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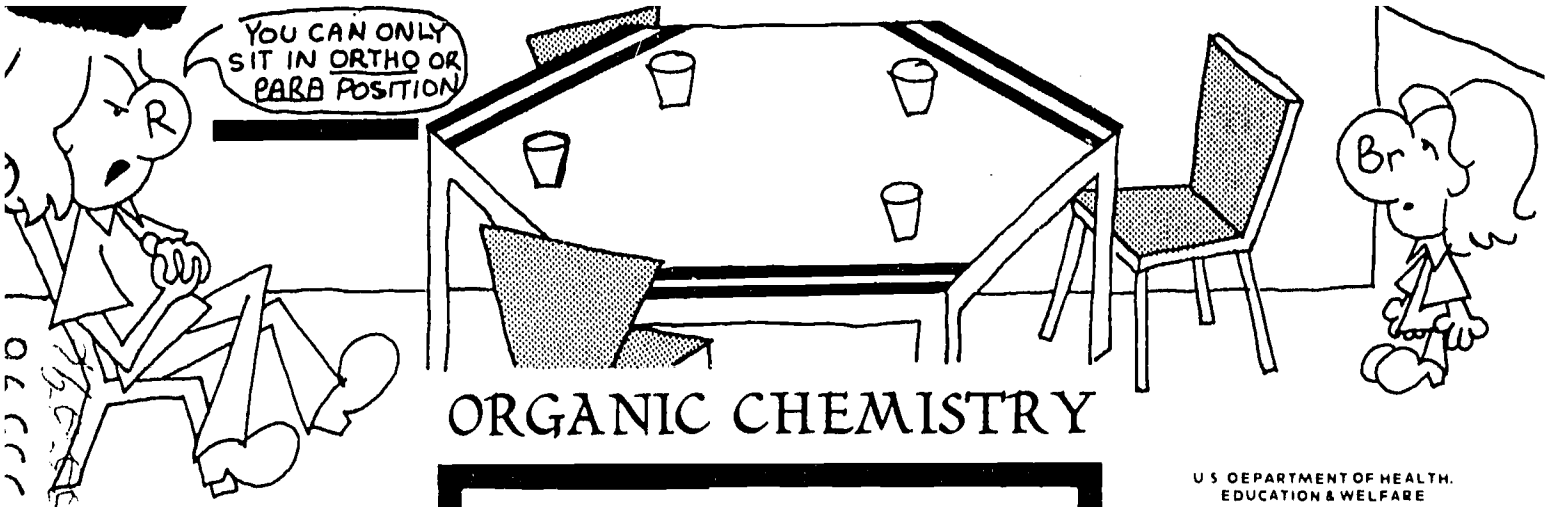
ABSTRACT

This booklet, one of a series of 17 developed at Prince George's Community College, Largo, Maryland, provides an individualized, self-paced undergraduate organic chemistry instruction module designed to augment any course in organic chemistry but particularly those taught using the text "Organic Chemistry" by Morrison and Boyd. The entire series of modules covers the first 13 chapters of the Morrison-Boyd text in great detail. Each module has been provided with from one to three audiotapes, available from Prince George's Community College, to provide students additional explanations of particular concepts. Each module includes a self-evaluation exercise, a reference guide, worksheets to be completed with the audiotapes, answer sheets for the worksheets, a progress evaluation, an answer sheet for the progress evaluation, an answer sheet for the self-evaluation exercise, an introduction to the topic covered by the module, and student performance objectives for the module. The topic of this module is aromatic compounds, effects of substituents. (SL)



ORGANIC CHEMISTRY

V. Zdravkovich

16

S elf

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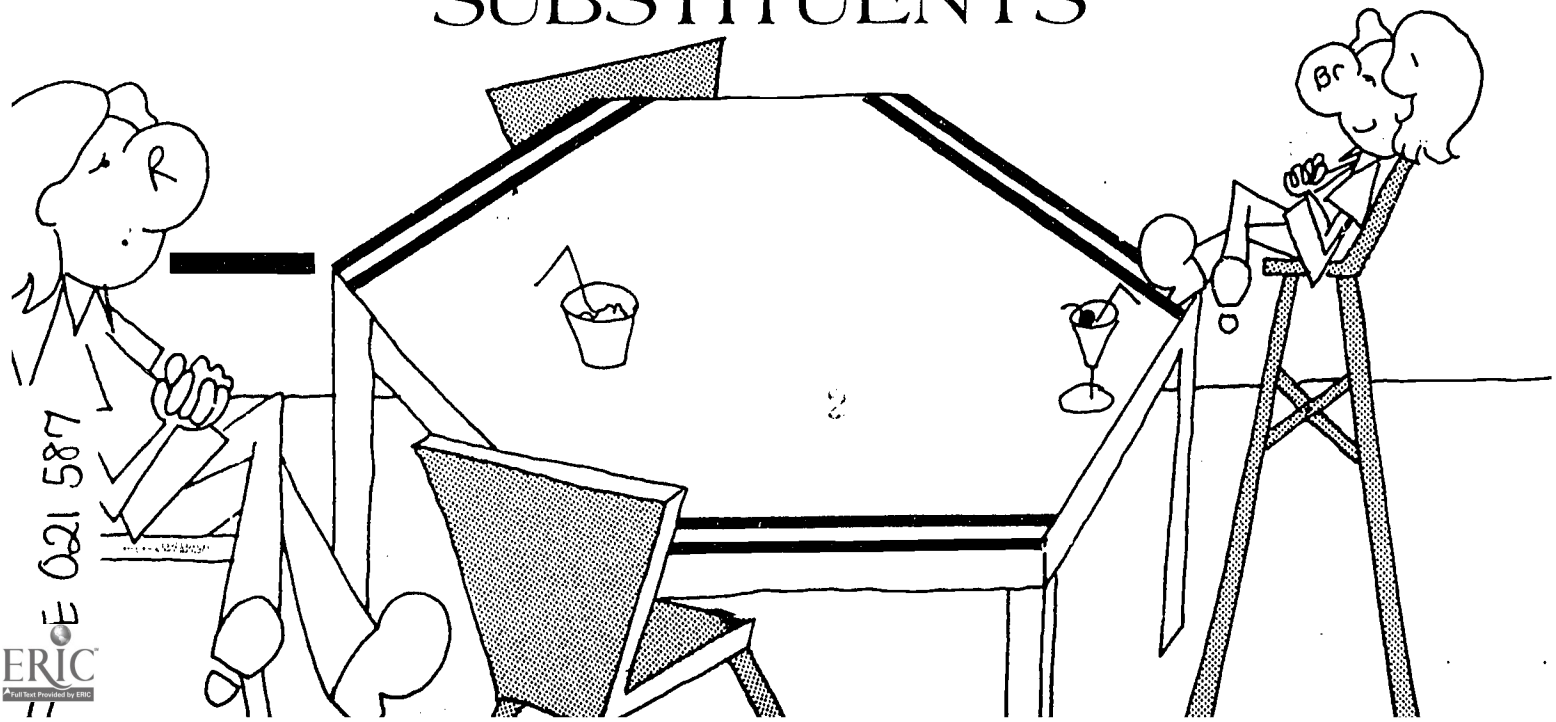
V. Zdravkovich

AROMATIC CHEMISTRY EFFECT OF SUBSTITUENTS



Self Instructional Sequence in

ORGANIC CHEMISTRY

There's hardly a thing that man can name
Of use or beauty in life's small game
But you can extract from alembic or jar
From the physical basis of black coal tar
Oil and ointment, wax and wine
And the lovely colors called aniline
You can make anything from a salve to a star
If you only know how, from black coal tar.
---Punch Magazine, 1884

The heating of bituminous coal to 1000-1300°C in the absence of air produces coal gas and a viscous, black material known as coal tar. Fractional distillation of the coal tar reveals a presence of large number of different aromatic compounds. Some of these are benzene derivatives such as phenols, aniline, toluene. Some contain nitrogen as an integral part of the ring and are better known as heterocyclic aromatic compounds. Some are polycyclic or condensed aromatic compounds.

For many centuries coal tar was an undesirable by-product in the production of coal gas. It was and it still is used as a source of heat and illumination. With the emergence and rapid development of the chemical industry in the nineteenth and twentieth century, the demand for the aromatic compounds of the coal tar increased significantly.

With the emerging industry, so dependent on the constituents of coal tar, the study of the chemistry of aromatic compounds began in earnest, and has continued to expand to the present day. There are many questions still unanswered, and many mysteries still unsolved, but the wonders of nature and capacities of the human brain being as they are will eventually provide us with the answers.

Self Instructional Package No. 16
Form A - List of Objectives

AROMATIC COMPOUNDS

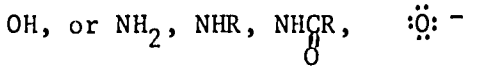
EFFECT OF SUBSTITUENTS

Definitions -

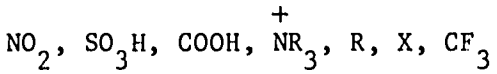
The student will be able to define and illustrate with appropriate examples where applicable the following terms: ELECTRON WITHDRAWING INDUCTIVE EFFECT, ELECTRON RELEASING INDUCTIVE EFFECT, RESONANCE EFFECT, ACTIVATING GROUP, DEACTIVATING GROUP, ORTHO, META AND PARA DIRECTING GROUPS.

Mechanism -

The student will be able to draw the resonance structures of the intermediate carbonium ion and demonstrate resonance stabilization for groups such as:



The student will be able to draw resonance structures of the intermediate carbonium ion and explain the different inductive effects of the given substituent groups such as:



Reactions -

The student will be able to predict the products in different reactions.

The student will be able to identify the reagents required for the synthesis of different compounds.

AROMATIC CHEMISTRY

EFFECT OF SUBSTITUENTS

Identify the statements below as True or False by placing a capital T or F in the spaces provided to the left.

1. _____ An alkyl group attached to benzene is an activator because of its electron releasing inductive effect.

2. _____ OH group in phenol is an activator because of its electron releasing inductive effect.

3. _____ NH_2 group in aniline is an o. p director because of the resonance effect which results in the increased electron density in o and p positions.

4. _____ NO_2 group in nitrobenzene is meta director because it generates a negative charge in m position.

5. _____ An alkyl group attached to the ring is an o and p director because it stabilizes o and p positions more.

6. _____ COOH group in benzoic acid is deactivator because of its electron withdrawing inductive effect.

7. _____ A halogen attached to the ring exhibits an electron withdrawing inductive effect.

8. _____ $\overset{+}{N}(CH_3)_3$ activates the ring toward further electrophilic aromatic substitution.

9. _____ NH_2 group in aniline exhibits an electron releasing inductive effect.

10. _____ $NH\overset{O}{\overset{\|}{C}}R$ group activates the ring more than the NH_2 group.

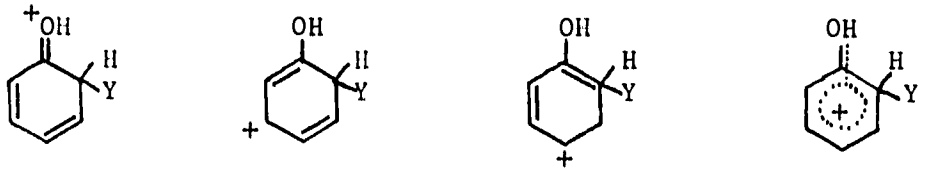
11. _____ NHR group activates the ring more than the NH_2 group.

12. _____ Resonance effect in phenol is caused by the interaction of nonbonding electrons on oxygen with π electrons on the ring.

SIP No. 16
Form B - Self Evaluation Exercise

Blacken out the correct answer or answers in the following questions:

13. The correct resonance structures showing ortho attach in phenol are:



I II III IV

a) I

b) II

c) III

d) IV

14. The correct resonance structures showing para attack in aniline are:

I II III IV

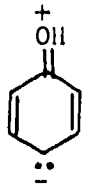
a) I

b) II

c) III

d) IV

15. The resonance structures which illustrate the o and p directing effect of the OH group are:



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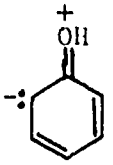

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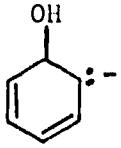

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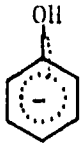


IV

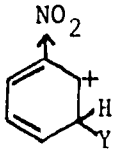
a) I

b) II

c) IV

d) IV

16. Resonance structures which illustrate m attack in nitrobenzene are:



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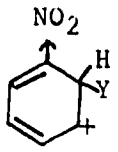

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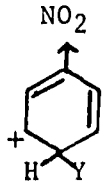

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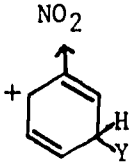


IV

16. (continued)

a) I

b) II

c) III

d) IV

17. The correct statements about the nitration reaction of phenol are:

a) the major product in the reaction is o-nitrophenol

b) the major product in the reaction is m-nitrophenol

c) the major product in the reaction is p-nitrophenol

d) the reaction occurs faster than with benzene

18. The correct statements about the nitration reaction of bromobenzene are:

a) the major product in the reaction is o-nitrobromobenzene

b) the major product in the reaction is m-nitrobromobenzene

c) the major product in the reaction is p-nitrobromobenzene

d) the reaction occurs faster than with benzene

19. The major product or products in the bromination reaction of 2-nitrotoluene are:

a) 2-nitro-3-bromo toluene

b) 2-nitro-4-bromo toluene

c) 2-nitro-5-bromo toluene

d) 2-nitro-6-bromo toluene

20. The major product or products in the bromination of p-ethyl phenol are:

    a) 2-bromo-4-ethyl phenol

    b) 3-bromo-4-ethyl phenol

    c) 5-bromo-4-ethyl phenol

    d) 6-bromo-4-ethyl phenol

21. The major product or products in the nitration of m-nitrophenol are:

    a) 2,3-dinitrophenol

    b) 3,4-dinitrophenol

    c) 3,5-dinitrophenol

    d) 2,5-dinitrophenol

22. The reagents required for the synthesis of p-bromo benzoic acid from benzene are:

    a) hot $KMnO_4$, Br_2, Fe

    b) CH_3Cl, $AlCl_3$, Br_2, Fe, hot $KMnO_4$

    c) Br_2, Fe, CH_3Cl, $AlCl_3$, hot $KMnO_4$

    d) CH_3Cl, $AlCl_3$, hot $KMnO_4$, Br_2, Fe

23. The reagents required for the synthesis of p-iodo toluene from benzene are:

    a) CH_3Cl, $AlCl_3$, I_2, Fe

    b) I_2, Fe, CH_3Cl, $AlCl_3$

    c) I_2, Fe, $Tl(OOCCF_3)$, CH_3Cl, $AlCl_3$

    d) CH_3Cl, $AlCl_3$, $Tl(OOCCF_3)_3$, KI

AROMATIC CHEMISTRY

EFFECT OF SUBSTITUENTS

The Reference Guide should be used in conjunction with From B or the Self Evaluation Exercise. The references give correlation between the questions in Form B and the available material in the textbook and in form of tapes.

Questions 1, 4, 5, 6, 8, 10, 16	Chapter 11, Sections 18, 19
Questions 2, 3, 9, 10, 11, 12, 13, 14, 15	Chapter 11, Section 20
Question 7	Chapter 11, Sections 21, 22 Morrison & Boyd Organic Chemistry
Questions 17, 18	Chapter 11, Sections 2, 3, 4, 5
Questions 19, 20, 21	Chapter 11, Section 6
Questions 22, 23	Chapter 11, Section 7

For Questions 17, 18, 19, 20, 21, 22, 23 additional explanations and examples are provided in Tape 1 - Effect of Substituent Groups on Electrophilic Aromatic Substitution.

For Questions 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16 additional explanations and examples are provided in Tape 2 - Inductive and Resonance Effects of Substituent Groups.

AROMATIC CHEMISTRY

Effect of Substituent Groups on Electrophilic Aromatic Substitution

Table No. 1 - Classification of Substituent Groups

Activating Groups

Strongly Activating

$-NH_2$ $-NHR$ $-NR_2$ (amino)

$-OH$ (phenol)

Moderately Activating

$-OR$ (alcoxy)

$-NHCR$ (acetanilido)

Weakly Activating

$-C_6H_5$ -(Phenyl) Group

$-R$ (Alkyl)

Deactivating Groups

$-NO_2$ (nitro)

$-N^+(R)_3$

$-C\equiv N$ (nitrile)

$-\overset{O}{\overset{\|}{C}}-OH$ or COOH (acid)

$-\overset{O}{\overset{\|}{C}}-OR$ or COOR (ester)

$-SO_3H$ (sulfonic acid)

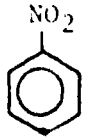
$-\overset{O}{\overset{\|}{C}}-H$ or -CHO (aldehyde)

$-\overset{O}{\overset{\|}{C}}-R$ or COR (ketone)

-X -(halo)-F, -Cl, -Br, -I

Assignment No. 1

Arrange the compounds in each series in decreasing order of reactivity toward ring nitration. Identify the most reactive and the least reactive compound in each series.

a) I 

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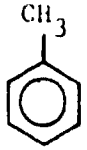
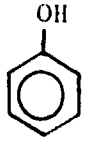
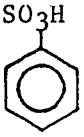
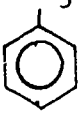
III 

IV 

Assignment No. 1 (continued)

b) I  II  III  IV 

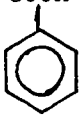
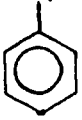
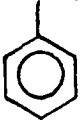
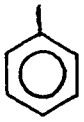
c) I  II  III  IV 

Table II - Orientation of Nitration of

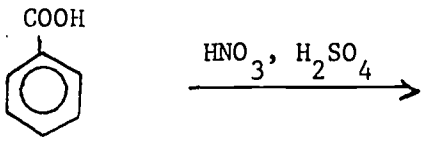
Z	Ortho	Para	Ortho + Para	Meta
-OH	50-55	45-50	100	--
-NHCO CH_3	19	79	98	2
$-CH_3$	58	38	96	4
-F	12	88	100	--
-Cl	30	70	100	--
-Br	37	62	99	1
-I	38	60	98	2
$-NO_2$	6.4	0.3	6.7	93.3
$-\overset{+}{N}R_3$	---	11	11	89
$-C\equiv N$	---	---	19	81
$-SO_3H$	21	7	28	72
-CHO	---	---	28	72
-COOH	19	1	20	80

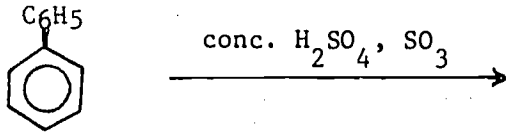
Table No. III - Orientation of Substitution in Toluene

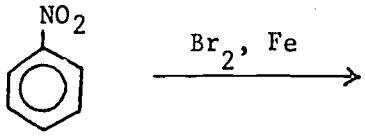
	Ortho	Para	Meta
Nitration	58	38	4
Bromination	53	67	-
Sulfonation	32	62	6

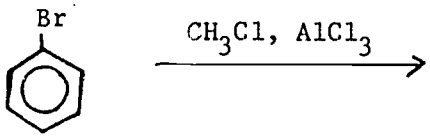
Assignment No. 2

In each reaction name the products, draw their structure and where more than one product is obtained identify the major product.

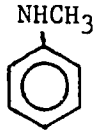
a) 

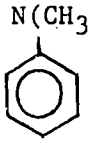
b) 

c) 

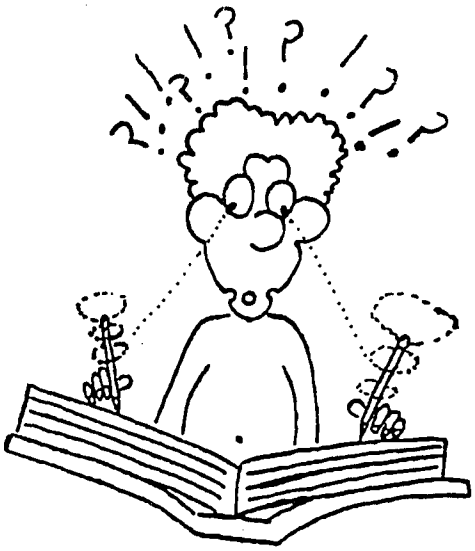
d) 

e)  $\xrightarrow{HNO_3,\ H_2SO_4}$

f)  $\xrightarrow{Br_2,\ Fe}$

g)  $\xrightarrow{\text{Fuming } H_2SO_4}$

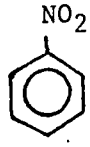
h)  $\xrightarrow{Cl\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3,\ AlCl_3}$



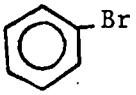
Assignment No. 3

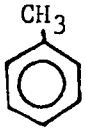
Confused Clyde was asked to complete a number of reactions, name the products, draw their structure and identify the major product where applicable. He has written the answers in the wrong place and applied it to the wrong question. It is your task to match the right question with the right answer.

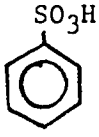
Questions:

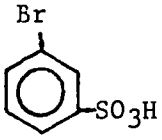
a)  $\xrightarrow{CH_3Cl,\ AlCl_3}$

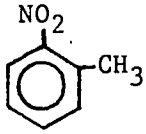
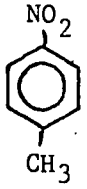
b)  $\xrightarrow{H_2SO_4,\ SO_3}$

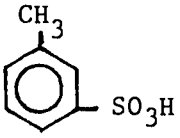
c)  $\xrightarrow{H_2SO_4,\ HNO_3}$

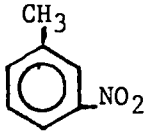
d)  $\xrightarrow{H_2SO_4,\ HNO_3}$

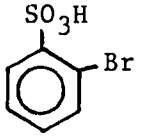
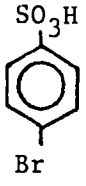
e)  $\xrightarrow{CH_3Cl,\ AlCl_3}$

a. 

b.  + 

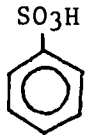
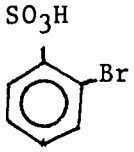
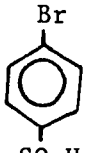
c. 

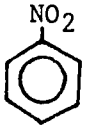
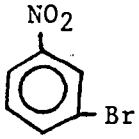
d. 

e.  + 

15

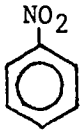
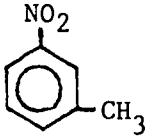
Assignment No. 3 (continued)

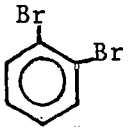
f)  $\xrightarrow{Br_2, Fe}$ f.  + 

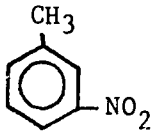
g)  $\xrightarrow{Br_2, Fe}$ g. 

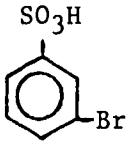
Assignment No. 4

Saturated Sam was asked to complete the given reactions, name the products, draw their structure and identify the major product where applicable. He has made several mistakes. Identify his mistakes and correct them.

a)  $\xrightarrow{CH_3Cl, AlCl_3}$  + 

b)  $\xrightarrow{Br_2, Fe}$ 

c)  $\xrightarrow{HNO_3, H^+}$ 

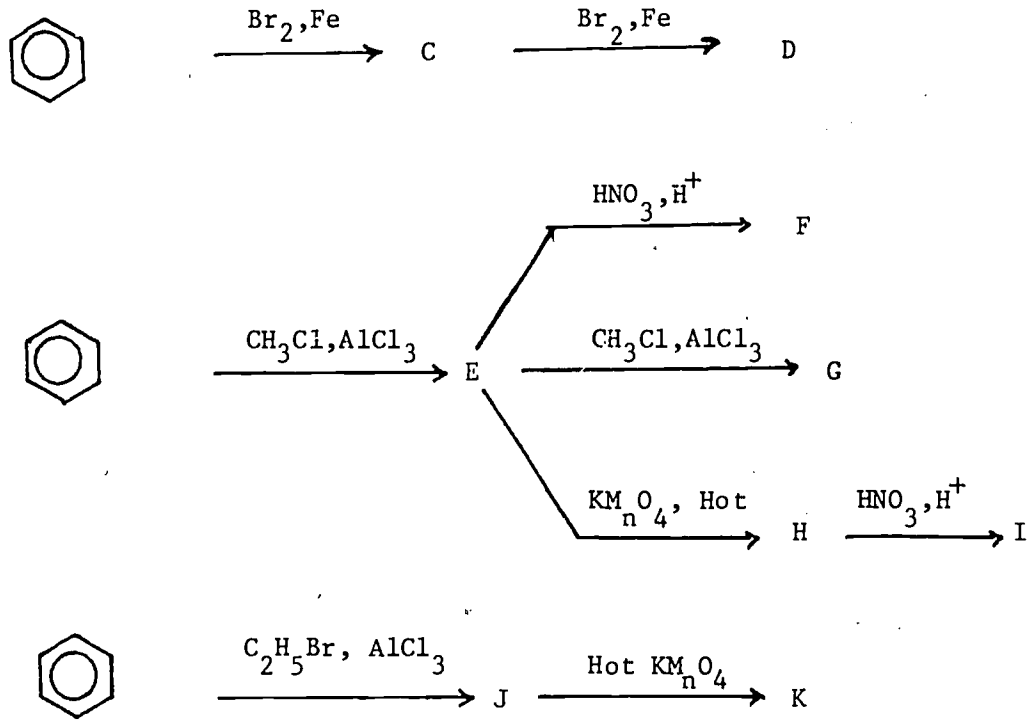
d)  $\xrightarrow{Br_2, Fe}$ 

Assignment No. 5

Identify (draw the structures and name) compounds A ⟶ K.

 $\xrightarrow{HNO_3, H^+}$ A $\xrightarrow{Br_2, Fe}$ B

Assignment No. 5 (continued)



Assignment No. 6

How can you synthesize compound listed below from benzene? Identify all the reagents.

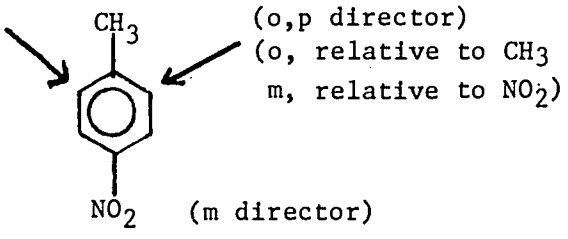
a) o-bromo benzoic acid

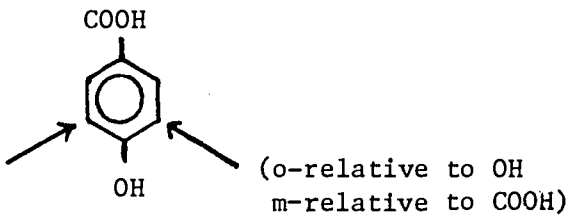
b) m-bromo benzoic acid

c) p-bromo nitro benzene

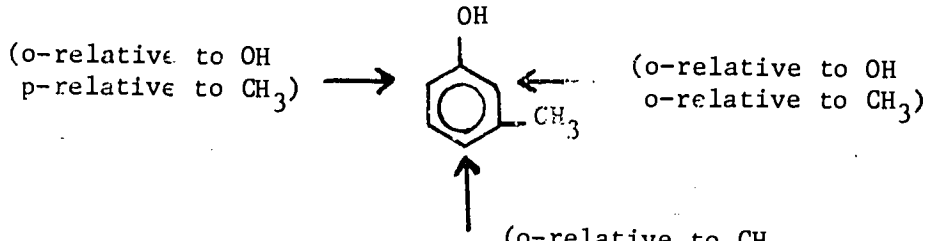
d) p-nitro toluene

Example No. 1 (Directive influence of one group reinforces that of the other)

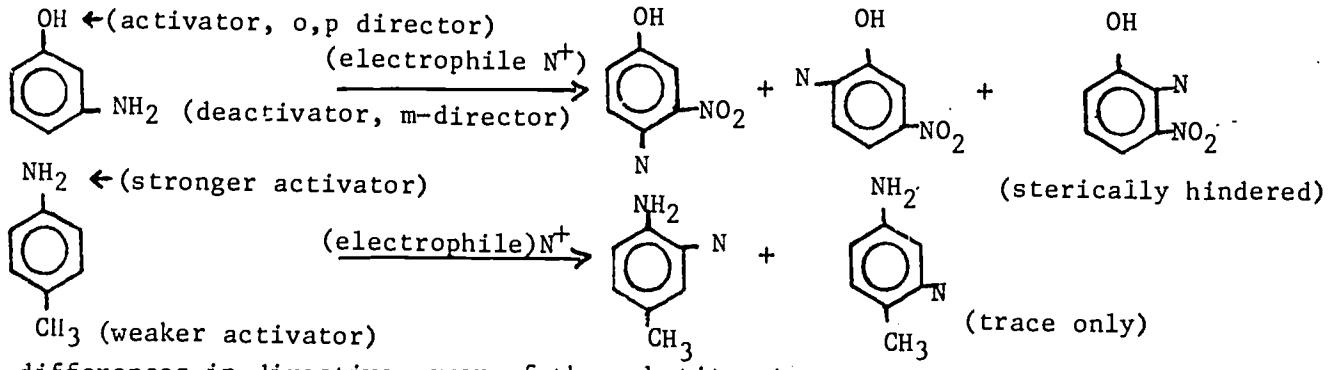




Example No. 1 (continued)



Example No. 2



The differences in directive power of the substituent groups:

$-NH_2$ or $-NHR$ or $-NR_2$, $-OH$ > $-OR$, $-NHCOCH_3$ > $-C_6H_5$, $-R$ > X > m-directors

Assignment No. 7

Complete the reactions below. Name the products, draw their structures and identify the major product in each reaction.

a) o-nitro phenol $\xrightarrow{HNO_3, H^+}$

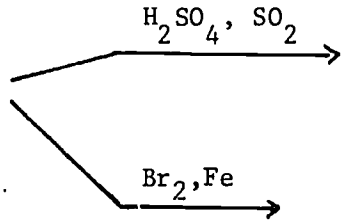
b) o-ethyl benzoic acid $\xrightarrow{Br_2, Fe}$

c) p-methyl aniline $\xrightarrow{CH_3Cl,\ AlCl_3}$

p-methyl aniline $\xrightarrow{HNO_3, H^+}$

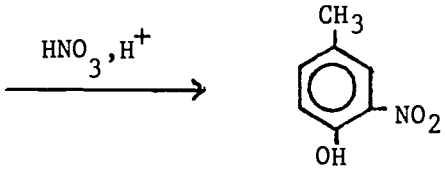
Assignment No. 7 (continued)

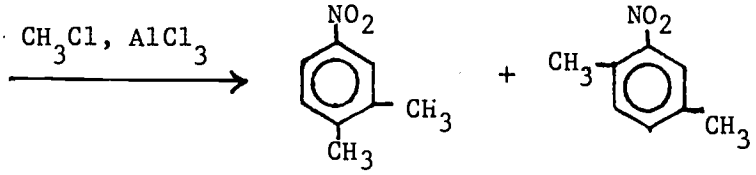
d) m-nitro toluene

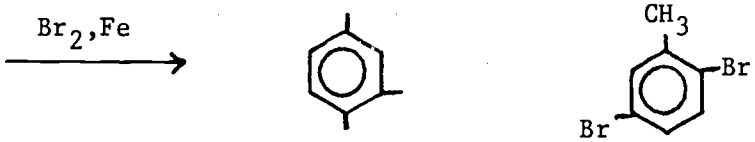


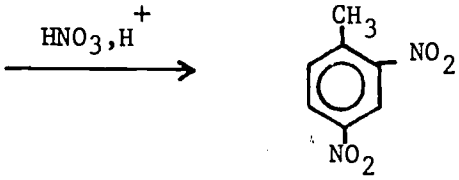
Assignment No. 8

Identify the reactants in the answers below submitted by Forgetful Frieda.

a) 

b) 

c) 

d) 

Assignment No. 9

Inert Irma has been asked to complete a number of reactions, name the products, draw their structure and indicate the major products where applicable. Identify the mistakes Irma has made and correct them.

SIP No. 16
Tape 1 - Work Sheet

a) p-methyl phenol $\xrightarrow{Br_2, Fe}$ 3-bromo-4-methyl phenol

b) m-nitro toluene $\xrightarrow{HNO_3, H^+}$ 3,4-dinitro toluene + 3,5-dinitrotoluene + 2,5-dinitro toluene + 2,3-dinitrotoluene

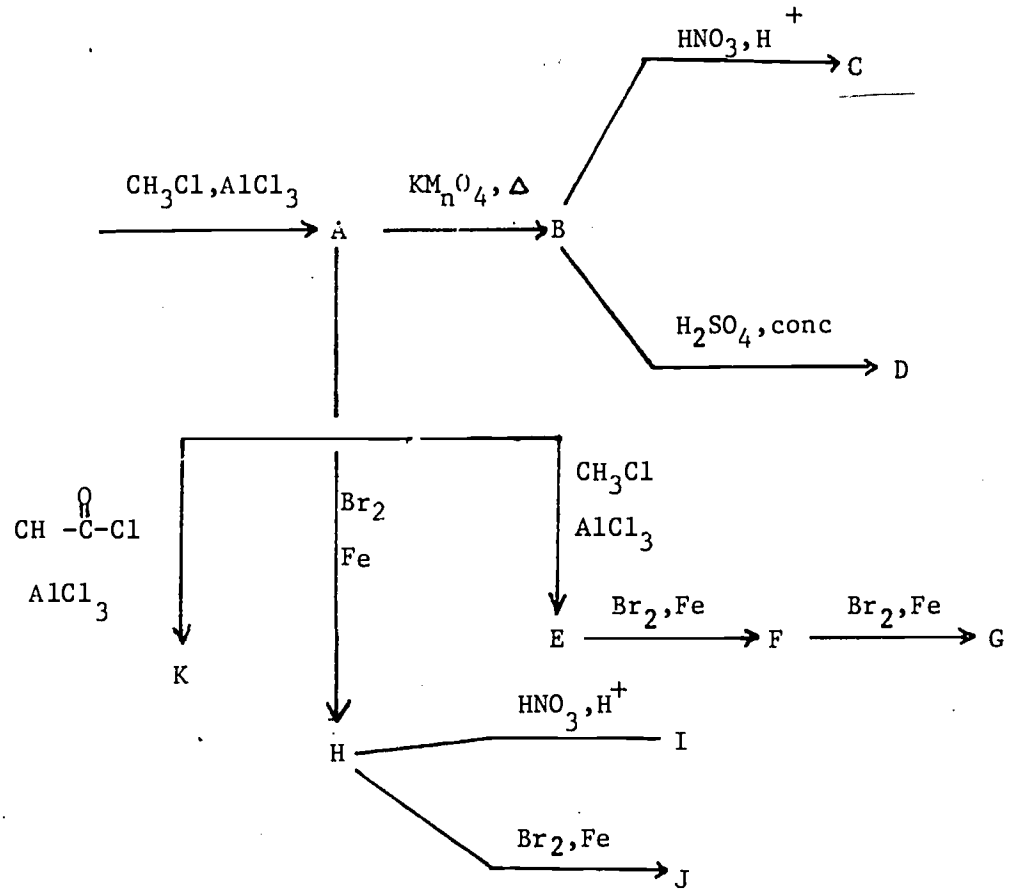
c) p-bromo phenol $\xrightarrow{Br_2, hv}$ 3,4-dibromophenol + 2,4-dibromophenol

d) 2-nitro-4-bromo phenol $\xrightarrow{Br_2, Fe}$ 2,4-dibromo-6-nitrophenol + 3,4-dibromo-6-nitro phenol

e) 2-methyl-4-nitro phenol $\xrightarrow{HNO_3, H^+}$ 4,6-dinitro-2-methyl phenol + 3,4-dinitro-6-metnyl phenol

Assignment No. 10

Identify (draw the structures and name) compounds A through K in a reaction sequence given below:



Assignment No. 11

Outline all the steps and identify all the reagents required for the laboratory synthesis of the compounds below from benzene.

a) 3,4-dibromobenzoic acid

b) 3,4-dinitro benzoic acid

c) 3,5-dinitrobenzoic acid

d) 2,4-dinitrobenzoic acid

e) 2-nitro-4-bromo benzoic acid

AROMATIC CHEMISTRY

Effect of Substituent Groups on Electrophilic Aromatic Substitution

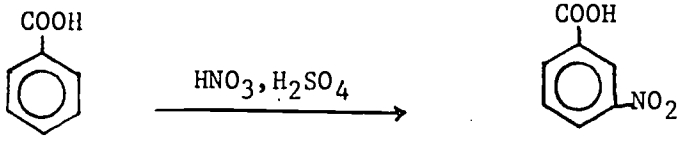
Assignment No. 1

a) IV > III > II > I

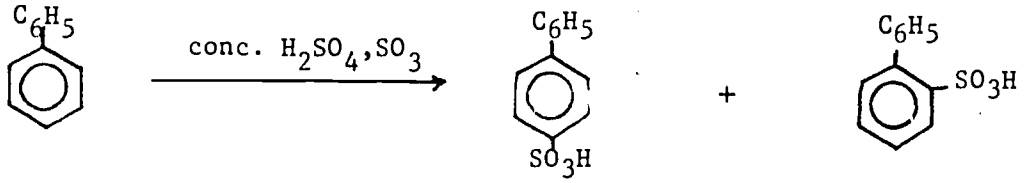
b) III ≈ IV > I > II

c) III > IV > II > I

Assignment No. 2

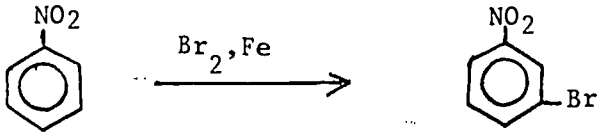
a) 

m-nitrobenzoic acid

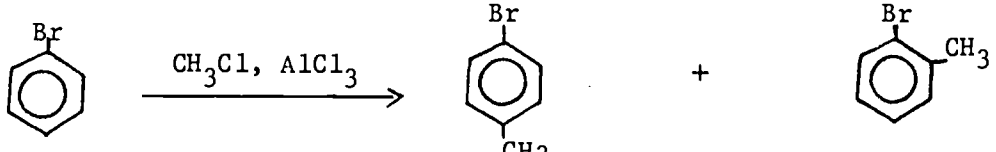
b) 

p-phenylbenzene sulfonic acid major product

o-phenylbenzene sulfonic acid

c) 

m-bromo nitrobenzene

d) 

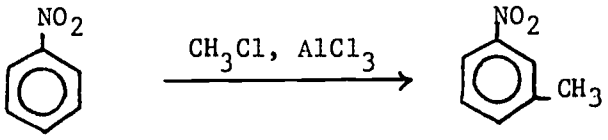
p-bromotoluene

o-bromotoluene

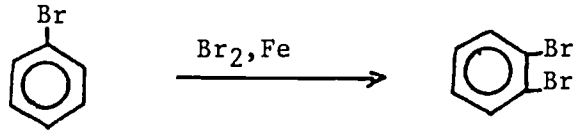
Assignment No. 3

A - d	E - c	C - e	F - g
B - f	F - a	D - b	

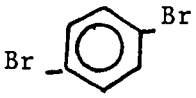
Assignment No. 4

a) 

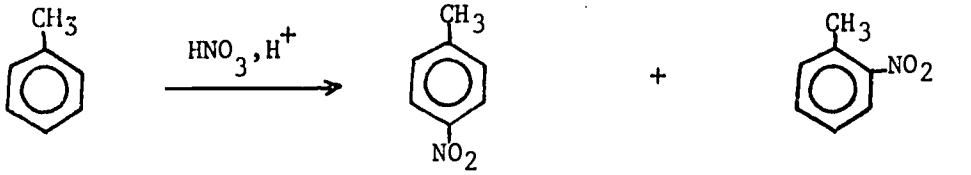
(in theory only since deactivated rings do not not undergo Friedel-Crafts reaction)

b) 

o-dibromo benzene



p-dibromobenzene

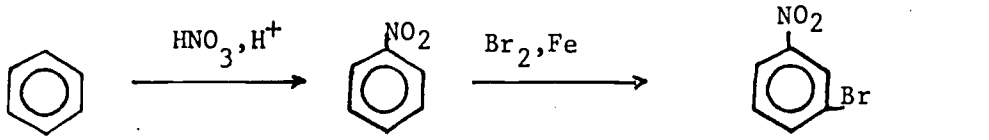
c) 

p-nitrotoluene

o-nitrotoluene

d) m-bromo benzenesulfonic acid - correct

Assignment No. 5



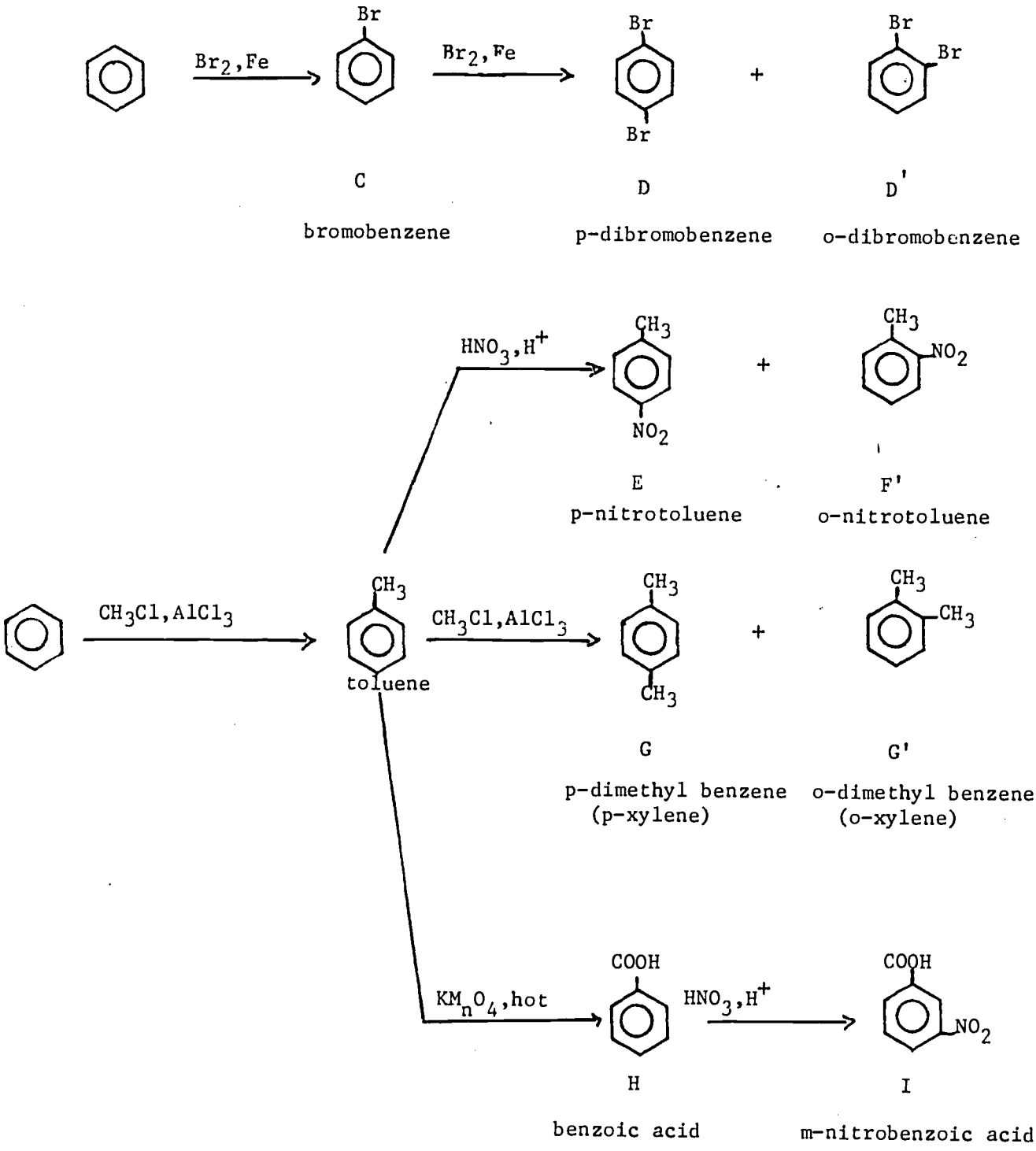
nitrobenzene

A

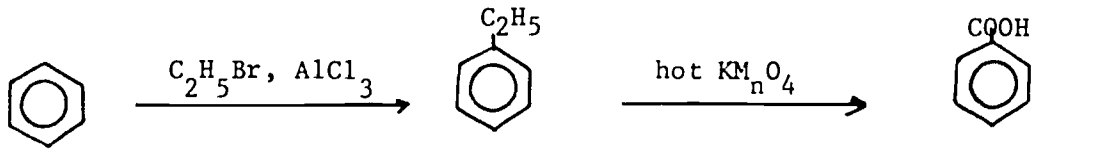
m-bromo nitrobenzene

B

Assignment No. 5 (continued)



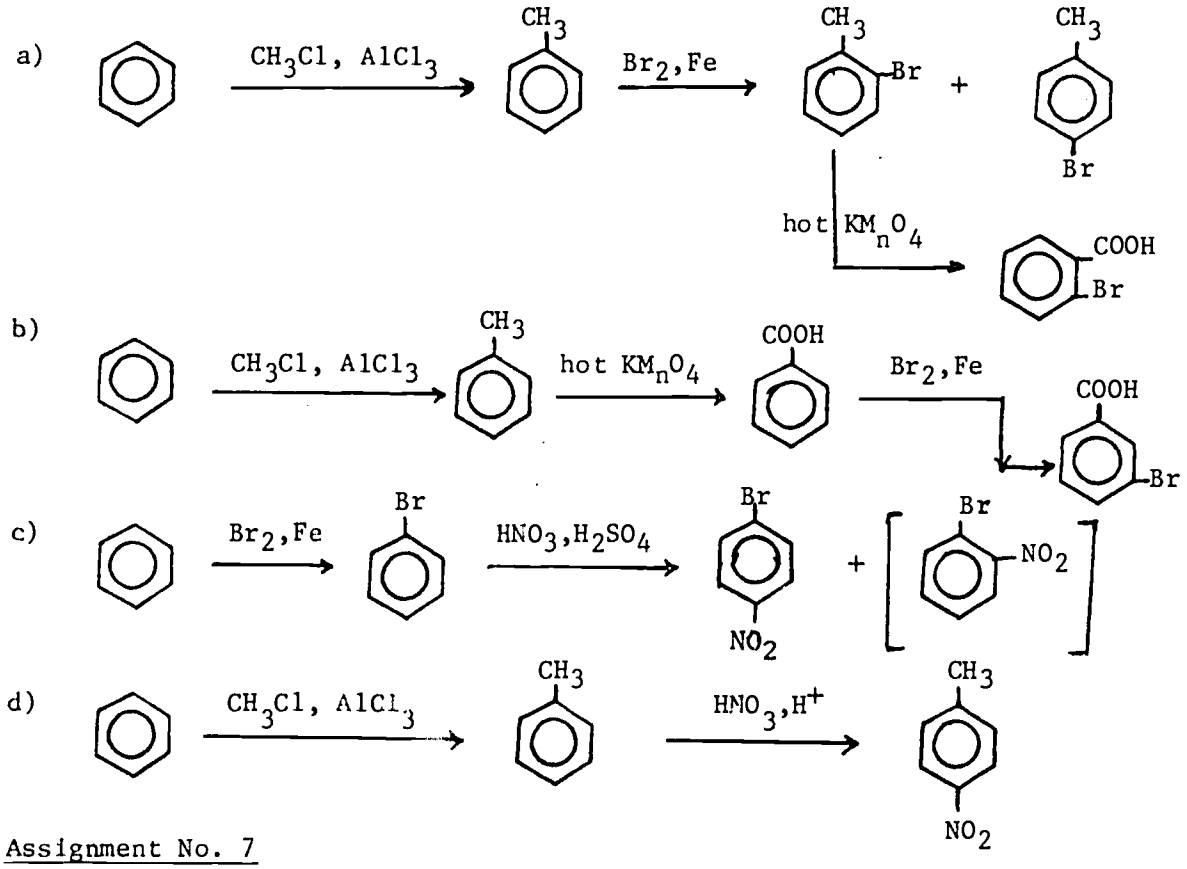
Assignment No. 5 (continued)



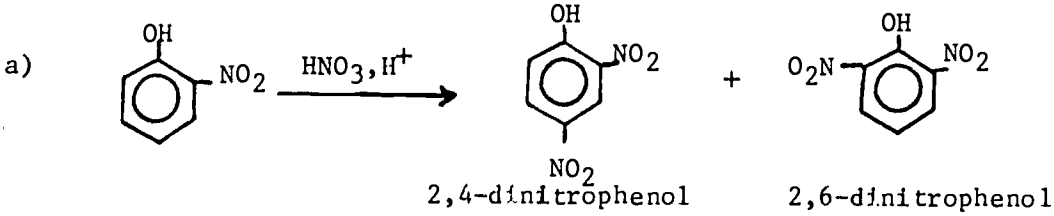
ethylbenzene — J

benzoic acid — K

Assignment No. 6

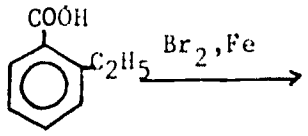


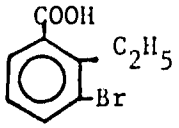
Assignment No. 7



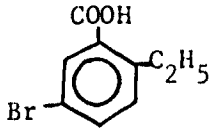
2,4-dinitrophenol — 2,6-dinitrophenol

Assignment No. 7 (continued)

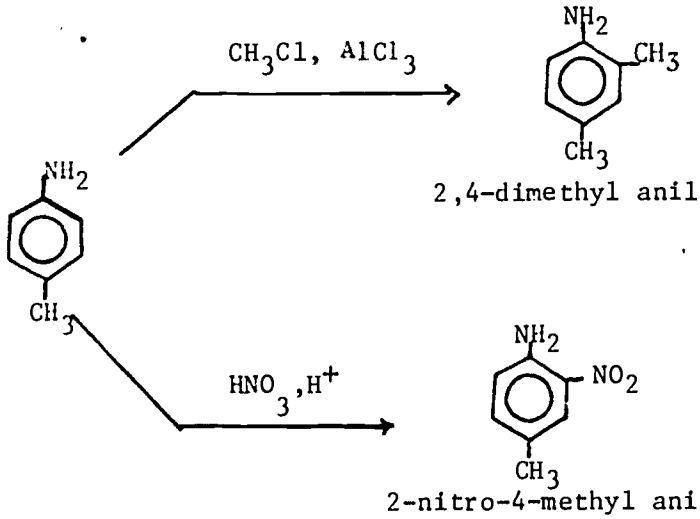
b) 



2-ethyl-3-bromobenzoic acid



2-ethyl-5-bromo benzoic acid

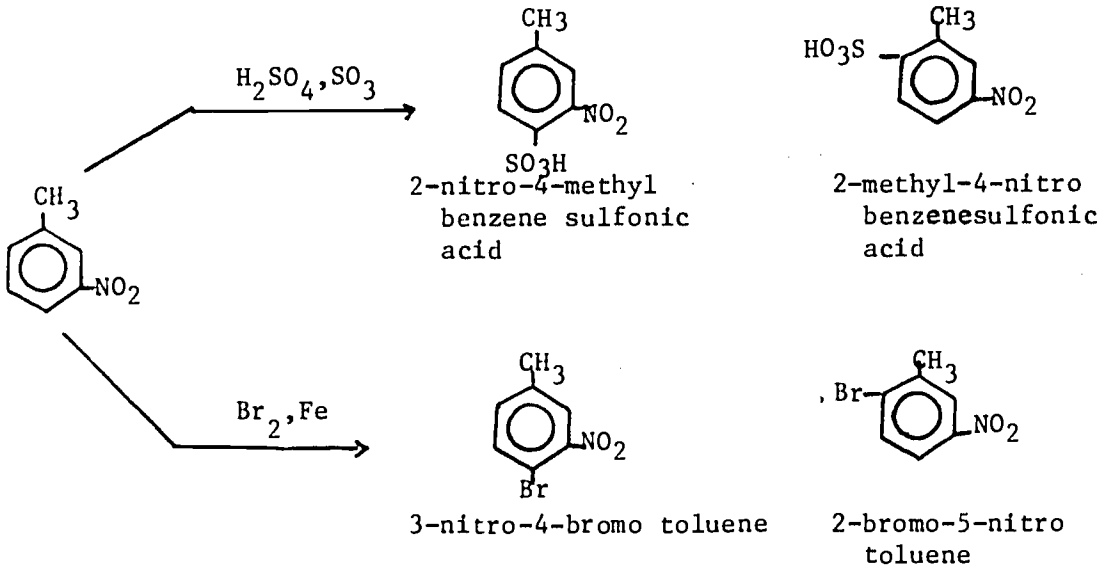
c) 

(major product)

2,4-dimethyl aniline

(chief product)

2-nitro-4-methyl aniline



2-nitro-4-methyl benzene sulfonic acid

2-methyl-4-nitro benzenesulfonic acid

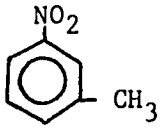
3-nitro-4-bromo toluene

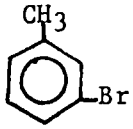
2-bromo-5-nitro toluene

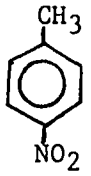
SIP No. 16
Tape 1 - Answer Sheet

Assignment No. 8

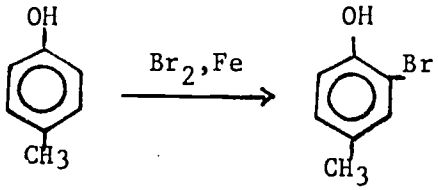
a)  p-methyl phenol

b)  m-nitrotoluene

c)  m-bromotoluene

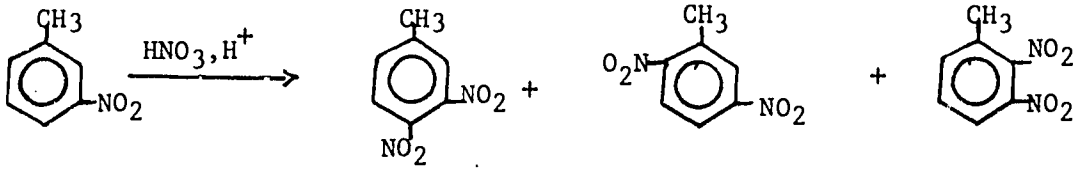
d)  p-nitro toluene

Assignment No. 9 - correct answers

a) 

2-bromo-4-methyl phenol

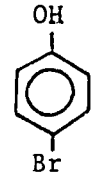
(OH is a stronger activator than CH_3 group)

b 

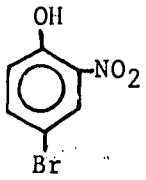
3,4-dinitro toluene

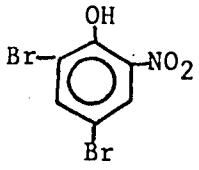
2,5-dinitro toluene

2,3-dinitro toluene

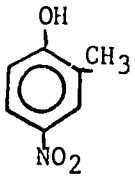
c) 

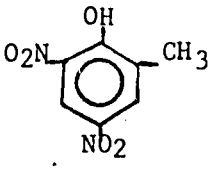
Br_2, hv ——— No Reaction

d) 

Br_2, Fe → 

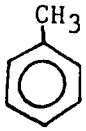
2,4-dibromo-6-nitro-phenol

e) 

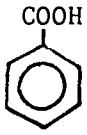
HNO_3, H^+ → 

2,4-dinitro-6-methyl phenol

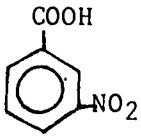
Assignment No. 10

A 

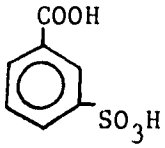
toluene

B 

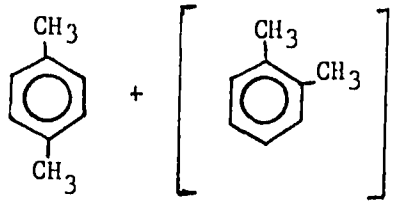
benzoic acid

C 

m-nitrobenzoic acid

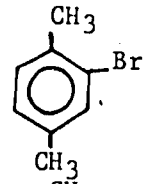
D 

m-sulfobenzoic acid

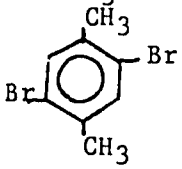
E 

p-dimethyl benzene (p-xylene_

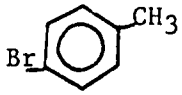
o-dimethyl benzene (o-xylene)

F 

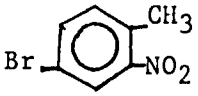
2-bromo-4-methyl toluene

G 

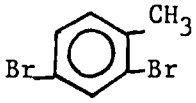
2,5-dibromo-4-methyl toluene

H 

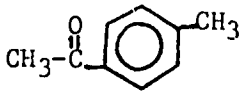
p-bromotoluene

I 

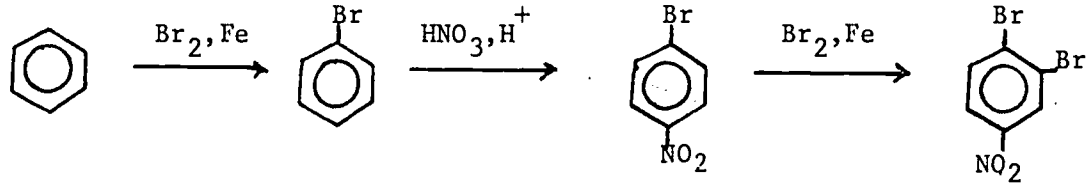
2-nitro-4-bromo toluene

J 

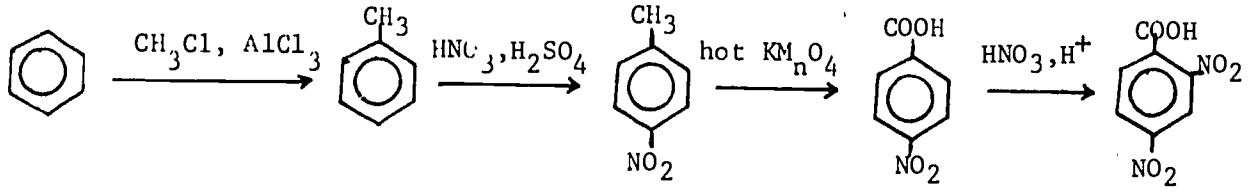
2,4-dibromotoluene

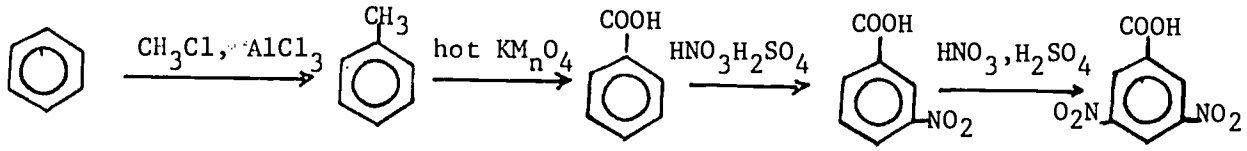
K 

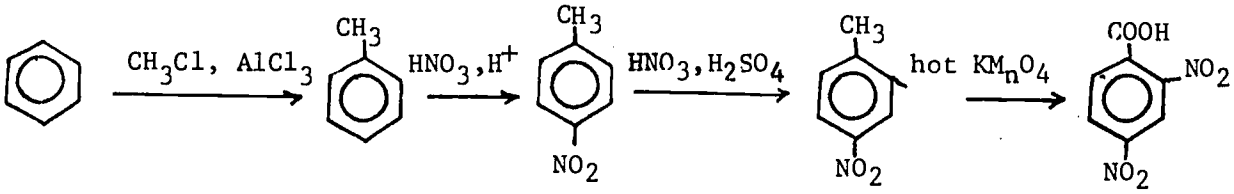
Assignment No. 11

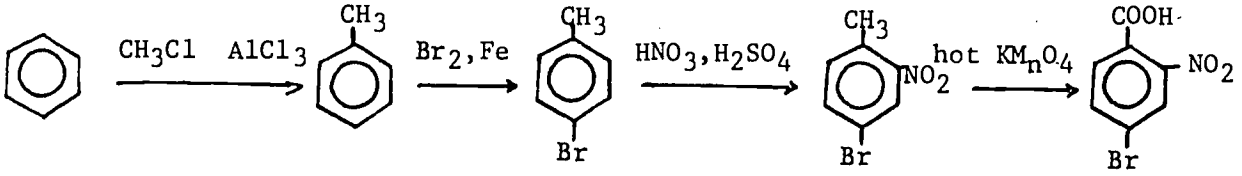
a) 

Assignment No. 11 (continued)

b) 

c) 

d) 

e) 

I wish he would explain his explanations.
---Bryon

AROMATIC CHEMISTRY

The Inductive and the Resonance Effect of the Substituent Groups

Example No. 1

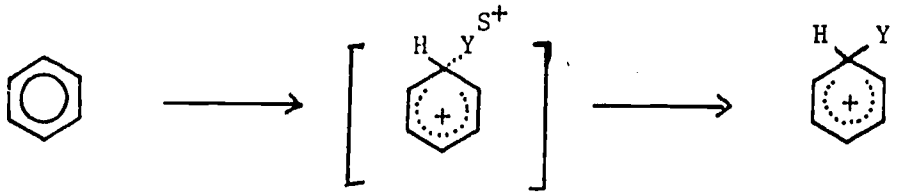
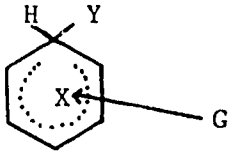


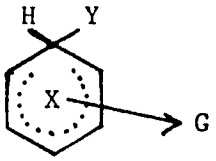
Table No. 1



G-Releases electrons;
Stablilizes carbonium ion;

ACTIVATES

G = NH_2 -NHR $-NR_2$
-OH
-OR
$-NHCOOH_3$
$-C_6H_5$
-R



G-Withdraws electrons;
Destabilizes carbonium ion;

DEACTIVATES

G = $\overset{+}{N}R_3$
NO_2
SO_3H
COOH
CHO
COR
X

Assignment No. 1

a) Compare the effect of the following four groups: CH_3, CH_2F, CHF_2 and CF_3 on the reactivity of benzene ring.

b) Do they stabilize or destabilize the intermediate carbonium ion?

c) Do they increase or decrease the electron density of the ring?

d) What effect does methyl group exhibit - electron withdrawing or electron releasing inductive effect?

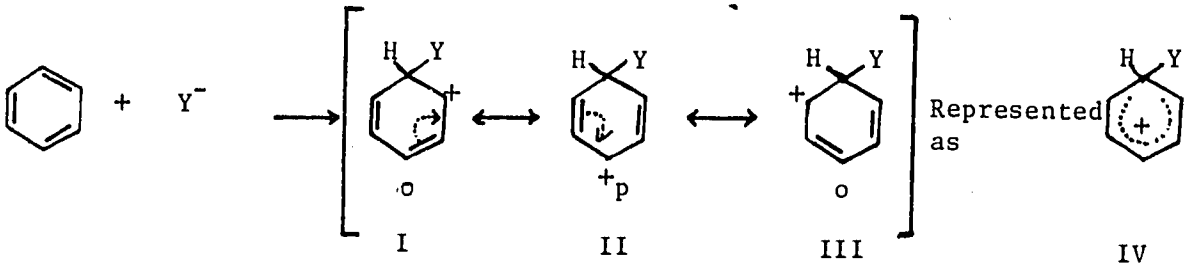
e) What effect does tribluoromethyl group exhibit?-- electron releasing or electron withdrawing inductive effect?

The inductive and the resonance effect in electrophilic aromatic substitution.

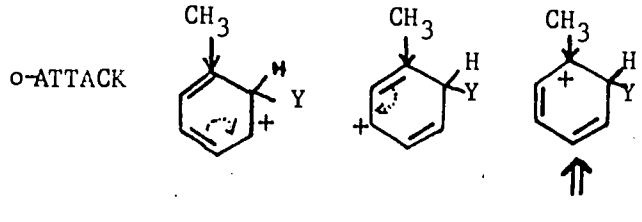
Example No. 2 - Mechanism of electrophilic aromatic substitution

Step 1: Formation of electrophile Y^+ i.e. NO_2^+, X^+, CH_3^+, R^+, SO_3,-----

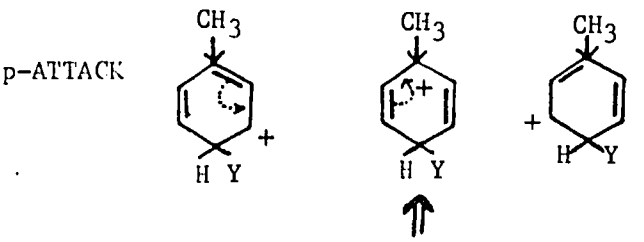
Step 2: Formation of the carbonium ion and its stabilization through resonance and delocalization of positive charge



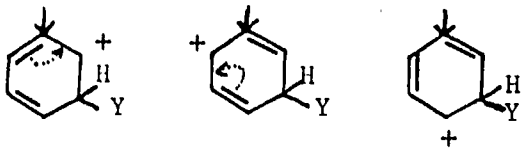
Resonance structures representing an o, m or p-attack on an activated ring



Methyl group stabilizes the carbonium ion particularly if in o-position

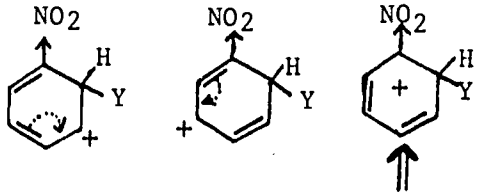


Methyl Group stabilizes the carbonium ion particularly if in p-position

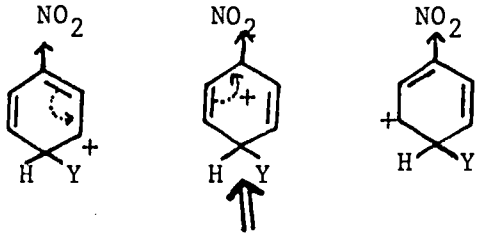
m-attack 

No position is stablized particularly in a meta attack.

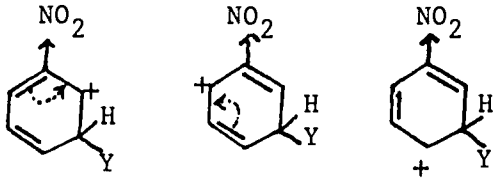
Resonance structures representing an o, m or p-attack on a deactivated ring

o-attack 

Nitro group destabilizies the carbonium ion particularly in o-position

p-attack 

Nitro group destablizes the carbonium ion particularly if in p-position

m-attack 

No position is particularly destablized in a meta attack.

The inductive and the resonance effect in electrophilic aromatic substitution

Assignment No. 2

Identify the statements given below as True or False by placing a capital letter T or F in front of each statement.

a) _____ Nitro group is a meta director because it stabilizes m-position more than o and p positions.

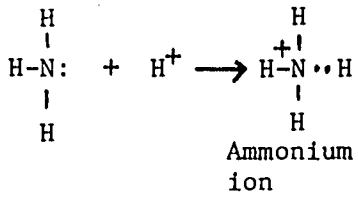
b) _____ Methyl group is an o and p director because it destabilizes m position more than o and p positions.

c) _____ Activators increase electron density in the ring.

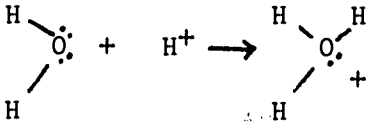
d) _____ Strongly activating groups such as NH_2, OH, etc. increase the electron density in the ring to greater extent than the weakly activating groups such as CH_3 or C_6H_5.

e) _____ Deactivating groups such as NO_2, COOH, SO_3H decrease the electron density in the ring particularly in o and p positions.

Example No. 3



Ammonium ion

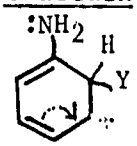


Water Hydronium ion

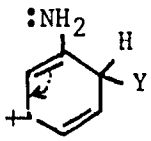
SIP No. 16
Tape 2 - Work Sheet

Example No. 4

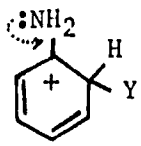
o-attack



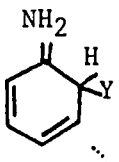
I



II



III

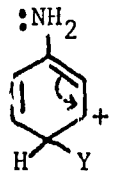


IV

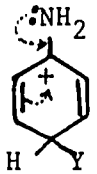
IV and VIII especially stable.

Every atom has octet.

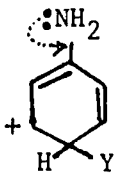
p-attack



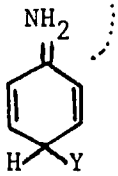
V



VI



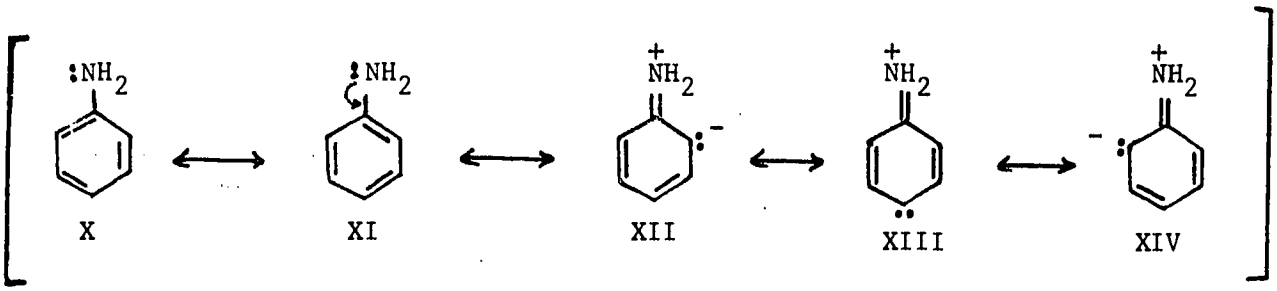
VII



VIII

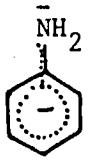
m-attack

Resonance structures of aniline



X XI XII XIII XIV

Increase in electron density is particularly strong in o and p positions



overall structure

XV

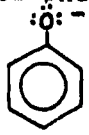
SIP No. 16
Tape 2 - Work Sheet

Assignment No. 3

a) Draw resonance structures for the carbonium ion during an o, m, p attack on phenol. Identify the structures with maximum stability.

b) Draw the resonance structures for phenol. Explain how they are related to the activating and the o and p directing effect of phenol.

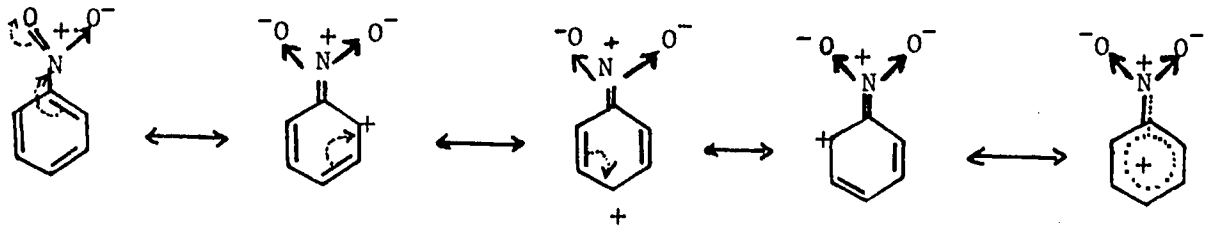
c) Draw the resonance structures of phenolate anion
Why is a phenolate anion even more activating than phenol? Be specific.



Assignment No. 4

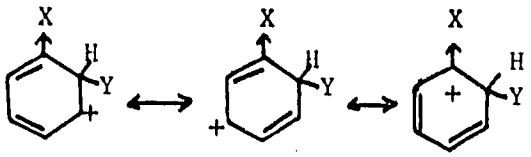
Compare the activating effects of NH CH_2 CH_3 group and $NHCOCH_3$ group. Which of the two is a stronger activator? Why? What effect does oxygen have on the activating effect of $NHCOCH_3$ group? Why?

Example No. 5 - Resonance structures of nitro benzene

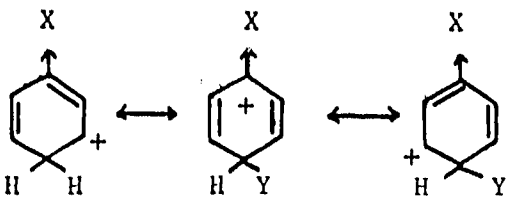


Example No. 6 - Electron withdrawing effect of halogen:

o-attack



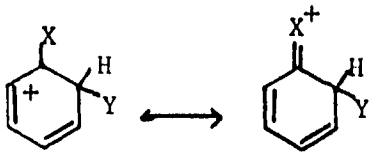
p-attack



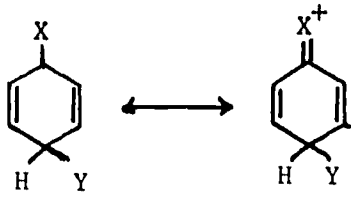
The inductive and the resonance effect in electrophilic aromatic substitution

Resonance effect in o and p attack

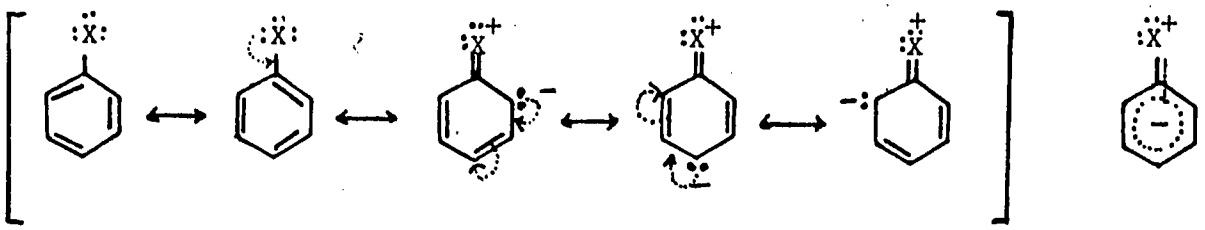
o-attack



p-attack



Resonance structures of halo benzene



Assignment No. 5

Identify the statements below as True or False by placing T or F in front of each statement.

a) _____ OH group activates the ring through an electron releasing inductive effect.

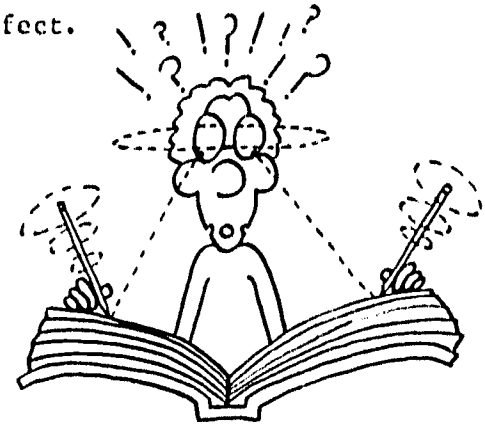
b) _____ Nitro group is a meta director because it generates higher electron density in meta position.

Assignment No. 5 (continued)

c) _____ NH_2 group is an o.p director because it generates excess electron density in those positions.

d) _____ X is a deactivator because of its prominent resonance effect.

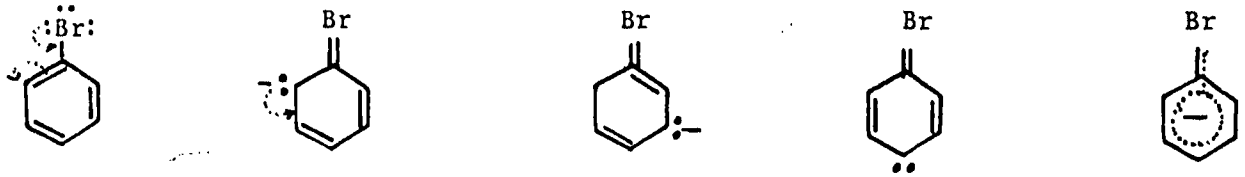
e) _____ X is an o.p director due to its resonance effect.



Assignment No. 6

Confused Clyde was asked to draw resonance structures which will explain the reactivity and orientation in phenol and bromobenzene and to explain it. His answers are given below. It is your task to correct them.

I II III IV V



I II III IV V

Self Instructional Package No. 16
Tape No. 2 - Answer Sheet

AROMATIC COMPOUNDS

Inductive and Resonance Effect of Substituent Groups

Assignment No. 1

a) CH_3 > CH_2F > CHF_2 > CF_3

activating — deactivating

b) CH_3 > CH_2F > CHF_2 > CF_3

stabilizes — destabilizes

c) CH_3 > CH_2F > CHF_2 > CF_3

increase the electron density — decrease the electron density

d) CH_3 - electron releasing inductive effect

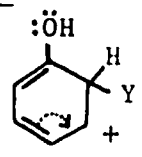
e) CF_3 - electron withdrawing inductive effect due to the highly electronegative fluorine atoms

Assignment No. 2

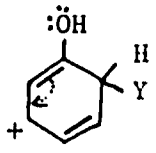
a) F b) F c) T d) T e) T

Assignment No. 3

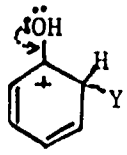
o-attack



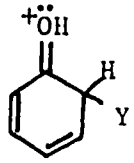
I,



II

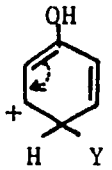


III

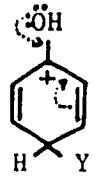


IV

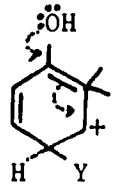
p-attack



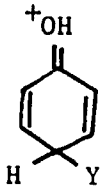
V



VI

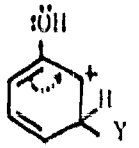


VII

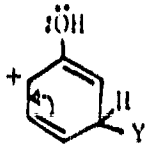


VIII

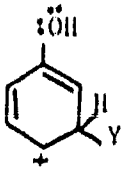
m-attack



IX

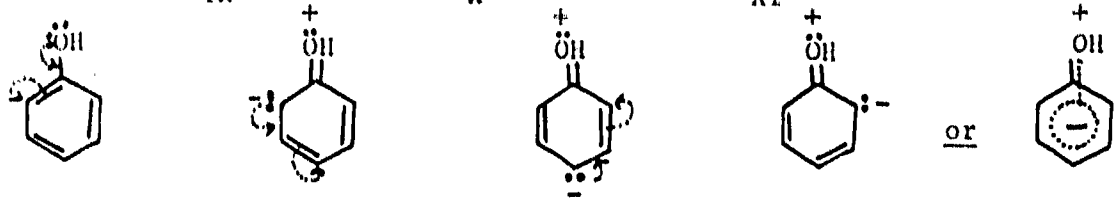


X



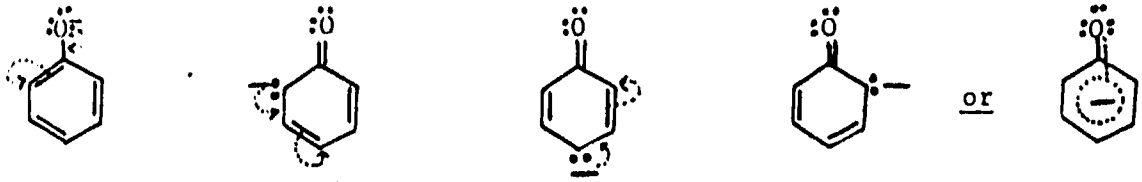
XI

b)



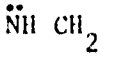
The resonance structures show an increase in electron density in o and p positions causing the o and p directing effect of the OH group.

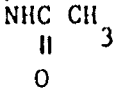
c)



Phenolate anion is stabilized through resonance. The negative charge from oxygen is delocalized over the ring.

Assignment No. 4

 - Stronger activator

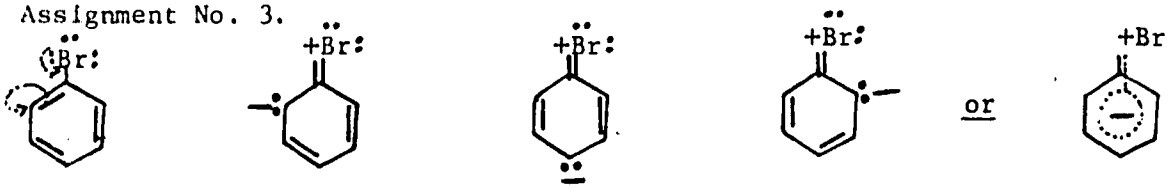
 - Weaker activator. The nonbonding electrons are pulled by the strongly electronegative oxygen.

Assignment No. 5

a) F b) F c) T d) F e) T

Assignment No. 6 - correct answers:

For phenol the correct resonance structures can be seen in the answer to Assignment No. 3.



The resonance structures show the increase in the electron density in o and p positions that cause the o and p directing effect of bromine.

Self Instructional Package No. 16
Form D - Progress Check Evaluation

AROMATIC CHEMISTRY

EFFECT OF SUBSTITUENTS

Identify the statements below as True or False by placing a capital T or capital F in the space provided to the left.

1. _____ NO_2 group in nitrobenzene is deactivator due to its electron withdrawing inductive effect.

2. _____ OR group attached to benzene is an o.p director because of its resonance effect.

3. _____ Resonance effect of the amino group in aniline stems from the interaction of nonbonding electrons on nitrogen with π electrons in the ring.

4. _____ Halogens attached to the ring exhibit an electron releasing inductive effect.

5. _____ Halogens attached to the ring are o and p directors due to the resonance effect.

6. _____ In bromobenzene the inductive and the resonance effect oppose each other.

7. _____ CF_3 group is a deactivator due to the strong electron withdrawing inductive effect.

8. _____ NH_2 is a stronger activator than NHCOR group.

9. _____ SO_3H deactivates the ring because of the resonance effect.

10. _____ Phenolate anion $C_6H_5O^-$ is stabilized through resonance. The negative charge is delocalized over the ring.

11. _____ A carbonyl group $\overset{O}{\overset{\|}{C}}$ when attached to the ring activates the ring through resonance.

Blacken out the correct answer or answers in the questions below.

12. The correct resonance structures showing the o and p directing effect of anion group in aniline are:

12. (continued)

I II III IV

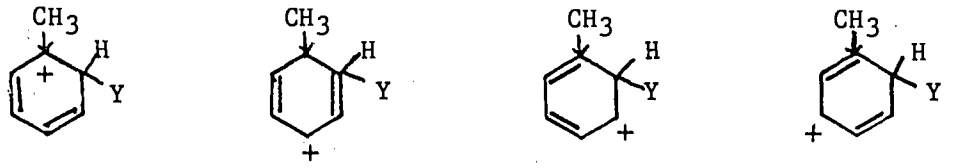
a) I

b) II

c) III

d) IV

13. The correct resonance structures which illustrate an ortho attack in toluene are:



I II III IV

a) I

b) II

c) III

d) IV

14. The correct resonance structures which illustrate a meta attack in benezenesulfuric acid are:

I II III IV

a) I c) III

b) II d) IV

15. The correct statements about the sulfanation reaction are:

    a) the attacking species is SO_3^+

    b) the attacking species is sulfurtrioxide

    c) it is reversible

    d) it exhibits a small isotope effect

16. The correct statements about the bromination of aniline is/are:

    a) the major product in the reaction is o-bromoaniline

    b) the major product in the reaction is m-bromoaniline

    c) the major product in the reaction is p-bromoaniline

    d) the reaction occurs faster than with benzene.

17. The correct statements about the nitration of benzoic acid are:

    a) the major product in the reaction is o-nitrobenzoic acid

    b) the major product in the reaction is m-nitrobenzoic acid

    c) the major product in the reaction is p-nitrobenzoic acid

    d) the reaction occurs faster than with benzene.

18. The major product or products in the nitration of m-nitrophenol are:

    a) 2,3-dinitro phenol

    b) 3,4-dinitro phenol

    c) 3,5-dinotro phenol

    d) 2,5-dinitro phenol

19. The major product or products in the methylation of o-methyl phenol are:

    a) 2,3-dimethyl phenol

    b) 2,4-dimethyl phenol

    c) 2,5-dimethyl phenol

    d) 2,6-dimethyl phenol

20. The reagents required for the synthesis of 2-nitro-4-bromo toluene are:

a) HNO_3, H_2SO_4, Br_2, Fe CH_3Cl, $AlCl_3$

b) CH_3Cl, $AlCl_3$, HNO_3, H_2SO_4, Br_2, Fe

c) CH_3Cl, $AlCl_3$, Br_2, Fe HNO_3, H_2SO_4

d) Br_2, Fe, CH_3Cl, $AlCl_3$, HNO_3, H_2SO_4

21. The reagents required for the synthesis of 3,5-dinitrobenzoic acid are:

a) CH_3Cl, $AlCl_3$, HNO_3, H_2SO_4, HNO_3, H_2SO_4, hot KM_nO_4

b) CH_3Cl, $AlCl_3$, hot KM_nO_4, HNO_3, H_2SO_4, HNO_3, H_2SO_4

c) HNO_3, H_2SO_4, CH_3Cl, $AlCl_3$, hot KM_nO_4, HNO_3, H_2SO_4

d) HNO_3, H_2SO_4, HNO_3, H_2SO_4, CH_3Cl, $AlCl_3$, hot KM_nO_4

Self Instructional Package No. 16
Form B^1 - Self Evaluation Exercise - Answers

AROMATIC CHEMISTRY

EFFECT OF SUBSTITUENTS

1.	T	13.	a, b, d
2.	F	14.	a, c, d
3.	T	15.	a, b
4.	F	16.	a, d
5.	T	17.	a, c, d
6.	T	18.	a, c
7.	T	19.	b, d
8.	F	20.	a
9.	F	21.	a, b, d
10.	F	22.	b
11.	T	23.	d
12.	T		

Self Instructional Package No. 16
Form D1 - Progress Check Evaluation - Answers

AROMATIC CHEMISTRY

EFFECT OF SUBSTITUENTS

1.	T	12.	a, d
2.	T	13.	a, c, d
3.	T	14.	b, c
4.	F	15.	b, c, d
5.	T	16.	a, c, d
6.	T	17.	b
7.	T	18.	a, b, d
8.	T	19.	b, d
9.	F	20.	c
10.	T	21.	b
11.	F		