organisms than aliphatic molecules, but developments in recent times have indicated that, for example, aromatics which were long considered as barely degradable can indeed be broken down. Typical of this development are the recent results in the field of biochemical degradation of lignin and brown coal.

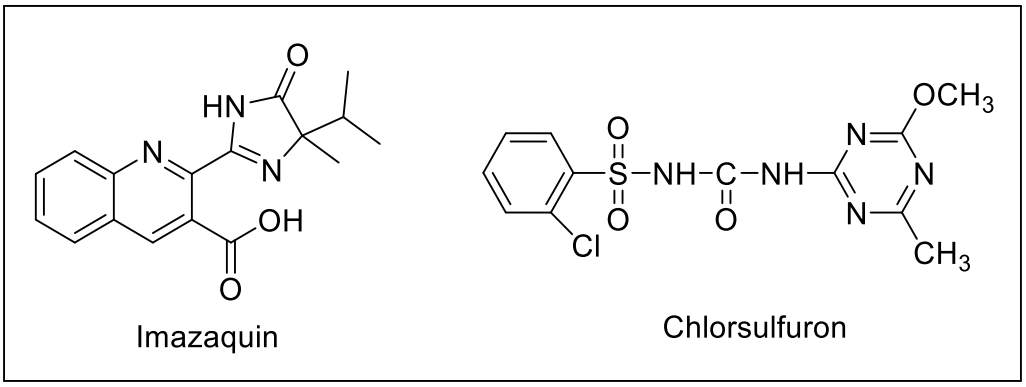
The association of biotechnology with pharmaceutical chemistry will continue to provide significant impulses for the aromatic chemistry in the future. A large number of chemicals which play a dominant role in natural processes are of aromatic character, for example, tryptophan, the alkaloids quinine and morphine, and nucleic acids. Complex molecules with aromatic moieties, such as vitamin E, penicillins and more simple aromatics such as acetylsalicylic acid, paracetamol and ephedrine serve as traditional drugs. The increased use of biotechnical processes in the production of pharmaceutically effective compounds thus offers interesting prospects for the future.

There are constant new developments in the synthetic production of drugs using heterocyclics and mono- and polynuclear aromatics; one of the most recent examples is the antimycotic naftifine, an allylamine derivative of naphthalene.



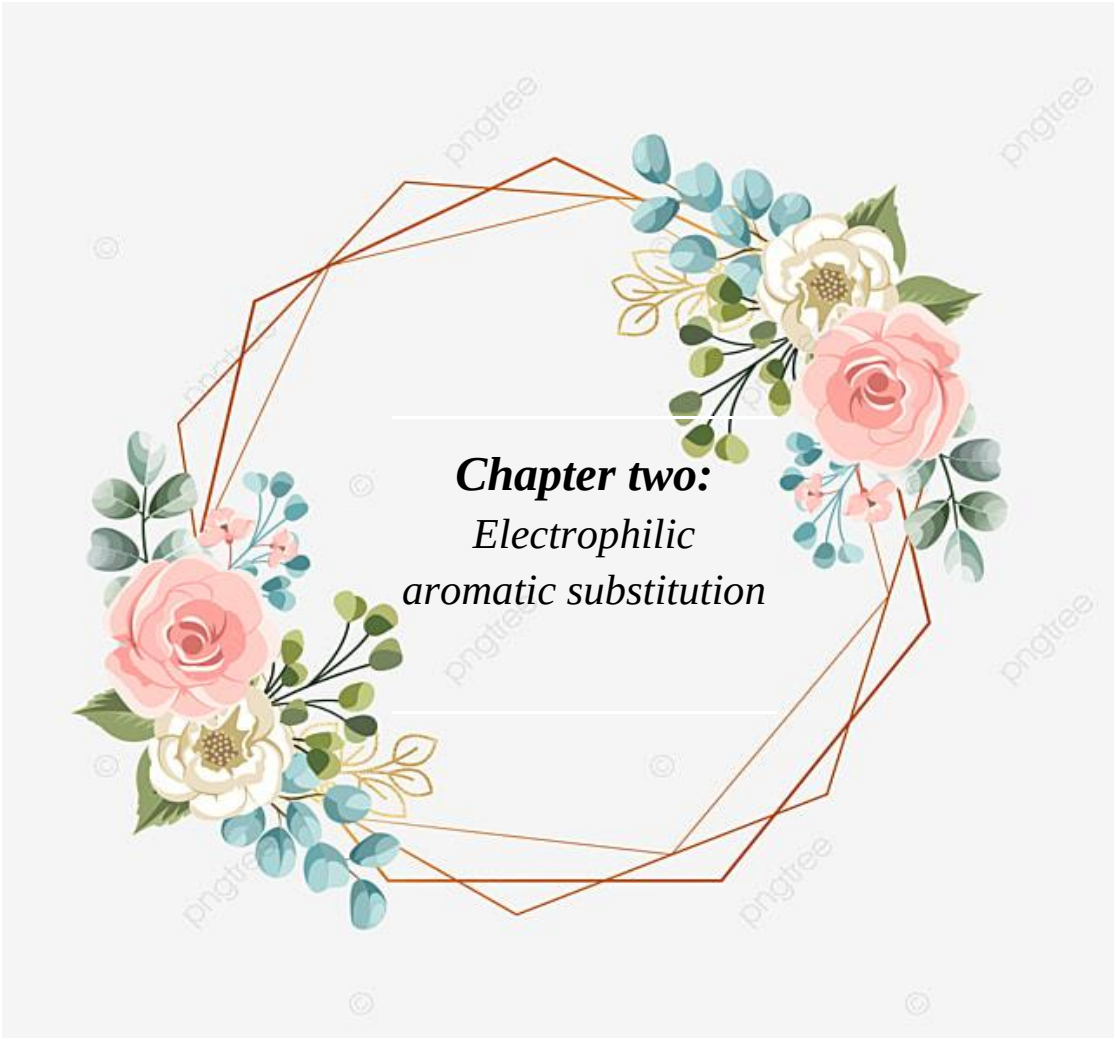
Figure(I-3-) :Naftifine

In the development of new plant protection agents, future pesticides will be distinguished by higher selectivity with lower dosages of application, together with adjusted biodegradability and the formation of non-toxic degradation products.
Once again, aromatics have an important role to play, as evidenced by the example of synthetic pyrethroid insecticides or by the herbicides imazaquin, a derivative of quinoline, and chlorsulfuron.



Figure(I-4) :Imazaquin, Chlorsulfuron

The potential to form pre-oriented phases (liquid crystals) offers additional areas of application for aromatics, especially for engineering plastics for high value composites.
Industrial aromatic chemistry will therefore continue to provide a field of rich potential for the chemist and the process engineer [6].



Chapter two:

Electrophilic aromatic substitution

II-Chapter two: Electrophilic aromatic substitution

II-1-Difinition of the electrophilic aromatic substitution:

Electrophilic aromatic substitution is one of the most important synthetic organic reactions. Since its discovery in the 1870s by Charles Friedel and James Crafts, it has become a general route to functionalized aromatic compounds. The chemistry is used extensively in the chemical industry, providing millions of tons of aromatic products annually for chemical feed stock, commodity chemicals, and consumer applications [7].

Many electrophiles can replace hydrogen on an aromatic ring. A halogen atom, usually chlorine or bromine, adds to the ring through a halogenation reaction. The nitro group (—NO_2) and the sulfonic acid group (—SO_3H) add in nitration and sulfonation reactions. Alkylation and acylation reactions introduce alkyl (—R) and acyl groups (—COR). These reactions all occur by the same general reaction mechanism [8].

The scope of electrophilic aromatic substitution is quite large; both the arene and the electrophilic reagent are capable of wide variation. Indeed, it is this breadth of scope that makes electrophilic aromatic substitution so important. Electrophilic aromatic substitution is the method by which substituted derivatives of benzene are prepared. We can gain a feeling for these reactions by examining a few typical examples in which benzene is the substrate [9].

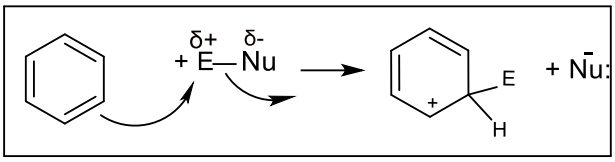
II-1-2-Mechanism of Electrophilic Aromatic Substitution:

The reaction mechanism consists two steps:

In the first step of electrophilic aromatic substitution, this resembles the addition of electrophiles.to alkenes, the electrophile accepts a pair of electrons from the aromatic ring. However, because this electron pair forms part of a delocalized aromatic sextet, aromatic compounds are significantly less reactive than alkenes.

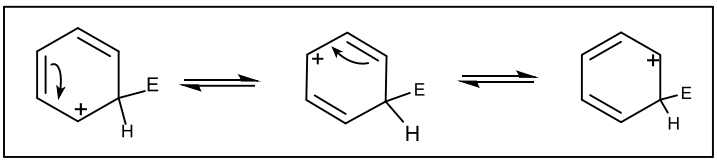
When the electrophile adds to the aromatic ring, it produces a carbocation intermediate.

The first step of electrophilic aromatic substitution is usually the rate-determining step. Since a new sigma bond forms in the first step, the intermediate is called a sigma complex, or intermediate Melland.



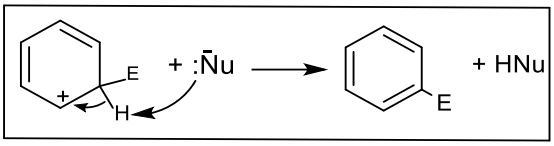
Figure(II-1-) : General case of EAS "step1"

This carbocation is resonance stabilized, but is not aromatic because it has only four p electrons. Therefore, the sigma complex is much more reactive than the original aromatic ring.



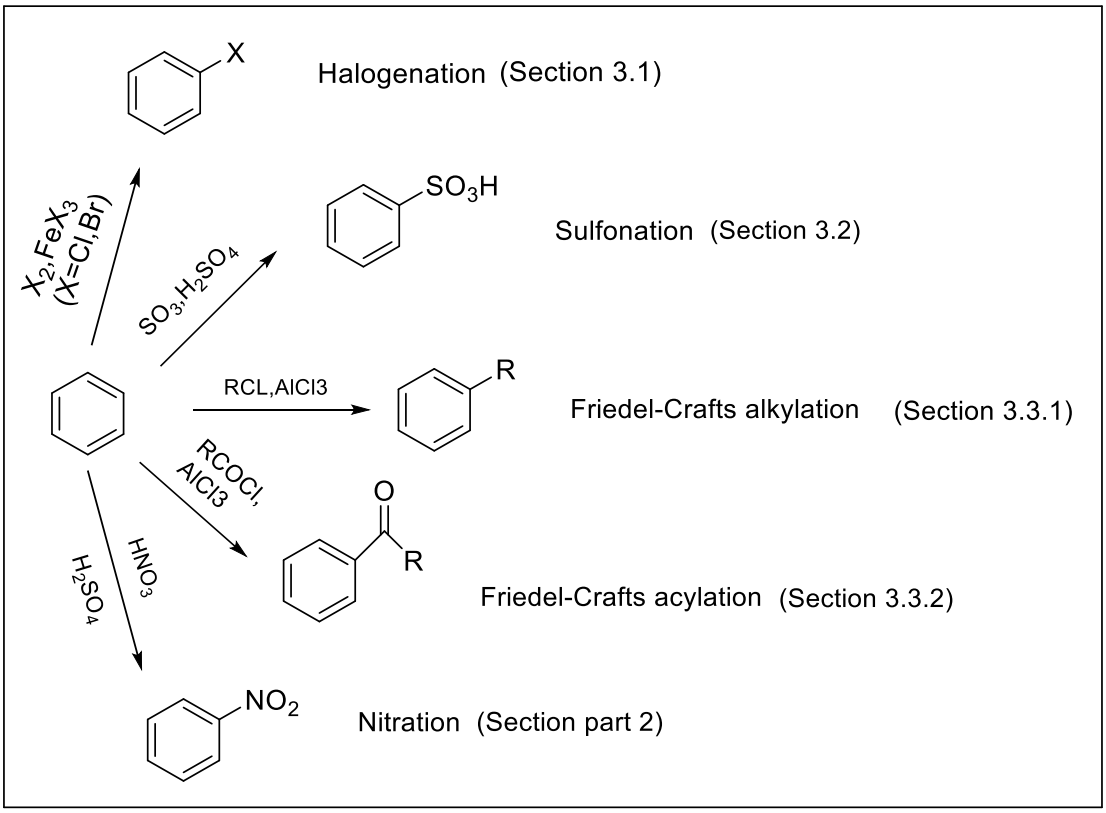
Figure(II-2-) : Resonance form of the substituted benzene ring

In the faster second step of the electrophilic substitution mechanism, the proton bound to the sp3-hybridized ring carbon atom leaves, restoring the aromatic p system.
A nucleophile, acting as a base, extracts the leaving proton [10].



Figure(II-3-) : General case of EAS "step2"

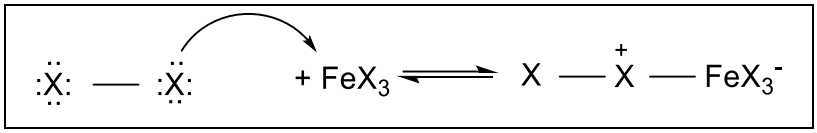
II-1-3-Types of electrophilic aromatic substitution:



Figure(II-4-) : Types of the electrophilic aromatic substitution[11].

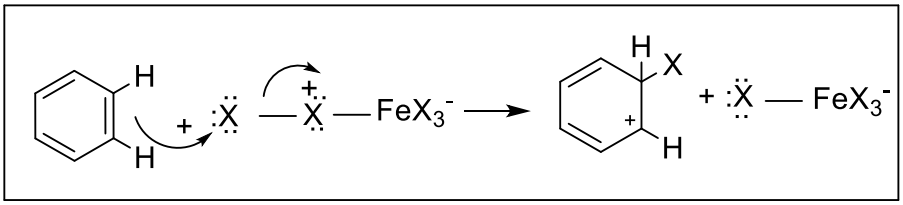
II-1-4-1-Halogenation:

1. Generation of the electrophile:



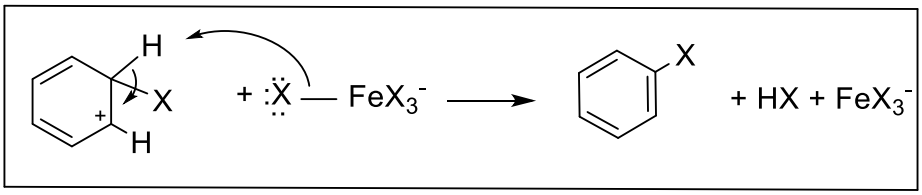
Figure(II-5-) : General case of Halogenation "step1"

2. Attack of the aromatic ring forming the cationic intermediate:



Figure(II-6-) : General case of Halogenation "step2"

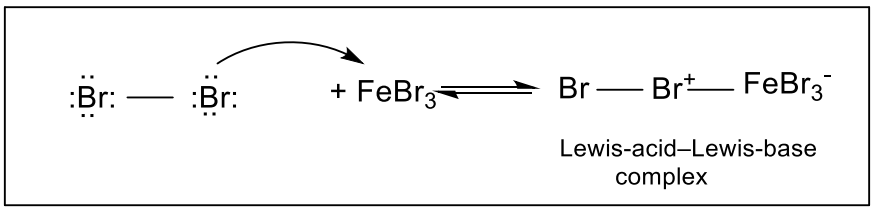
2. Deprotonation:



Figure(II-7-) : General case of Halogenation"step3"

Example:"X=Br"
1. Generation of the electrophile:

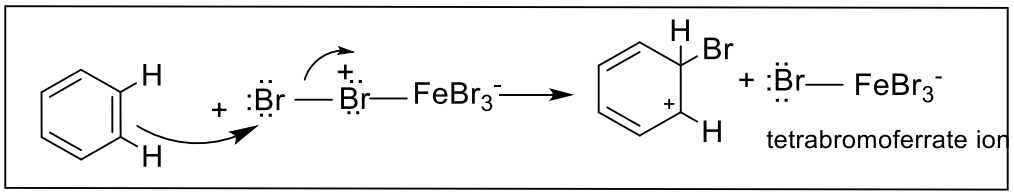
In the presence of a strong Lewis acid, bromine and chlorine halogenate aromatic rings. Bromination requires both Br2 and a Lewis acid catalyst, FeBr3. The catalyst generates a Lewis acid–Lewis base complex with a weakened Br—Br bond. The bromine atom bonded to iron carries a formal positive charge. It is the electrophile [12].



Figure(II-8-) : Halogenation "step 1"

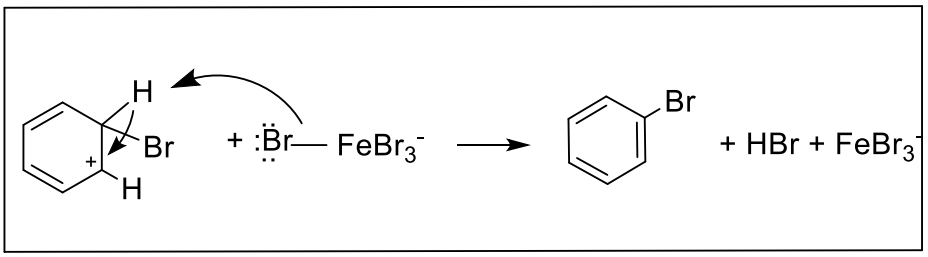
2. Attack of the aromatic ring:

The Lewis acid-base complex reacts with the benzene ring to form the cyclohexadienyl ion. This step also forms the tetrabromo ion, which removes a proton from the cyclohexadienyl ion in a later step. This step also regenerates iron (III) bromide, which continues to act as a reaction catalyst [12].



Figure(II-9-) : Halogenation "step 2"

3. Deprotonation:



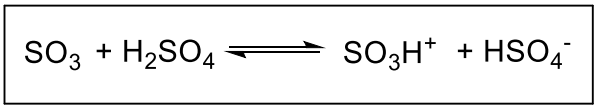
Figure(II-10-) : Halogenation "stap 3"

Electrophilic halogenation is applied on a large scale, for example, in the production of chlorobenzenes.

II-1-4-2-Sulfonation:

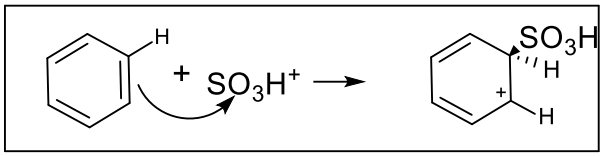
1. Generation of the electrophile:

We can add a sulfonic acid group (-SO_3H) to an aromatic ring by sulfonation. The reaction requires a mixture of SO3 and sulfuric acid, called fuming sulfuric acid. The electrophile is SO_3H^+ [12].



Figure(II-11-) : Sulfonation "step 1"

2. Attack of the aromatic ring:



Figure(II-12-) : Sulfonation "step 2"

3. Deprotonation:

Figure(II-13-) : Sulfonation "step 3"

The sulfonation reaction is less exothermic than halogenation or nitration. Hence, it is reversible, and desulfonation occurs in dilute aqueous acid. The reversibility of sulfonation forms the basis of the synthesis of some aromatic compounds because the sulfonic acid group may block a position on an aromatic ring, preventing substitution at that point. The sulfonic acid group is removed at the end of the synthesis.

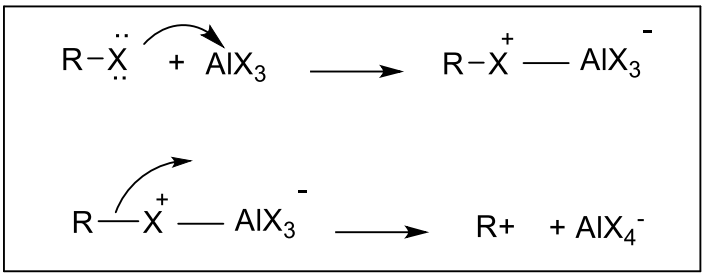
The sulfonic acid functional group, commonly found in azo dyes, affects both the color of a compound and its solubility in water. A sulfonic acid group can be converted to a sulfonamide group to form sulfa drugs [12].

Historically, sulfonation has been one of the most important electrophilic aromatic substitutions, particularly in the production of 1- and 2-naphthol, as well as alizarin. Unlike the previously mentioned electrophilic reactions, it is frequently reversible. SO_3, which occurs in low concentration in sulfuric acid, acts as the electrophilic agent [13].

II-1-4-3- The Friedel–Crafts Reactions:

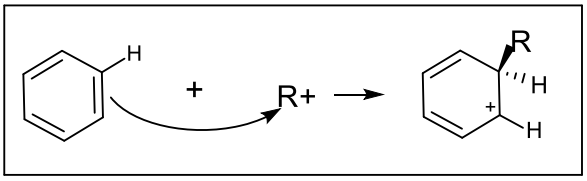
II-1-4-3-1- Alkylation:

1. Generation of the electrophile:



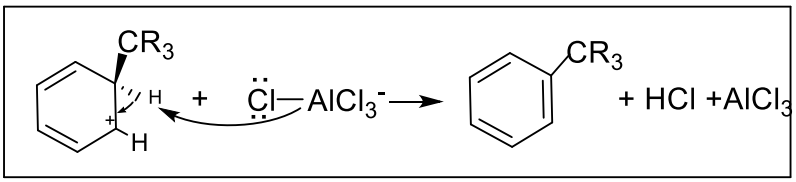
Figure(II-14-) : General case of Alkylation "step1"

2.Attack of the aromatic ring:



Figure(II-15-) : General case of Alkylation "step2"

3. Deprotonation:



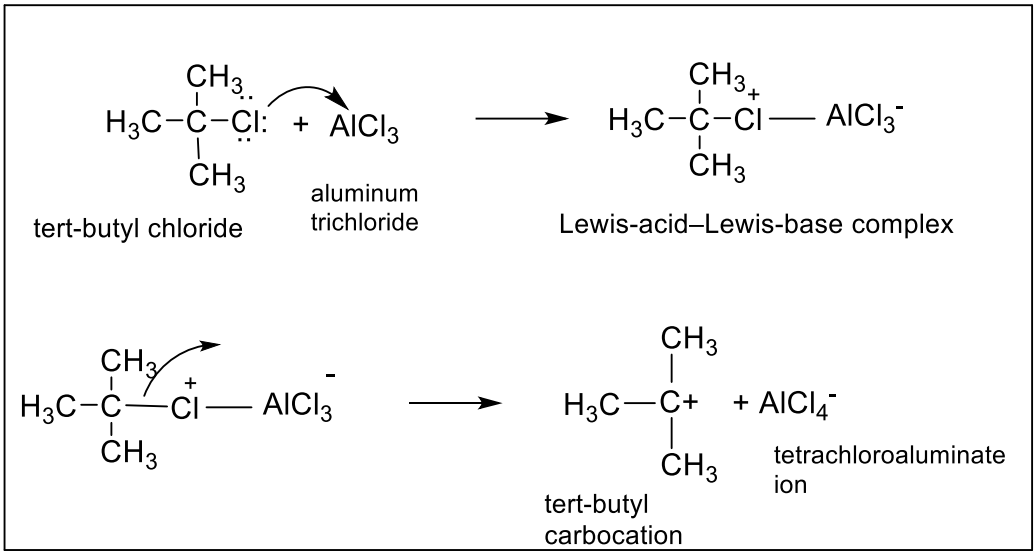
Figure(II-16-) : General case of Alkylation "step3"

Example:*"RX= $(CH_3)_3CCl$"*

1. Generation of the electrophile:

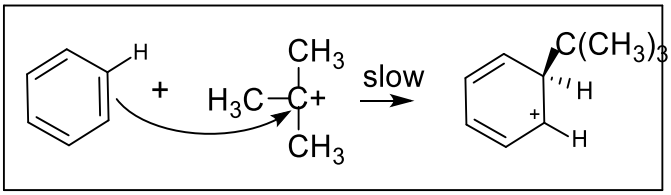
An alkyl group can replace a hydrogen atom of benzene in the Friedel–Crafts alkylation reaction. This reaction requires an alkyl halide, with an aluminum trihalide

as the catalyst. The catalyst produces an Electrophilic species, The reaction is commonly carried out only with alkyl bromides or alkyl chlorides [12].



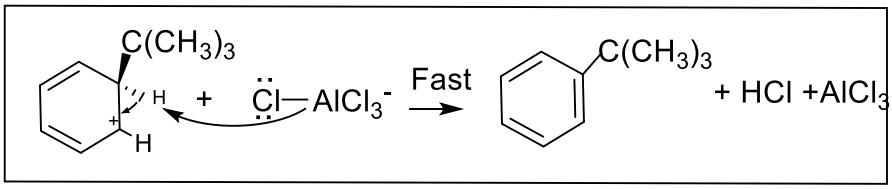
Figure(II-17-) : Alkylation "step 1"

2. Attack of the aromatic ring forming the cationic intermediate:



Figure(II-18-) : Alkylation "step 2"

3. Deprotonation:



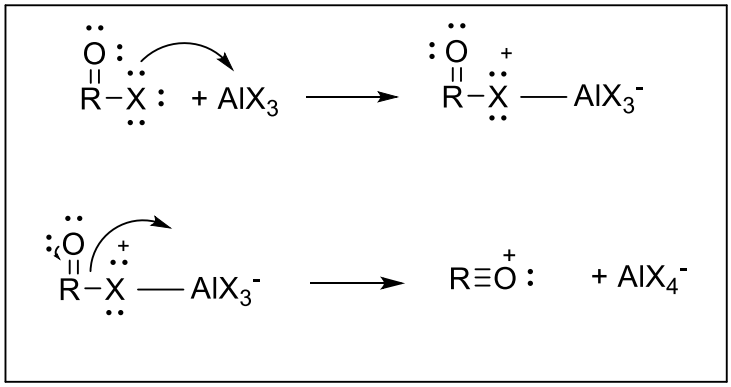
Figure(II-19-) : Alkylation "step 3"

Secondary alkyl halides react with benzene by forming a secondary carbocation. However, primary alkyl halides do not form carbocations under Friedel–Crafts conditions. Instead, the alkyl group transfers directly to the aromatic ring from the

Lewis acid–Lewis base complex, which has a highly polarized carbon halogen bond [12].
Care should be taken in Friedel Crafts alkylation since the alkyl aromatic produced displays increased reactivity in comparison with the original unsubstituted aromatic, because of the activating effect of the alkyl group, so that the formation of by-products is unavoidable [14].

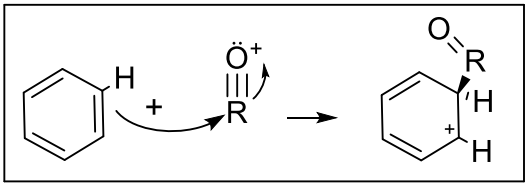
II-1-4-3-2-Acylation:

1. Generation of the electrophile:



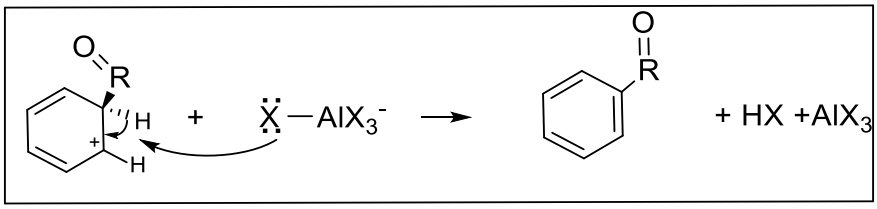
Figure(II-20-) : General case of Acylation "step1"

2. Attack of the aromatic ring:



Figure(II-21-) : General case of Acylation "step2"

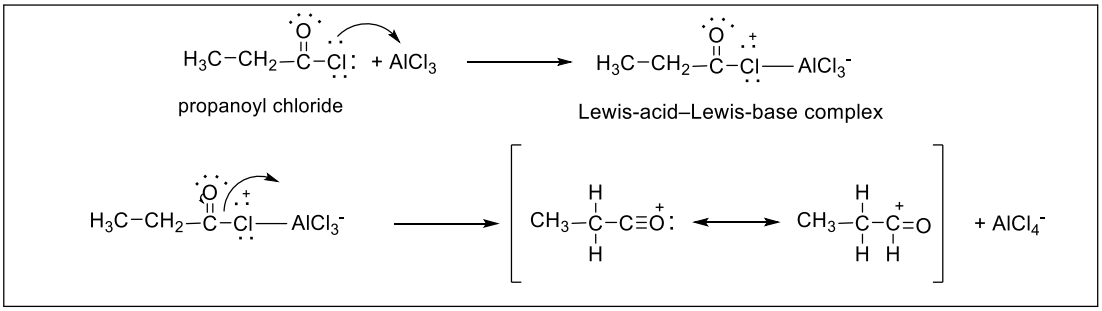
3. Deprotonation:



Figure(II-22-) : General case of Acylation "step3"

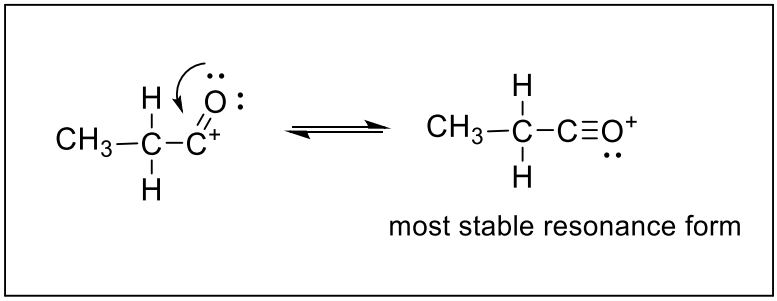
Example:"ROX=CH_3CH_2COCL"
1. Generation of the electrophile:

An acyl group can replace hydrogen in an aromatic ring by a reaction called Friedel–Crafts acylation. The reaction requires an acyl halide and the corresponding aluminum trihalide. The reaction is commonly carried out only with acyl chlorides.
The electrophile is shown as an acyl cation, called an acylium ion, forms from a Lewis acid–Lewis base complex of aluminum trichloride and the acyl chloride [12].

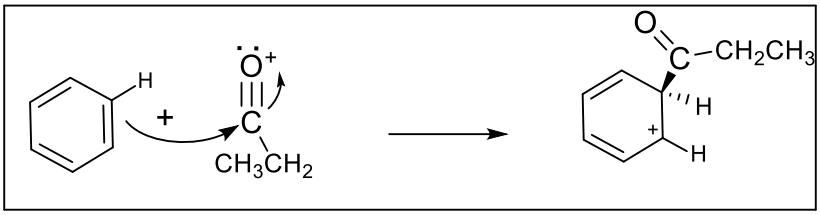


Figure(II-23-) : Acylation "step 1"

The acyl cations are stabilized by resonance. The most stable form has eight bits of electrons on the carbon and oxygen atoms, and an official positive charge on the oxygen atom. However, to give a stable product, the acylation reaction must occur [12].

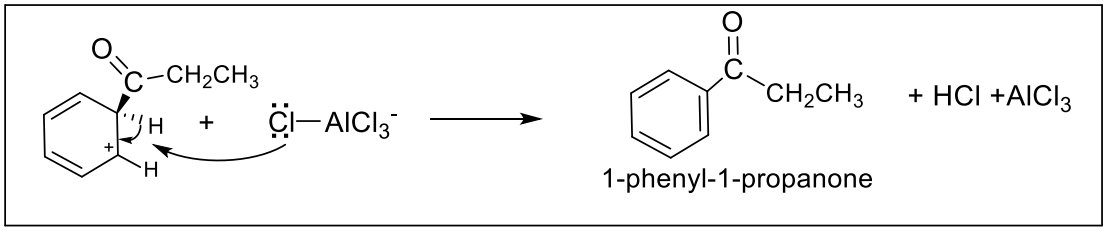


2. Attack of the aromatic ring forming the cationic intermediate:



Figure(II-24-) : Acylation "step 2"

3. Deprotonation:



Figure(II-25-) : Acylation "step3"

Friedel-Crafts acylation is related to Friedel-Crafts alkylation, with an acylium cation acting as the electrophile. However, in industrial aromatic chemistry, because of the high consumption of catalyst, this reaction is of much less importance than Friedel-Crafts alkylation.

Nonetheless, it has been used, for example, in the manufacture of anthraquinone from phthalic anhydride and benzene [14].

Part one:

Nitration reaction

II-2-Difinition of a nitration reaction:

Some of the most common and important organic reactions involve nitration of various organic compounds. Nitrated organic compounds find wide use in many applications. Majority of energetic materials, for example, are organic compounds, which derive their energy from the nitro group serving as an intramolecular oxidizer. Nitrated aromatics are of particular interest as they are widely used as solvents, dyes, explosives, pharmaceuticals, and perfumes. In addition, they serve as intermediates in preparation of other compounds [15].

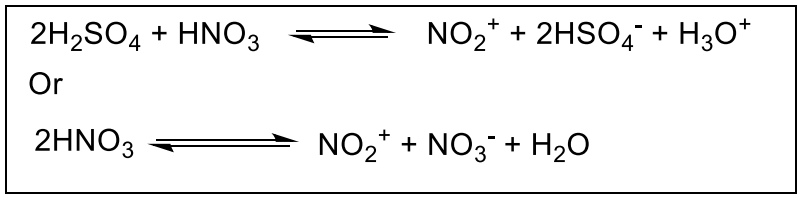
II-2-1-The importance of nitration:

Nitration is important for two reasons:
Firstly, because it is the most general process for the preparation of aromatic nitro compounds.
Secondly, because of the part which it has played in the development of theoretical organic chemistry. It is of interest because of its own characteristics as an electrophilic substitution. The first nitration to be reported was that of benzene itself. Mitscherlich in 1834 prepared nitrobenzene by treating benzene with fuming nitric acid. Not long afterwards the important method of effecting nitration with a mixture of nitric and sulphuric acids ('mixed acid') was introduced, evidently in a patent by Mansfield; the poor quality of early nitric acid was probably the reason why the method was developed. Since these beginnings, nitration has been the subject of continuous study [16].

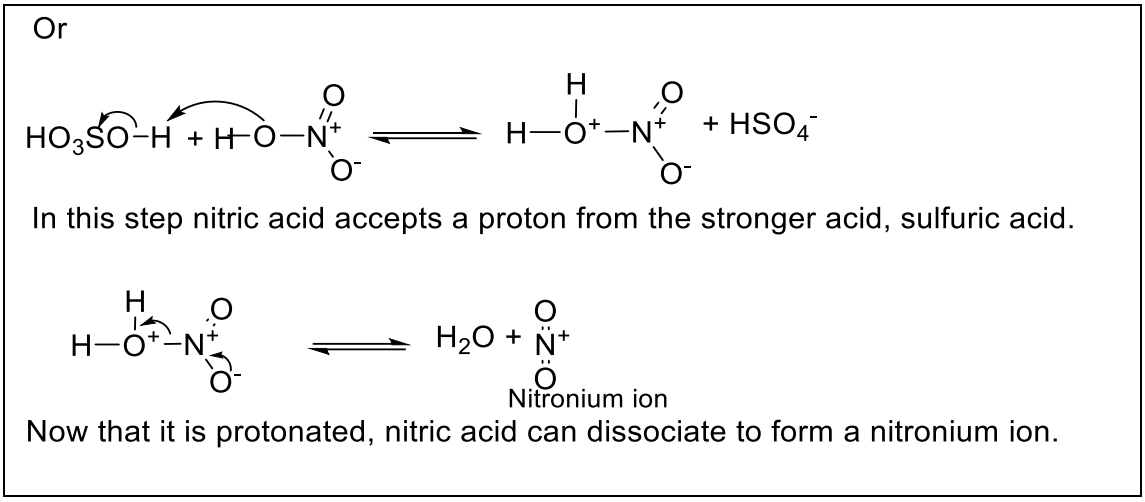
II-2-2-Mechanism of nitration:

As anticipated from the general mechanism for electrophilic substitution, there are three distinct steps.
Conditions under which each of the first two steps is rate determining have been recognized. The third step is usually very fast.

1. Generation of the electrophile:

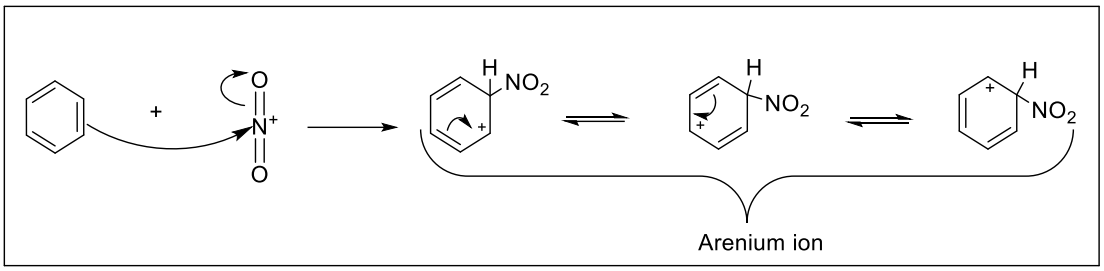


Figure(II-26-) : Nitration "step1" using 2 moles of the acids



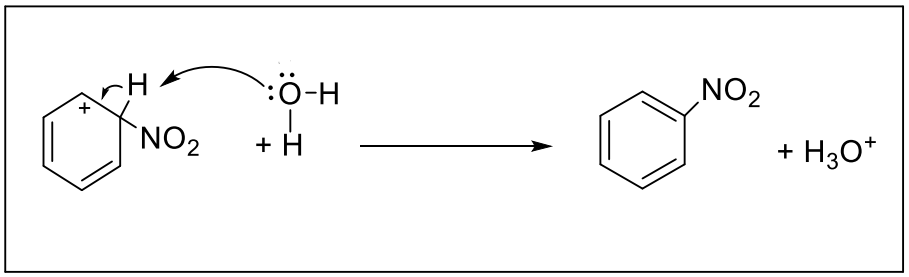
Figure(II-27-) : Nitration "step1" using both acides

2. Attack of the aromatic ring forming the cationic intermediate:



Figure(II-28-) : Nitration "step2"

3. Deprotonation:

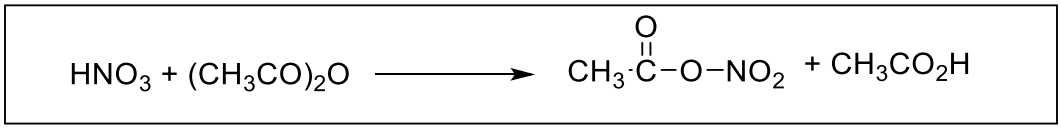


Figure(II-29-) : Nitration "step3"

There are three general types of kinetic situations that have been observed for aromatic nitration. Aromatics of modest reactivity exhibit second-order kinetics in mixtures of nitric acid with the stronger sulfuric or perchloric acid. Under these conditions, the formation of the nitronium ion is a fast pre equilibrium and Step 2 of the nitration mechanism is rate controlling. If nitration is conducted in inert organic solvents, such as nitromethane or carbon tetrachloride in the absence of a strong acid, the rate of formation of nitronium ion is slower and becomes rate limiting. Finally, some very reactive aromatics, including alkylbenzenes, can react so rapidly under conditions where nitronium ion concentration is high that the rate of nitration becomes governed by encounter rates. Under these circumstances mixing and diffusion control the rate of reaction and no differences are observed between the reactants.

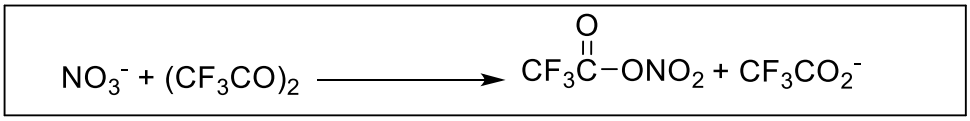
With very few exceptions, the final step in the nitration mechanism, the deprotonation of the δ complex, is fast and has no effect on the observed kinetics. The fast deprotonation can be confirmed by the absence of an isotope effect when deuterium or tritium is introduced at the substitution site. Several compounds such as benzene, toluene, bromobenzene, and fluorobenzene were subjected to this test and did not exhibit isotope effects during nitration. The only case where a primary isotope effect has been seen is with 1,3,5-tri-t-butylbenzene, where steric hindrance evidently makes deprotonation the slow step.

There are several other synthetic methods for aromatic nitration. Nitric acid in acetic anhydride is a potent nitrating agent and effects nitration a higher rates than nitric acid in inert organic solvents. Acetyl nitrate is formed and it is the nitrating agent.



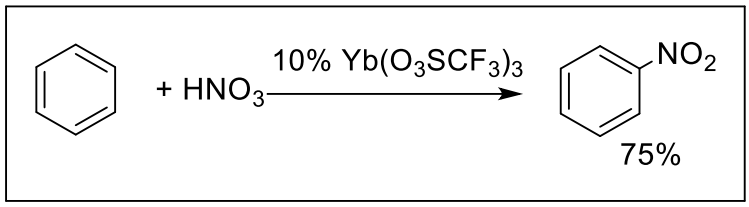
Fegure(II-30-) : Method of nitration using nitric acid in acetic anhydride

A very convenient synthetic procedure for nitration involves the mixing of a nitrate salt with trifluoroacetic anhydride. This generates trifluoroacetyl nitrate, which is even more reactive than acetyl nitrate.



Fegure(II-31-) : Method of nitration using a mixture of a nitrate salt with trifluoroacetic anhydride

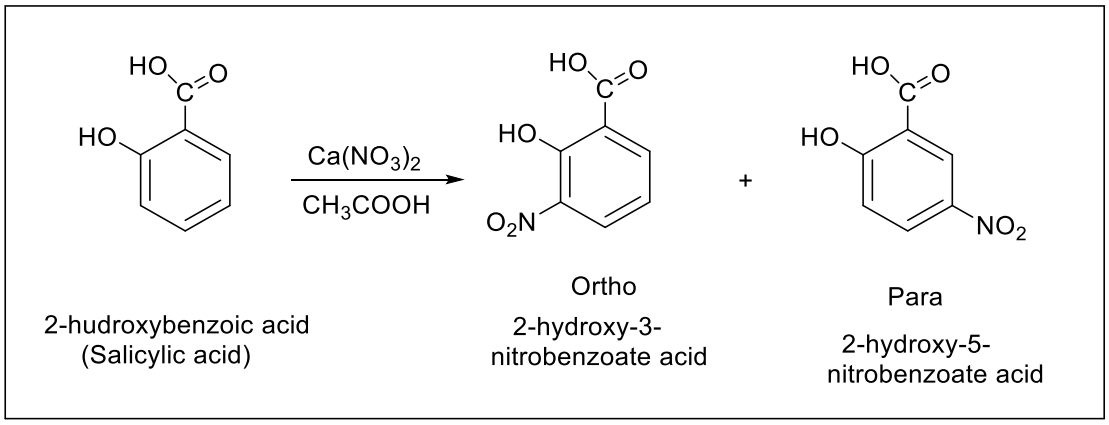
Benzene, toluene, and aromatics of similar reactivity can be nitrated using Yb(O3SCF3)3 and 69% nitric acid in an inert solvent. The catalyst remains active and can be reused. The active nitrating agent under these conditions is uncertain but must be some complex of nitrate with the oxyphilic lanthanide [17].



Figure(II-32-) : Nitration with $Yb(O_3SCF_3)_3$

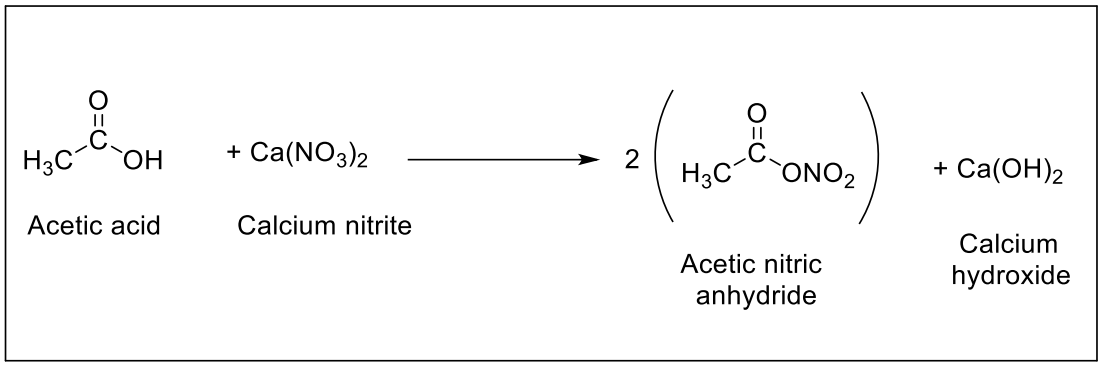
II-2-3-Example of nitration:

Using "$Ca(NO_3)_2$, CH_3COOH:



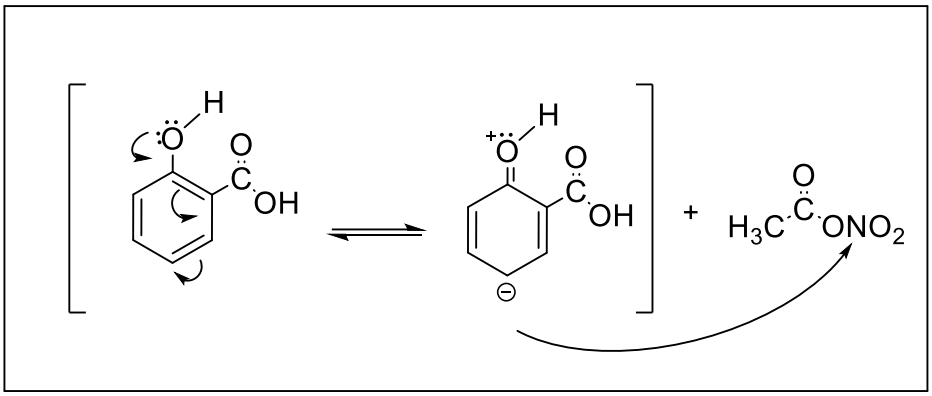
Figure(II- 33-) : Nitration of salicylic acid

1. Generation of the electrophile:



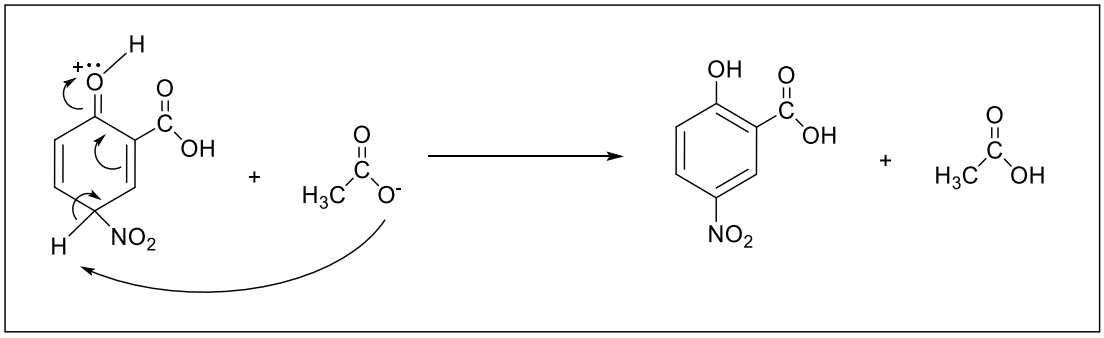
Figure(II-34-) : Nitration of salicylic acid "step 1"

2. Attack of the aromatic ring forming the cationic intermediate:



Figure(II-35-) : Nitration of salicylic acid "step 2"

3. Deprotonation:

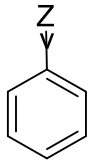


Figure(II-36-) : Nitration of salicylic acid "step 3"

II-2-4- Orientation of the Incoming Groups:

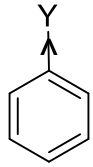
- A substituent can make the ring more reactive than benzene (i.e., it can make the compound react faster than benzene reacts). Such a group is called an activating group.
- A substituent can make the ring less reactive than benzene (i.e., it can make the compound react more slowly than benzene reacts). Such groups are called deactivating groups.

If a substituent that is already present on the ring makes the ring more electron rich by donating electrons to it, then the ring will be more reactive toward the electrophile and the reaction will take place faster.`



If Z donates electrons the ring is more electron rich and it reacts faster with an electrophile.

On the other hand, if the substituent on the ring withdraws electrons, the ring will be electron poor and an electrophile will react with the ring more slowly.



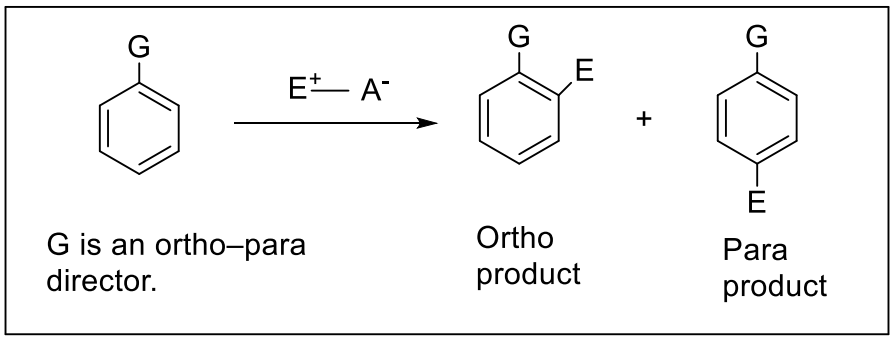
If Y withdraws electrons the ring is electron poor and it reacts more slowly with an electrophile.

II-2-4-1-Ortho–Para-Directing Groups and Meta-Directing Groups:

A substituent on the ring can also affect the orientation that the incoming group takes when it replaces a hydrogen atom on the ring. Substituents fall into two general classes:

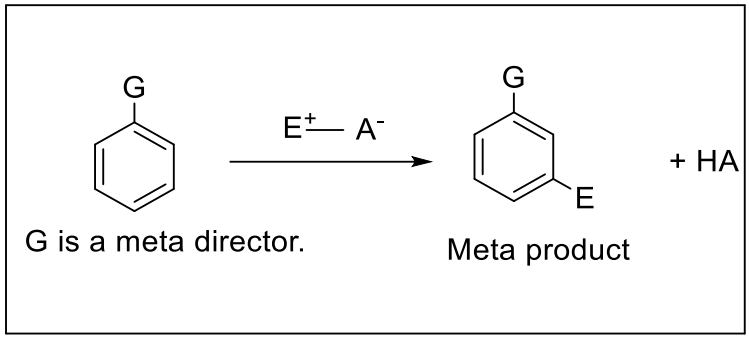
II-2-4-1-1-Ortho–para directors:

predominantly direct the incoming group to a position ortho or para to itself.



Figure(II-37-) : Ortho, para director reaction

II-2-4-1-2-Meta directors: predominantly direct the incoming group to a position meta to itself.

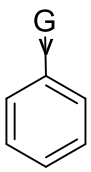


Fegure(II-38-) : Meta director reaction

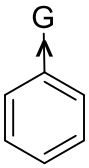
II-2-4-2-Electron-Donating and Electron-Withdrawing Substituents:

Whether a substituent is an activating group or a deactivating group, and whether it is an ortho–para director or a meta director, depends largely on whether the substituent donates electrons to the ring or whether it withdraws electrons.

- All electron-donating groups are activating groups and all are ortho–para directors.
- With the exception of halogen substituents, all electron-withdrawing groups are deactivating groups and all are meta directors.
- Halogen substituents are weakly deactivating groups and are ortho–para directors.



If G donates electrons the ring is activated; it reacts faster, and at an ortho or para position.

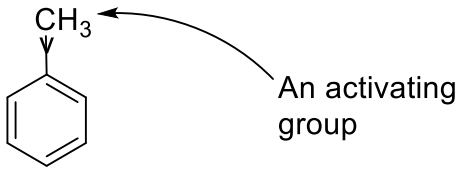


If G withdraws electrons the ring is deactivated; it reacts more slowly, and at a meta position (except when G is a halogen).

II-2-4-2-1-Groups: Ortho–Para directors:

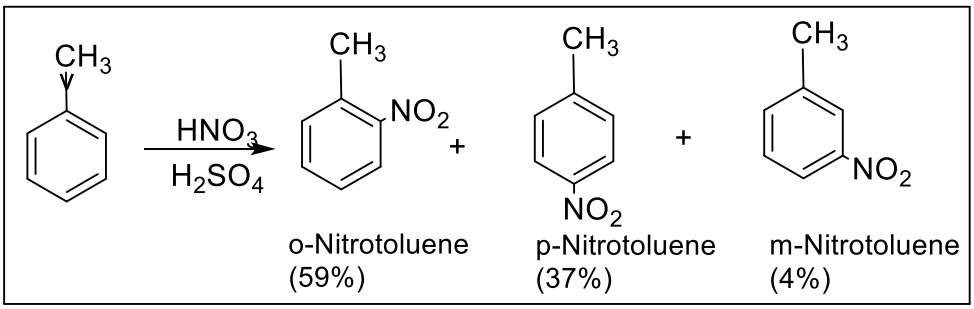
- Alkyl substituents are electron-donating groups and they are activating groups. They are also ortho–para directors.

Toluene, for example, reacts considerably faster than benzene in all electrophilic substitutions:



We observe the greater reactivity of toluene in several ways. We find, for example, that with toluene, milder conditions—lower temperatures and lower concentrations of the electrophile can be used in electrophilic substitutions than with benzene. We also find that under the same conditions toluene reacts faster than benzene. In nitration, for example, toluene reacts 25 times as fast as benzene.

We find, moreover, that when toluene undergoes electrophilic substitution, most of the substitution takes place at its ortho and para positions. When we nitrate toluene with nitric and sulfuric acids, we get mononitrotoluenes in the following relative proportions:



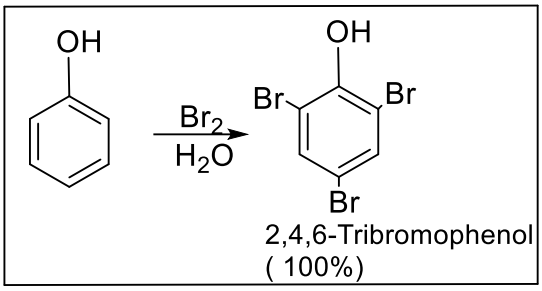
Fegure(II-39-) : Nitration reaction of Toluene

Of the mononitrotoluenes obtained from the reaction, 96% (59% _ 37%) have the nitro group in an ortho or para position. Only 4% have the nitro group in a meta position.

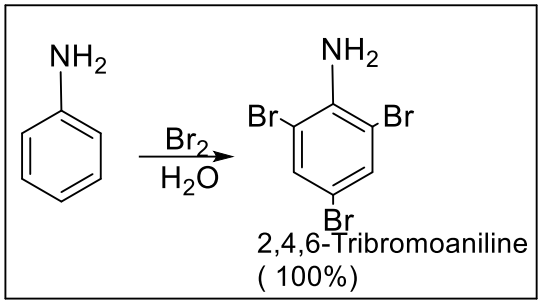
Predominant substitution of toluene at the ortho and para positions is not restricted to nitration reactions. The same behavior is observed in halogenation, sulfonation, and so forth.

- Groups that have an unshared electron pair on the atom attached to the aromatic ring, such as amino, hydroxyl, alkoxyl, and amides or esters with the oxygen or nitrogen directly bonded to the ring, are powerful activating groups and are strong ortho–para directors.

Phenol and aniline react with bromine in water (no catalyst is required) at room temperature to produce compounds in which both of the ortho positions and the para position become substituted.



Figure(II-40-) : Substitution reaction of Phenol

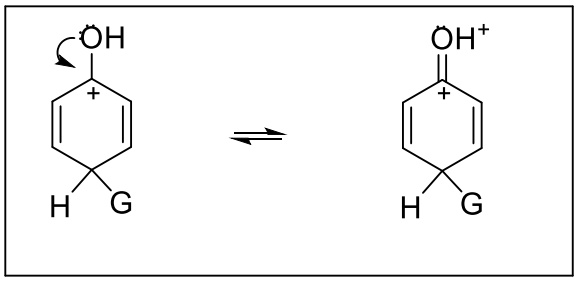


Figure(II-41-) : Substitution reactoin of Aniline

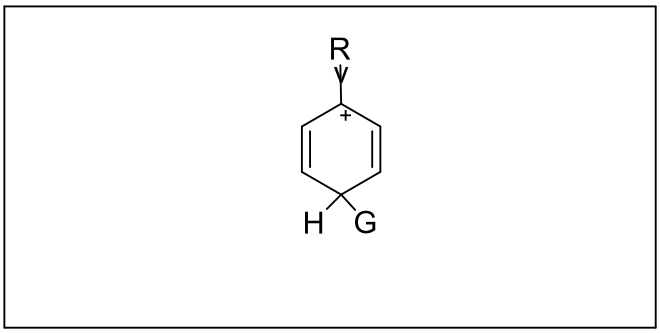
- In general, substituent groups with unshared electron pairs on the atom adjacent to the benzene ring (e.g., hydroxyl, amino) are stronger activating groups than groups without unshared electron pairs (i.e., alkyl groups).
- Contribution of electron density to the benzene ring through resonance is generally stronger than through an inductive effect.

As a corollary, even though amides and esters have an unshared electron pair on the atom adjacent to the ring, their activating effect is diminished because the carbonyl group provides a resonance structure where electron density is directed away from the benzene ring. This makes amides and esters less activating than groups where the only resonance possibilities involve donation of electron density toward the benzene ring.

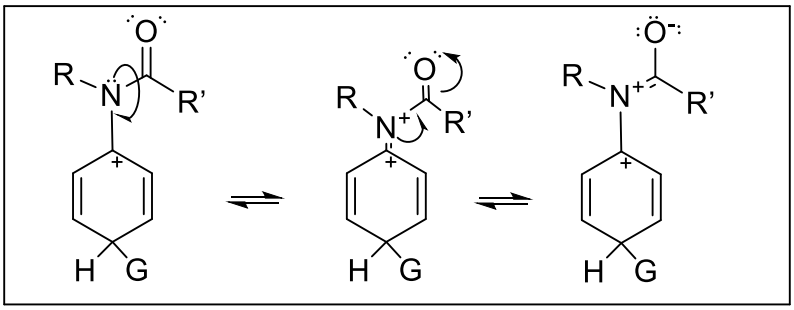
Examples of arenium ion stabilization by resonance and inductive effects:



Figure(II-42-) : Electron donation through resonance



Figure(II-43-) : Electron donation through the inductive effect

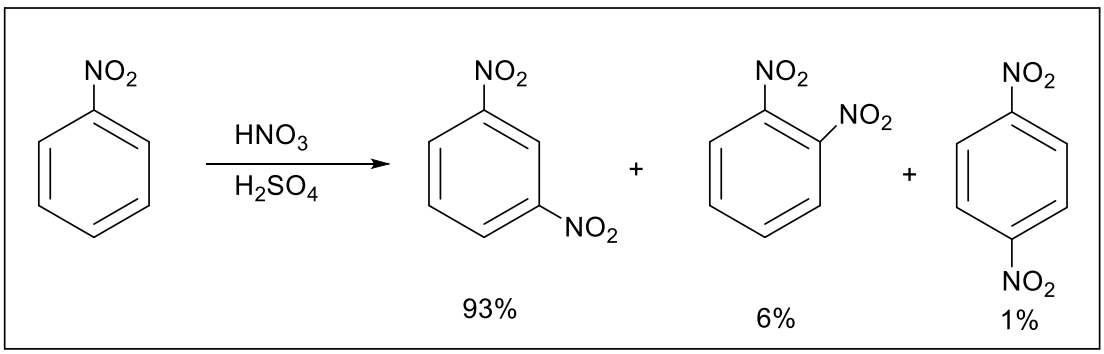


Figure(II-44-) : Electron donating far away from the ring

Electron donation to the ring by resonance is reduced when there is an alternative resonance pathway away from the ring.

II-2-4-2-2-Deactivating Groups: Meta Directors:

The nitro group is a very strong deactivating group and, because of the combined electronegativities of the nitrogen and oxygen atoms, it is a powerful electron withdrawing group.
Nitrobenzene undergoes nitration at a rate only 10^-4 times that of benzene. The nitro group is a meta director. When nitrobenzene is nitrated with nitric and sulfuric acids, 93% of the substitution occurs at the meta position:



Figure(II-45-) : Nitration reaction of nitrobenzene

The carboxyl group (-CO_2H), the sulfonic acid group (-SO_3H), and the trifluoromethyl group (-CF_3) are also deactivating groups; they are also meta directors.

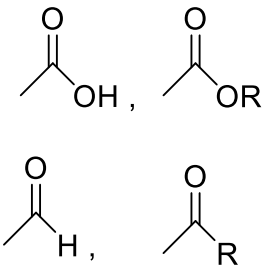
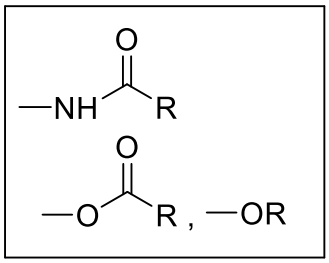
II-2-4-2-3-Halo Substituents: Deactivating Ortho–Para Directors:

The chloro and bromo groups are ortho–para directors. However, even though they contain unshared electron pairs, they are deactivating toward electrophilic aromatic substitution because of the electronegative effect of the halogens.
Chlorobenzene and bromobenzene, for example, undergo nitration at a rate approximately 30 times slower than benzene.

II-2-5-Classification of Substituents:

A summary of the effects of some substituents on reactivity and orientation is provided in this table [18]:

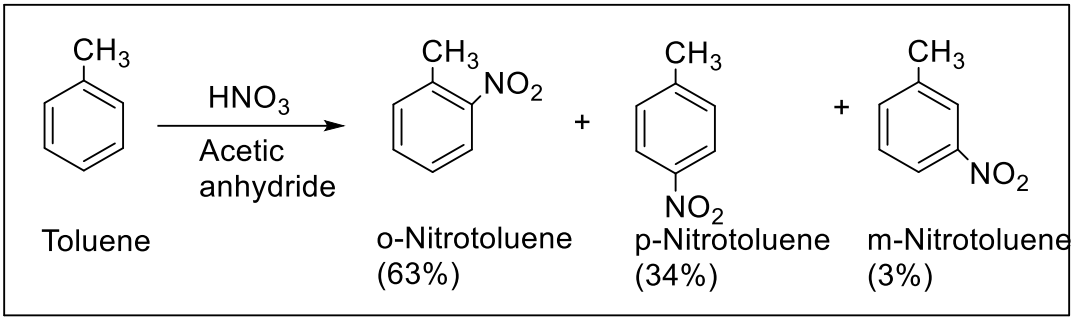
Table(I-1-) :Ortho, meta, para directors[18]

Ortho–Para Directors	Meta Directors
Strongly Activating —NH_2 , —NHR , —NR_2 —OH , —O^-	Moderately Deactivating —C≡N —SO_3H 
Moderately Activating 	Strongly Deactivating —NO_2 —NR_3^+ —CF_3 , —CCl_3
Weakly Activating —R (alkyl) —C_6H_5 (phenyl)	
Weakly Deactivating —F , —Cl , —Br , —I	

II-2-6-Examples of the regioselectivity:

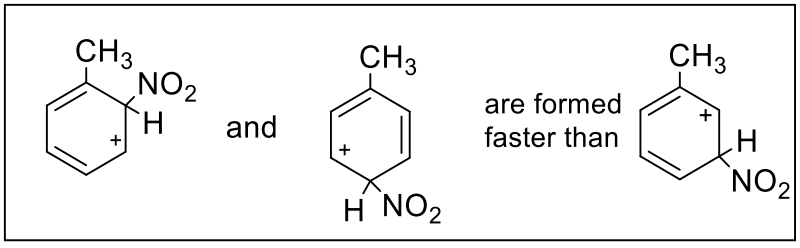
II-2-6-1-Regioselectivity in the nitration of Toluene:

Toluene undergoes nitration some 20–25 times faster than benzene. Because toluene is more reactive than benzene, we say that a methyl group activates the ring toward electrophilic aromatic substitution.
Three products are possible from nitration of toluene: o-nitrotoluene, m-nitrotoluene, and p-nitrotoluene. All are formed, but not in equal amounts. Together, the ortho and para-substituted isomers make up 97% of the product mixture; the meta only 3%.



Figure(II-46-) : Nitration of toluene"

Because substitution in toluene occurs primarily at positions ortho and para to methyl, we say that a methyl substituent is an ortho, para director.
Methyl is activating and ortho, para-directing; the first point to remember is that the regioselectivity of substitution is set once the cyclohexadienyl cation intermediate is formed.

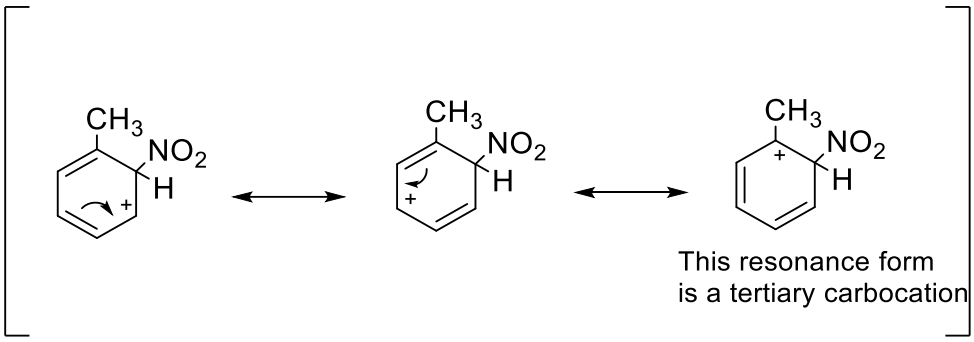


Figure(II-47-) : cyclohexadienyl cation intermediates

A more stable carbocation is formed faster than a less stable one. The most likely reason for the directing effect of methyl must be that the cyclohexadienyl cation precursors to o- and p-nitrotoluene are more stable than the one leading to m-nitrotoluene.

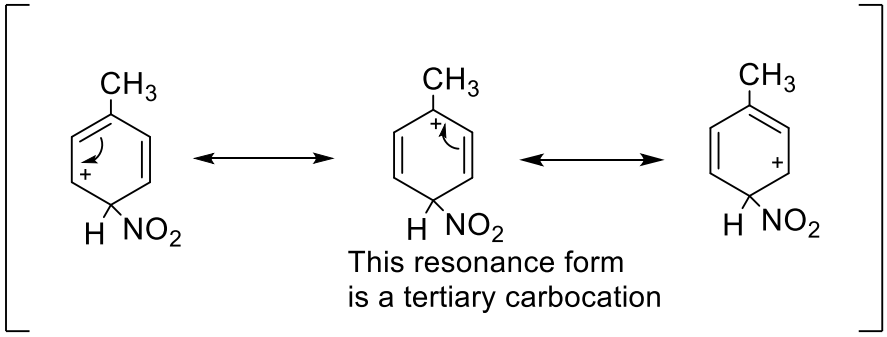
One way to assess the relative stabilities of these various intermediates is to examine electron delocalization in them using a resonance description. The cyclohexadienyl cations leading to o- and p-nitrotoluene have tertiary carbocation character. Each has a resonance form in which the positive charge resides on the carbon that bears the methyl group.

Ortho attack:



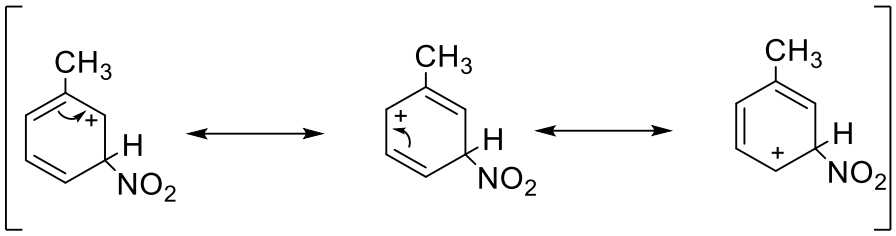
Figure(II-48-) : Resonance form of ortho attack

Para attack:



Figure(II-49-) : Resonance form of para attack

Meta attack:



Figure(II-50-) : Resonance form of meta attack

Because of their tertiary carbocation character the intermediates leading to ortho and to para substitution are more stable and are formed faster than the one leading to meta substitution. They are also more stable than the secondary cyclohexadienyl cation intermediate formed during nitration of benzene.

A methyl group is an activating substituent because it stabilizes the carbocation intermediate formed in the rate-determining step more than hydrogen does. It is ortho, para-directing because it stabilizes the carbocation formed by electrophilic attack at these positions more than it stabilizes the intermediate formed by attack at the meta position [19].

Part two:

Methyl-m-nitrobenzoate

II-3-Entrance to our target:

Generally, nitrations are performed in a mixture of concentrated nitric and concentrated sulfuric acids. The mixture of these acids generates the nitronium ion, which is the species that attacks the aromatic ring.

The nitrogen in industrial nitric acid originates in the air you breathe, which contains 78 % nitrogen.

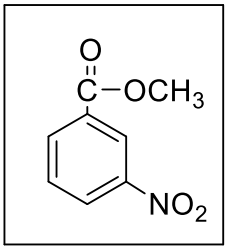
Much of the nitrogen in the food we eat comes from synthetic fertilizers manufactured using nitric acid.

Aromatic nitro compounds are used as explosives, antibiotics, and synthetic intermediates in the production of dyes, foams,analgesics,antidegradants for rubber, and synthetic fibers.

II-3-1-Chemical informations:

methyl 3-nitrobenzoate is a yellow needles crystals, It has a molar mass of 181.145g/mol and a density of 1.301g/cm^3 and a melting point of 76-80°C and a boiling point of 284.7°C, Its vapor pressure is 60 (279°C), and its solubility in "water: insoluble", "methanol: sparingly soluble", "ethanol: sparingly soluble", "diethyl ether: sparingly soluble".

Structurally, "Figure(II-51-)" methyl-m-nitrobenzoate consists of a benzene ring with a two substituents a nitro group "it is considered to be a versatile and unique functional group in medicinal chemistry" and a an ester "aromatic esters moiety has been vastly investigated in medicinal chemistry due to its lipophilic nature, which is an attractive property for diffusion across cell membranes. A variety of biological applications of these compounds exist, ranging from antihypertensive, anti-inflammatory, anti-tumor, and antimicrobial to antileishmanial".



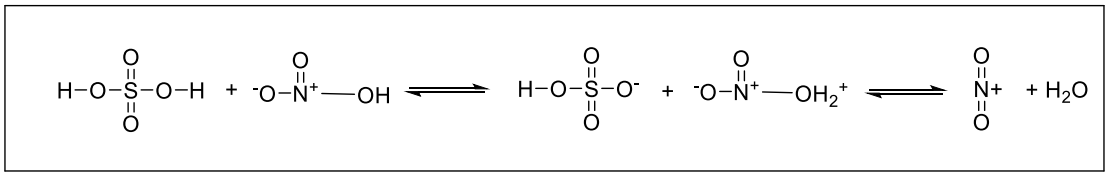
Figure(II-51-) :Chemical structure of nitrobenzene

Methyl-m-nitrobenzoate is manufactured by direct nitration of methyl benzoate with nitric acid, using sulfuric acid as catalyst and dehydrating agent. The purified product is used extensively in chemical manufacturing, especially in the synthesis of other industrial chemicals and intermediates, most important among these are aromatic amines such compounds occur widely. They are an industrially important class of organic compounds, they usually form stable salts with inorganic and also with many organic acids.

II-3-2-Synthesisof Methyl-m-nitrobenzoate:

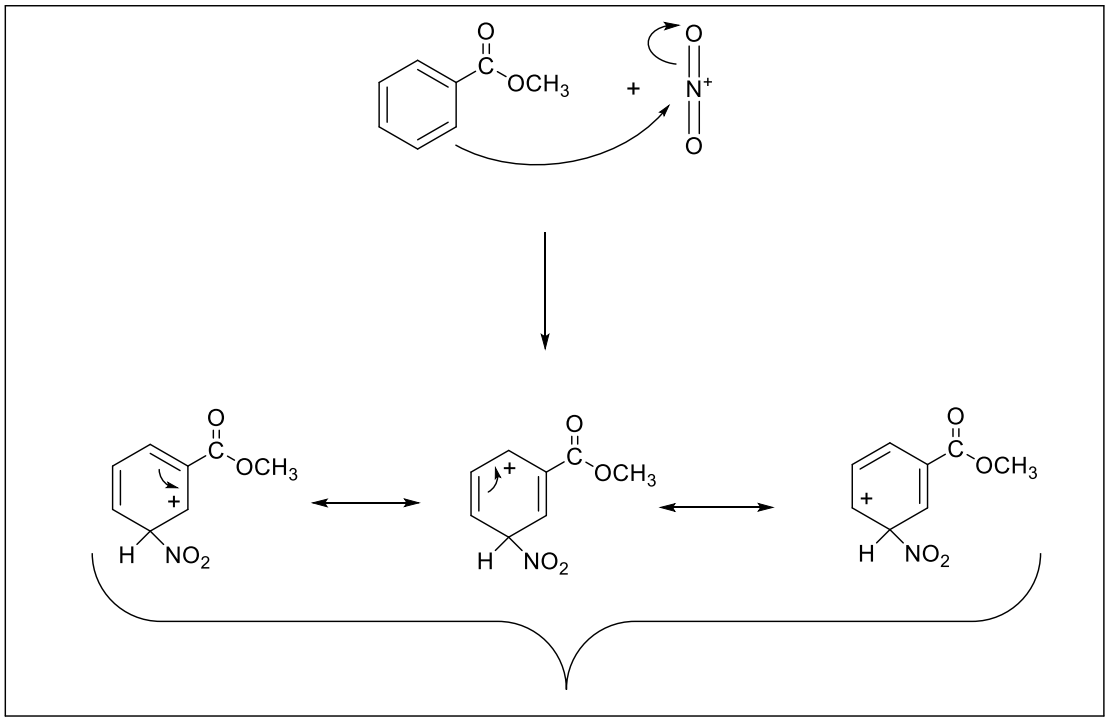
Because methyl benzoate is an electron deficient arene, a mixture of concentrated nitric acid and concentrated sulfuric acid is used to generate the nitronium ion.

1. Generation of the electrophile:



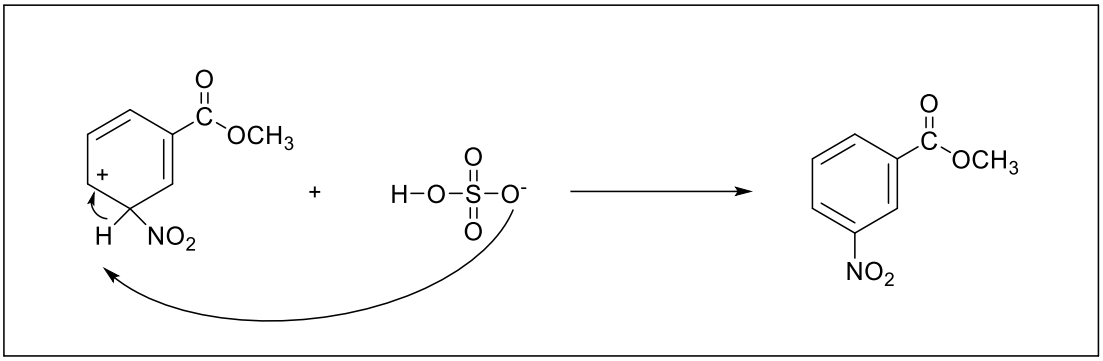
Figure(II-52-) : Nitration of methyle benzoate "step 1"

2. Attack on the aromatic ring forming the cationic intermediate:



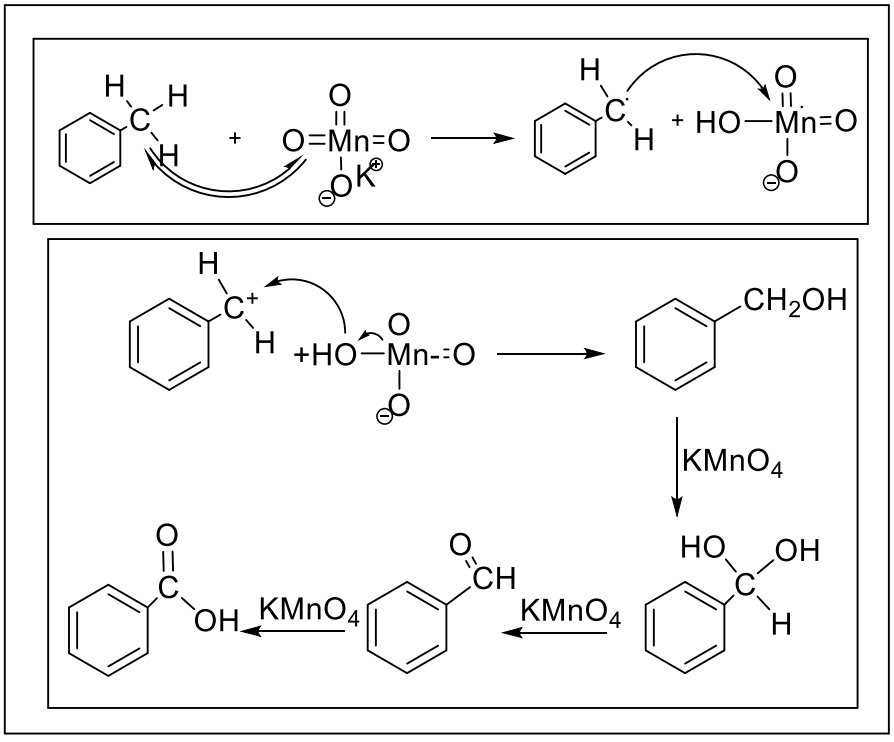
Figure(II-53-) : Nitration of methyl benzoate "step 2"

3. Deprotonation:

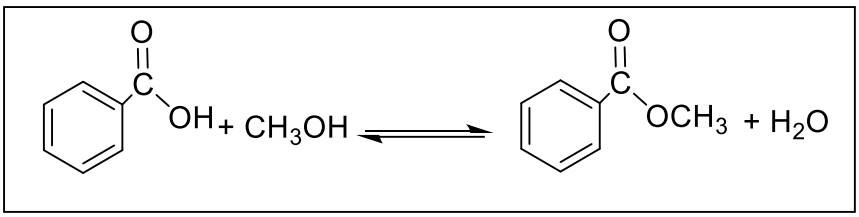


Figure(II-54-) : Nitration of methyl benzoate "step 3"

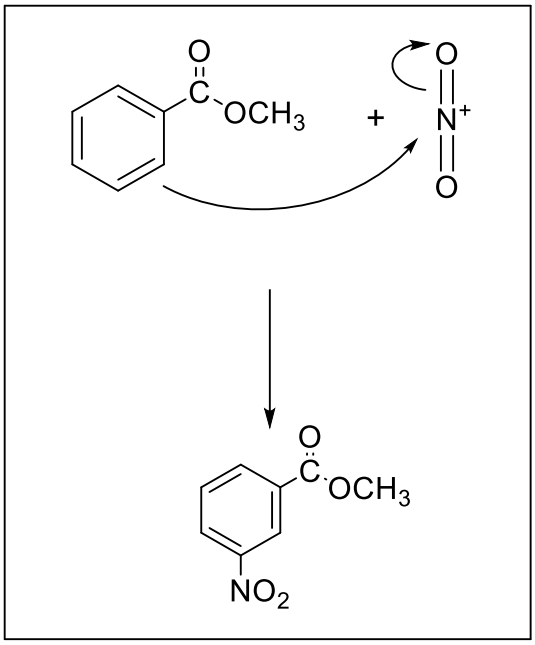
II-3-3-Synthesis of methyl-m-nitrobenzoate beginning with Toluene:



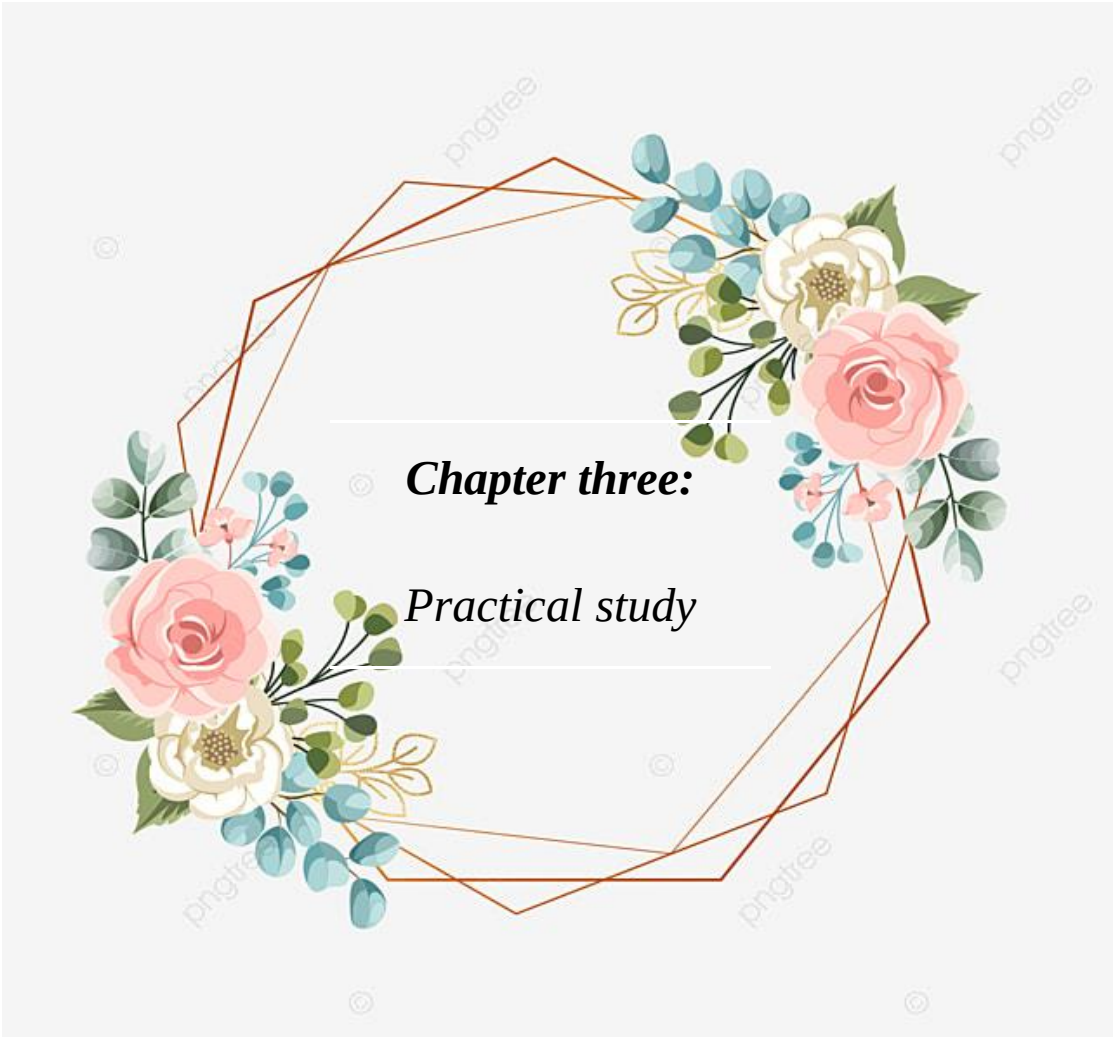
Figure(II-55-) : Oxidation of toluene



Figure(II-56-) : Esterification of benzoic acid



Figure(II-57-) : Nitration of methyl benzoate



Chapter three:

Practical study

III-Chapter three: practical part

III-1-Used materials and chemicals:

Table(III- 1-) : Used chemicals and materials

Chemicals	*Materials*
Sulphuric acid Nitric acid Methyl benzoate Methanol Ice bath	Beaker Glass rod Test tube Pasteur pipette Buchner funnel

III-1-1-experimental procedure:

1. 6 mL of concentrated sulphuric acid was added into a 100mL beaker.
2. The beaker was cooled in an ice bath for about 10 minutes.
3. 2.8 mL of methyl benzoate was added into a cold sulphuric acid in the beaker.
4. The mixture solution *(H_2SO_4/$C_8H_8O_2$)* was well mixed and cooled again to 0℃ for 5 minutes.
5. 2 mL of concentrated sulphuric acid and 2 mL of concentrated nitric acid was mixed together to perform mixture solution in order to produce electrophile.
6. The acid mixture solution *(H_2SO_4/HNO_3)* was cooled in the ice bath.
7. The acid mixture solution *(H_2SO_4/HNO_3)* was dropped wisely into the mixture solution prepared *(H_2SO_4/$C_8H_8O_2$)*. (Swirl for each acid mixture addition)
8. The mixture reaction was kept and done in an ice bath.
9. After complete addition, we let the mixture to settle down towards the room temperature.
10. The mixture had standed about 15 minutes as to allow the reaction to complete.
11. The mixture was poured in about 10g of crushed ice in a beaker.
12. Solid product had formed and the product was collected through vacuum filtration.

13. The filtrate solid product was rinsed with amount of ice cold 50% methanol. (mixture 1:1 The crude product was then recrystallize again by using methanol as recrystallization solvent.

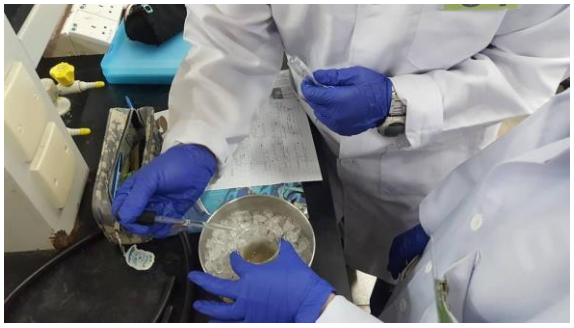
III-1-2-Observations:

Photo(III-1-) : Mixture of Conc. H_2SO_4& HNO_3 in an ice bath.

Photo(III-2-) : Mixture of Conc. H_2SO_4& Methyl Benzoate in an ice. bath.

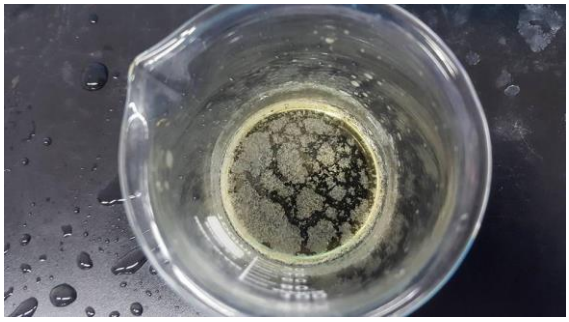
Photo(III-3-) : Complete solution was settled down to the room temperature.

Part two: Methyl-m-nitrobenzoate

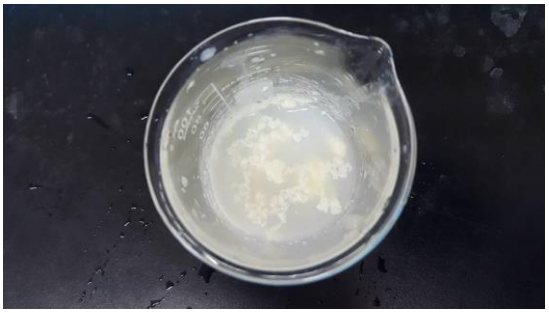


Photo(III-4-) : Mixing mixture solution of Conc.H_2SO_4& Conc.HNO_3 into Conc.H_2SO_4&Methyl Benzoate.

Photo(III-5) : Mixing was done with wisely dropping and swirlling.



Photo(III-6-) : Top view of the complete addition.



Photo(III-7-) : White crystal were formed once 10g of crushed ice was added into the acid mixture solution.

III-2-Used materials and chemicals:

Table(III-2-) : Used materials and chemicals"1"

Materials	***Chemicals***
Beaker Erlenmeyer flask Filter paper Filter funnel Heating plate Water bath	Calcium Nitrate Salt($Ca(NO_3)_2$) Salicylic acid($C_7H_6O_3$) Acetic acid(CH_3COOH) Distilled water Cold water

III-2-1-experimental procedure:

1-3.28g of $Ca(NO_3)_2$ was melted in 10 ml of acetic acid in 100ml beaker.

2-2g of salicylic acid was added.

3-The mixture was well mixed in a water bath for 1 minute.

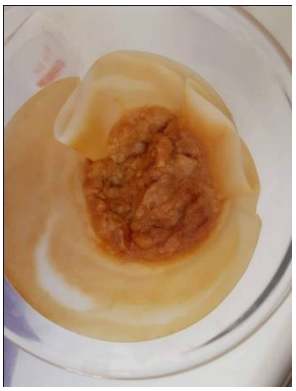
4-When the color became dark red we added 10ml of cooled water put in an ice bath until yellow crystals formed.

5-Crystals had formed and the product was collected through simple filtration and then washed with cold water then dried.

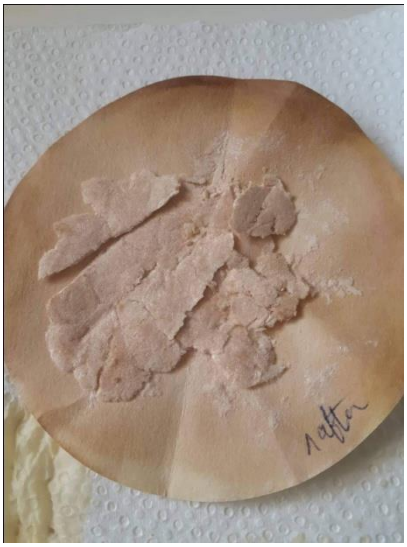
6-the product was melted in a small amount of ethanol and water in a water bath.

7-The crude product was then put in an ice bath till recrystallized then filtered and dried.

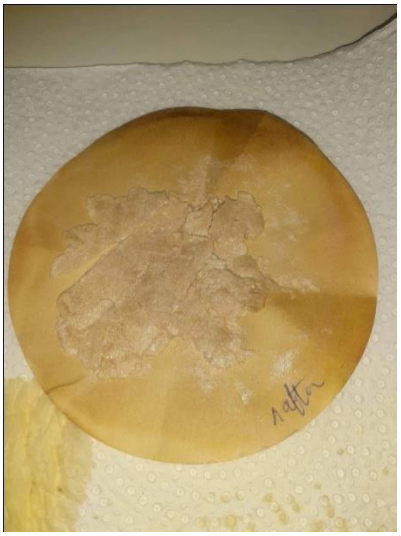
III-2-2-Observations:



Photo(III-8-) :Top view of the product while the filtration.



Photo(III-9-) : The final dried product without lighting.



Photo(III-10-) : The final dried product with lighting.

Photo(III-11-) : The product after filtrating the filtrete.

III-3-Used materials and chemicals:

Table(III-3-) : Used chemicals and materials"2"

Materials	***Chemicals***
Beaker Erlenmeyer flask Filter paper Filter funnel Heating plate Water bath	Nitric acid HNO_3 Sulphuric acid H_2SO_4 Salicylic acid($C_7H_6O_3$) Distilled water Cold water

III-3-1-experimental procedure:

1- 2.46ml of nitric acid HNO_3 with 10 ml of sulphuric acid H_2SO_4 was mixed together, added into a 100ml beaker.

2-2g of salicylic acid was added.

3-The mixture was well mixed in a water bath for 1 minute.

4-When the color became dark red we added 10ml of cooled water put in an ice bath until yellow crystals formed.

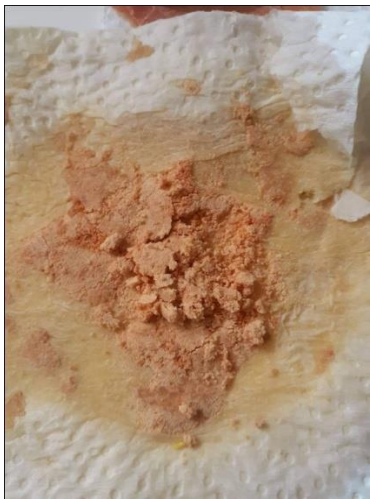
5-Crystals had formed and the product was collected through simple filtration and then washed with cold water then dried.

6-the product was melted in a small amount of ethanol and water in a water bath.

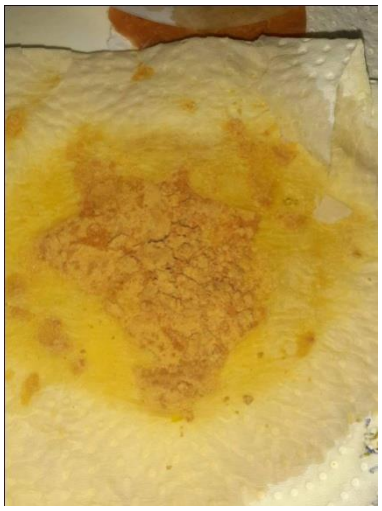
7-The crude product was then put in an ice bath till recrystallized then filtered and dried.

III-3-2-Observations:

Photo(III-12-) : Top view of the mixture.



Photo(III-13-) : The final dried product without lighting.



Photo(III-14-) : The final dried product with lighting.

Photo(III-15-) : The product after filtrating the filtrate.

III-4-Used materials and chemicals:

Table(III-4-) : Used chemicals and materials"3"

Chemicals	*Materials*
Sulphuric acid Nitric acid Benzaldehyde Methanol Ice bath	Beaker Glass rod Test tube Pasteur pipette Buchner funnel

III-4-1-experimental procedure:

1-6 mL of concentrated sulphuric acid was added into a 100mL beaker.

2-The beaker was cooled in an ice bath for about 10 minutes.

3-2.8 mL of benzaldehyde was added into a cold sulphuric acid in the beaker.

4-The mixture solution *(H_2SO_4/ C_6H_5CHO)* was well mixed and cooled again to 0℃ for 5 minutes.

5-2 mL of concentrated sulphuric acid and 2 mL of concentrated nitric acid was mixed together to perform mixture solution in order to produce electrophile.

6-The acid mixture solution *(H_2SO_4/HNO_3)* was cooled in the ice bath.

7-The acid mixture solution *(H_2SO_4/HNO_3)* was dropped wisely into the mixture solution prepared *(H_2SO_4/ C_6H_5CHO).* (Swirl for each acid mixture addition)

8-The mixture reaction was kept and done in an ice bath.

9-After complete addition, we let the mixture to settle down towards the room temperature.

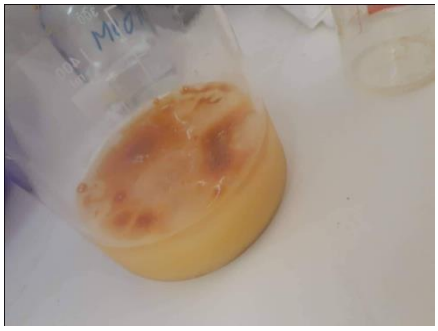
10-The mixture had standed about 15 minutes as to allow the reaction to complete.

11-The mixture was poured in about 10g of crushed ice in a beaker.

12-Solid product had formed and the product was collected through vacuum filtration.

13-The filtrate solid product was rinsed with amount of ice cold 50% methanol. (Mixture 1:1 the crude product was then recrystallize again by using methanol as recrystallization solvent.

III-4-2-Observatuions:



Photo(III-16-) : The mixture in crashed ice.

Photo(III-17-) : Top view of the finalresult.


Discussion

III-5-Discussion

III-5-1-Calculations 1 :

☺ Actual Weight of the product = 4.08599g.

☺ Molar mass of methyl-3-nitrobenzoate, $C_8H_7NO_4$ = 181.147 g/mol.

☺ Mole of methyl-3-nitrobenzoate = weight of $C_8H_7NO_4$/molar mass of $C_8H_7NO_4$ =4.08599g / 181.147 g/mol = 0.02257 g/mol.

☺ Density of Methyl Benzoate, $C_8H_8O_2$ = 1.094 g/mol.

☺ Mass of Methyl Benzoate, $C_8H_8O_2$= Density of Methyl Benzoate x volume of Methyl Benzoate used = 1.094g/mol x 2.8 ml = 3.0632g.

☺ Moles of Methyl Benzoate, C8H8O2 = Mass of Methyl Benzoate / Molecular mass

☺ 1 mol of methyl benzoate, $C_8H_8O_2$ produce 1 mol of methyl-3-nitrobenzoate, $C_8H_7NO_4$.

☺ 0.02249 mol of methyl benzoate, $C_8H_8O_2$produce0.02257 mol of methyl-3-nitrobenzoate, $C_8H_7NO_4$.

☺ Molar mass of methyl-3-nitrobenzoate, $C_8H_7NO_4$= 181.147 g/mol.

☺ Theoretical yield of methyl-3-nitrobenzoate, C8H7NO4 = 181.147 g/mol x 0.02249 mol = 4.0740 g.

☺ Actual yield = 3.0632g.

☺ Percentage yield of the product, methyl-3-nitrobenzoate, $C_8H_7NO_4$: (3.0632g / 4.0740 g) x 100% = 75.19%.

III-5-2-Calculations 2:

Salicylic acid: M = 138 g/mol, m = 2 g.

$n_S = m/M = \frac{2}{138}$ = 0,014 mol.

Acetic acid: M = 60 g/mol, ρ = 1,049 g/ cm3 , V= 10 ml.

$n_A = m/M = \rho \times V/M = \frac{1.049 \times 10}{60}$ = 0,17 mol.

Calcium Nitrate: M = 164 g/mol,nC = 0, 02mol , V= 20 ml.

$m_C = M_C \times n_C = 164 \times 0,02 = 3,28$ g.

Table(III-5-) : progress table

	Salicylic acid + Acetic acid → 5-nitro salicylic acid + calcium acetate + water				
T = 0	n_S = 0,014 mol	n_A = 0,04 mol	0	0	0
T= t_f	$n_S - X_{max}$	$n_A - X_{max}$	X_{max}	X_{max}	X_{max}

CalculatingX_{max}:

$n_A - X_{max} = 0 \rightarrow n_A = X_{max} = 0{,}04$ mol.

$n_S - X_{max} = 0 \rightarrow n_S = X_{max} = 0{,}014$ mol.

Calculation of the mass of the acid:

$n_{5.n.s.a} = m_{5.n.s.a} / M = X_{max}$

$m_{5.n.s.a} = M_{5.n.s.a} \times X_{max} = 183 \times 0.014 = 2.562$g.

Calculating the yield:

$m_{exp} = 2.333$

$R\% = m_{exp}/m_{5.n.s.a} \times 100\% = 2.333/2.562 \times 100 = 91.06\%$

III-5-3-Calculations 3:

☺Actual Weight of the product = 2.54 g.
☺Molar mass of DNS = 228.12 g/mol.
☺Mole of DNS = weightof DNS / molar mass of DNS = 2.54 g / 228.12 g/mol = 0.011 g/mol.

☺Mass of salicylic acid = 2 g.

☺Moles of salicylic acid = Mass of salicylic acid / Molecular mass = 2/138.12 = 0.014 mol

☺Theoretical yield of DNS = 228.12 g/mol x 0.014 mol = 3.193 g.

☺Actual yield = 2.54 g.

☺Percentage yield of the product, DNS = (2.54 g / 3.193 g) x 100% = 79.54%.

Conclusion

III-8-Conclusion:

The aim of this work was to prepare methyl-m-nitrobenzoate by the nitration of methyl benzoate, by this preparation we could have hitten 2 birds with one stone and use one product for two different functions , since it contains an ester so we use it as an arom, and it contains a nitro group that is used as a coloring, also the methyl-m-nitrobenzoate is considered as an intermediate material for the preparation of many other compounds such as amines, monomers such as "Toluene diisocyanate" the synthesis of it has no existence in Algeria so by making the methyl-m-nitrobenzoate undergo some reactions we could get Toluene diisocyanate , and this latter could be used to manufacture sponges, However, due to the huge lack, also the high prices, we couldn't afford the methyl benzoate so decided to replace it with an available, low price compounds as "salicylic acid, benzaldehyde and vaniline" and the main reason for choosing this compound is that they are similar to the methyl benzoate.

So by the nitration of salicylic acid the goal was to produce the widely used product especially in the pharmaceutical field, 5-nitrosalicylic acid by using 2 different nitrating systems: Ca(NO3)2/CH3COOH in the 01 experiment and HNO3/H2SO4 (mixed acid) in the second one, we can say that we obtained a good yield of the 3 isomers "3,5-dinitrosalicylic acid, 5-nitrosalicylic acid, 3-nitrosalicylic acid" in both of them, even though the product we wanted is the 5-nitrosalicylic acid but due to the lack of chemicals and equipment to be used, we couldn't afford the spectroscopic analysis to check the purity of the obtained compound, we couldn't go so far from this but in general we concluded that the use of the first system "Ca(NO3)2/CH3COOH" gives a better yield also it is more safe to use.

In the nitration of benzaldehyde we got two phases that needed to be separated, but due to the limited chemicals we couldn't afford the compounds the can separate the oily phase from the water phase , so we just stops and couldn't go farther then this.

We aimed and hoped to nitrate the vanillin as it was planned since the vanillin if available and cheap but couldn't because we were running out of time so we just so, we settled on studying it theoretically.

At the end we can say that we were successful in the nitration reactions we have made inspite of the limited resources.


Recommendations

Recommendations:

the nitration of the aromatic compounds is one of the most important type out of the 5 types of the electrophilic aromatic substitution and it gives such a widely used compounds such as our target that is going to receive more attention due to its importance and multiple uses, and as being the intermediate for the preparation of compounds of greater importance.

Highly recommend to do more synthesis based on the nitration reaction to get more useful monomers.

Refrences

References

[4]محمد بن إبراهيم عبد العزيز الحسن, سالم بن سليم سالم الذياب, حمد بن عبد الله فهد اللحيدان, الكيمياء العضوية الأروماتية, مطابع جامعة الملك سعود, الطبعة الأولى, 1992, ص. 10-11

[1]Francis A. Carey, Richard J. Sundberg, Advanced Organic Chemistry, 2007,Springer, 5th edition, p.713

[2]G.W. Robinette, did linzexu make morphine?, graffiti militante press, 2008, 1st edition, p.632

[3]H.-G. Franck, J.w. Stadelhofer, Industrial aromatic chemistry,Springer-Verlag, 1987, p.1-7

[5]Francis A. Carey,Organic chemistry,Mcgraw-hill,2000, 4thedition, p. 411

[6]H.-G. Franck, J.w.Stadelhofer, Industrial Aromatic Chemistry, Springer-Verlag, 1987, p. 447-448

[7]Jac ques Mortier, Arene chemistry,John Wiley & Sons, 2016,p. 3

[8]Robert J. Ouellette, J. David Rawn, Organic chemistry: structure, mechanism, and synthesis,elsevierinc,2014, 1stedition, , p.422

[9]Francis A. Carey,Organic chemistry, Mcgraw-hill2000, 4thedition, p.444

[10]Robert J. Ouellette, J. David Rawn, Organic Chemistry: Structure, Mechanism, and Synthesis,elsevierinc, 2014, 1stedition, p. 420-421

[11]T.W. Graham Solomons, Craig b. Fryhle, Organic chemistry, 10thedition,John Wiley & Sons, Inc, 2011,p.677

[12]Robert J. Ouellette, J. David Rawn, Organic Chemistry: Structure, Mechanism, and Synthesis,elsevierinc, 2014, 1stedition, p.422-425

[13]H.-G. Franck, J.w.Stadelhofer, Industrial Aromatic Chemistry, Springer-Verlag, 1987,p.16

[14]H.-G. Franck, J.w.Stadelhofer, Industrial Aromatic Chemistry,Springer-Verlag, 1987, p.14-15

[15]OlegShlomoLagoviyer, Mechanochemical nitration of aromaticcompounds,NJIT, 2018,p.1

[16]J. G. Hoggett, R. B. Moodiej, J. R. Penton & K. Schofield, Nitration and aromatic reactivity,Syndics of the Cambridge,1971, p.1

[17]Francis A. Carey, Richard J. Sundberg, Advanced Organic Chemistry, 5th edition,Springer, 2007, p.796-797

[18]T.W. Graham Solomons, Craig B. Fryhle, Organic chemistry, 10th edition,Wiley& Sons, Inc, 2011, p.691-696

[19] Francis A. Carey, Organic chemistry, Mcgraw-hill companies, 2000, 4th edition, p.458-459

Abstract:

The aim of this study is to prepare a methyl-metal-nitro-benzoate compound from the nitration of methyl benzoate or similar compounds such as salicylic acid, vanillin, benzaldehyde, but this study was a comparison of a theoretical results, so we nitrated some compounds that has a similar function group as the methyl benzoate we nitrated the above-mentioned compounds using two different ways: using $Ca(NO_3)_2/CH_3COOH$ at first and then nitrating them using HNO_3/H_2SO_4, there results have been compared.

The results showed a good yield in both of them, but couldn't afford the spectroscopic analysis "HNMR".

Generally we got a good yield of the nitrated compounds.

Key words: Electrophilic aromatic substitution, aromatic compounds, methyl benzoate, methyl-m-nitrobenzoate

الملخص:

الهدف من هذا الدراسة هو تحضير مركب ميثيل ميتا نيترو بنزوات انطلاقا من نترتة الميثيل بنزوات أو مركبات شبيهة به كحمض الساليسيك,الفانيلين, بنزوكربالدهيد, لكن هذه الدراسة كانت عبارة عن مقارنة لنتائج نظرية, فقمنا بتفاعل النترتة على مركبات مشابهة من حيث المجموعات الوظيفية للميثيل بنزوات . تمت نترتتها باستخدام طريقتين مختلفتين, تضمنت الأولى استعمال نترات الكالسيوم و حمض الخليك, أما الثانية فتمت باستعمال حمض النتريك و حمض السلفوريك, و المقارنة بين نتائجها.

أظهرت النتائج مردودا جيدا في كلا الطريقتين و لم نتمكن من القيام بالدراسة الطيفية للبروتون RMN, و لكن عموما فقد تحصلنا على مردود جيد للمركبات التي تمت نترتتها و هي كالتالي: حمض الساليسيك, الفانيلين, بنزوكربالدهيد.

الكلمات المفتاحية: الاستبدال العطري الإلكتروفيلي, المركبات العطرية, ميثيل بنزوات, ميثيل ميتا نيتروبنزوات.