SOME ORGANIC REACTION PATHWAYS

P SYKES

ETSG

CHEMISTRY CASSETTE

CHEMISTRY CASSETTES

General Editor:
Peter Groves
The University of Aston in Birmingham

Published 1975 by the Educational Techniques Subject Group, The Chemical Society, London.

ISBN 0 85186 999 8

USING THE CHEMISTRY CASSETTE

Please read this carefully before you start

This Chemistry Cassette presentation comprises an audio-cassette and this accompanying booklet. The two are designed to be used together and you should have the booklet with you as you work through the cassette. During the course of the presentation you will, from time to time, be asked to stop the tape and answer questions: you should, therefore, have paper and pencil ready before you start.

The material in this booklet consists of reaction schemes, figures, equations etc., each of which is clearly numbered. Dr. Sykes refers to these section numbers as he speaks, and you should locate the relevant section, and study its contents, as soon as you hear it referred to. Because some of the questions asked are answered in subsequent reaction schemes it is suggested that you cover, with a card or sheet of paper, any schemes beyond the last one referred to.

Tape recorded material has the important feature of being 'self-pacing'. This means that you can work through it at your own pace, *switching off the player*, whenever you want to think, to write some notes, to answer a question etc., and you can use the rewind control to repeat material that you may not have fully understood on a first hearing. To gain the greatest benefit from this presentation you should make full use of these features. You should make notes wherever appropriate: these will then supplement the material contained in the booklet and, together with this, will serve as an authoritative introduction to the subject.

The running time of the cassette is

Side A 34 min.

Side B 34 min.

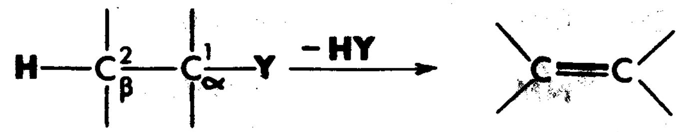
AUTHOR'S NOTE

Rather than attempt a very shallow treatment over the whole field of reaction mechanisms I have concentrated on two types of reaction only, namely **elimination** and **aromatic substitution**; both of them reactions that are of the very greatest importance in organic chemistry as a whole. The cassette begins, on side A, with elimination reactions: aromatic substitution follows on side B.

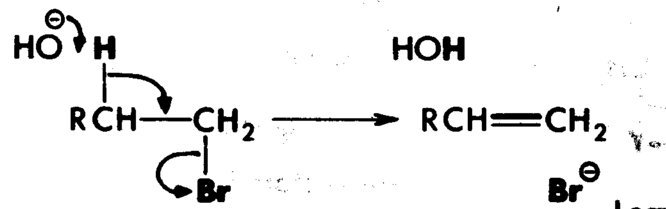
Side A

ELIMINATION

ELIMINATION

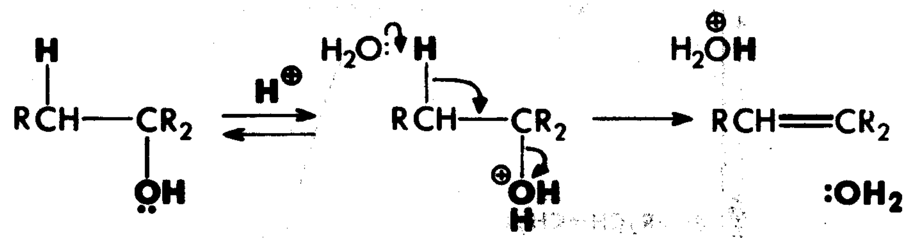


(1) ELIMINATION : GENERALISED FORM



Leaving group = $Br^{\ominus}$

(2) $-$HBr FROM BROMOALKANES

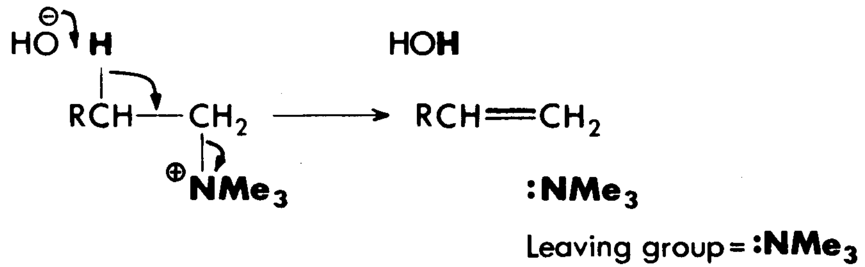


Leaving group = H_2O:

(3) $-H_2O$ FROM ALCOHOLS

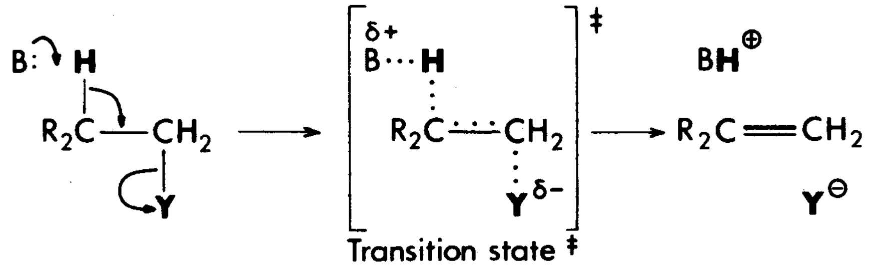
$$RCH_2{-}CH_2\overset{\oplus}{N}Me_3 \quad \overset{\ominus}{O}H$$

(4) ELIMINATION FROM A TETRAALKYLAMMONIUM HYDROXIDE ?



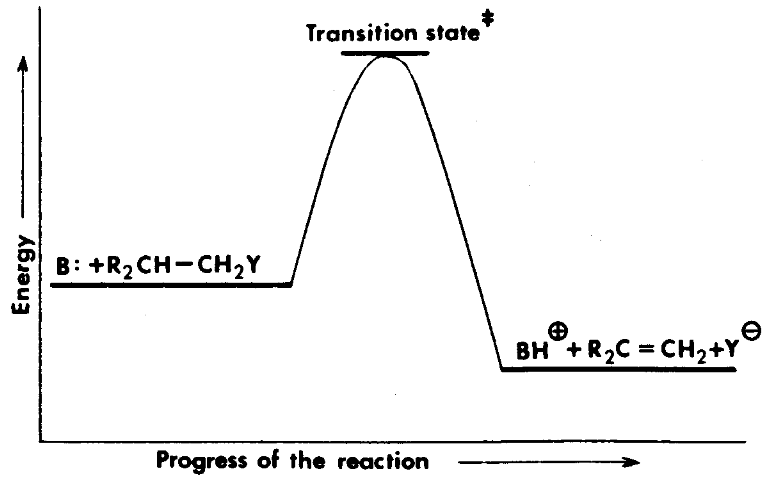
(5)

$-NMe_3$ FROM TETRAALKYLAMMONIUM HYDROXIDES



(6)

ELIMINATION: SINGLE STEP PATHWAY



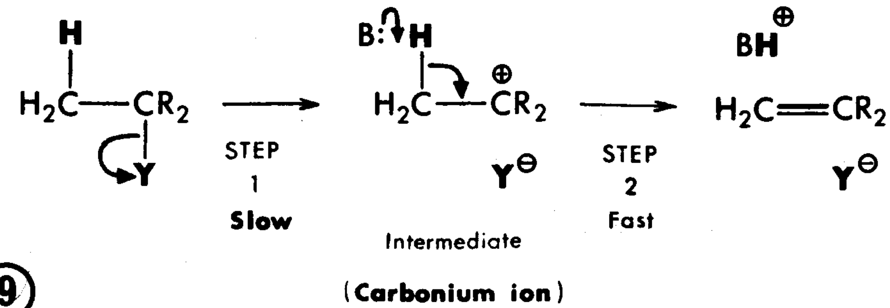
(7)

ENERGY PROFILE: SINGLE STEP PATHWAY

$$\text{RATE} = k\,[\mathbf{B:}]\,[\mathbf{R_2CH{-}CH_2Y}]$$

(8)

RATE LAW: SINGLE STEP PATHWAY



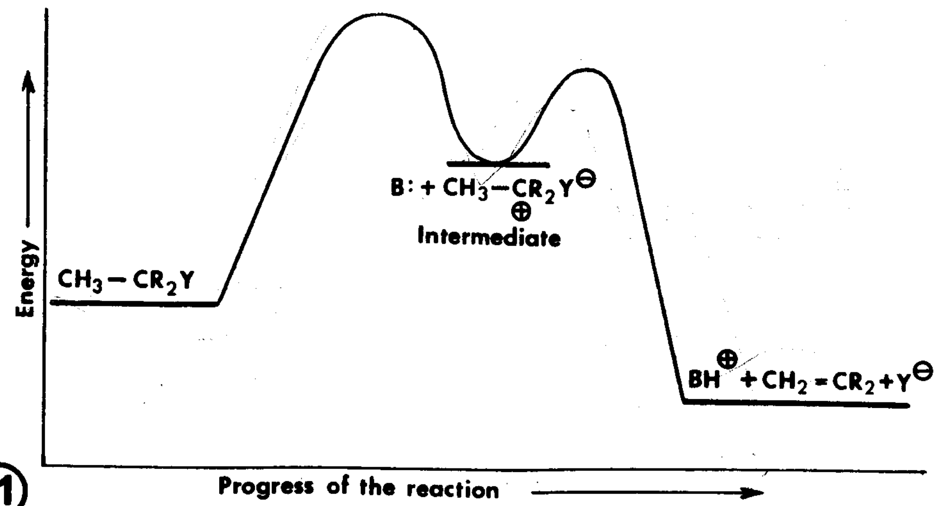
(9)

ELIMINATION: CARBONIUM ION PATHWAY

$$\text{RATE} = k\,[\mathbf{CH_3{-}CR_2Y}]$$

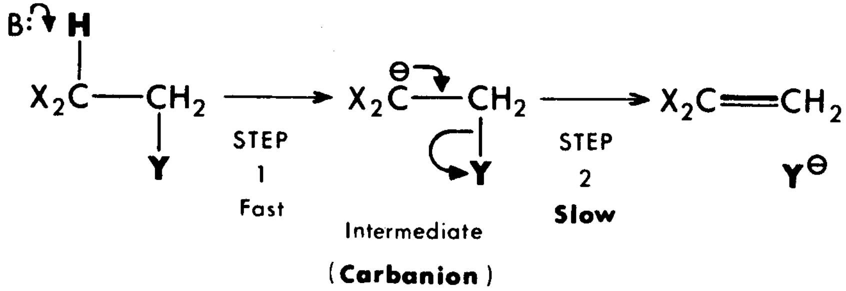
(10)

RATE LAW: CARBONIUM ION PATHWAY



(11)

ENERGY PROFILE: CARBONIUM ION PATHWAY



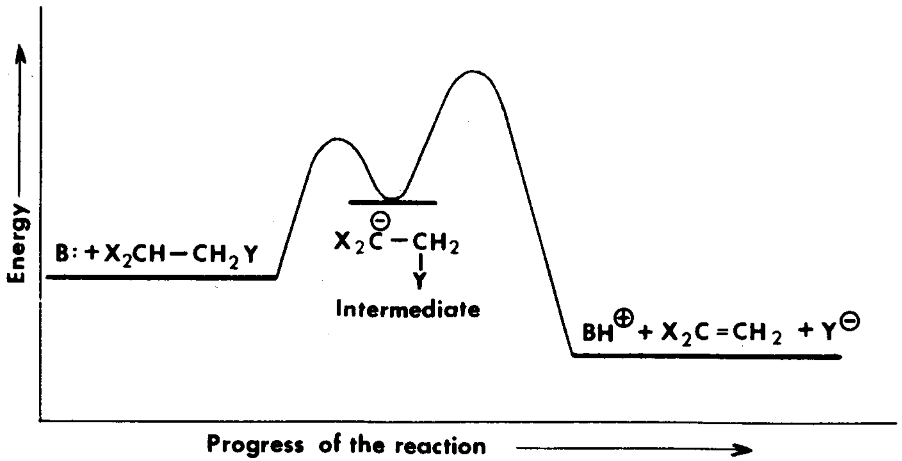
⑫

ELIMINATION: CARBANION PATHWAY

$$\text{RATE} = k\,[\mathbf{B:}]\,[\mathbf{X_2CH-CH_2Y}]$$

⑬

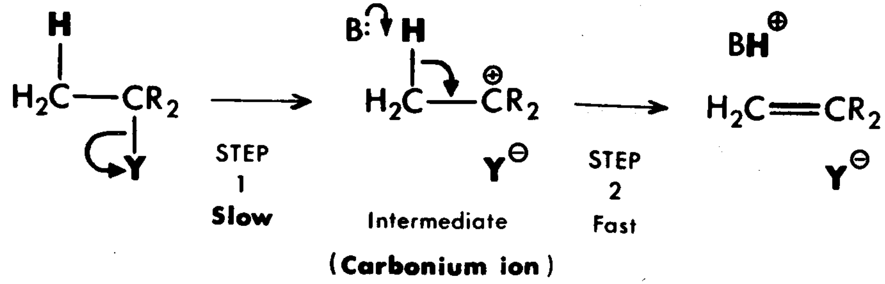
RATE LAW: CARBANION PATHWAY



⑭

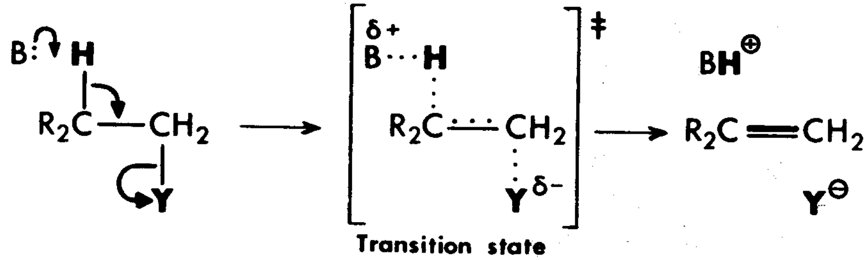
ENERGY PROFILE: CARBANION PATHWAY

COMPARISON OF THREE PATHWAYS



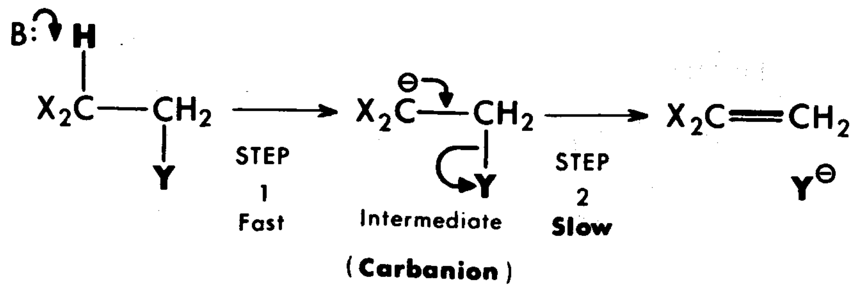
$$\text{RATE} = k\,[\mathbf{CH_3-CR_2Y}]$$

E1 PATHWAY



$$\text{RATE} = k\,[\mathbf{B:}]\,[\mathbf{R_2CH-CH_2Y}]$$

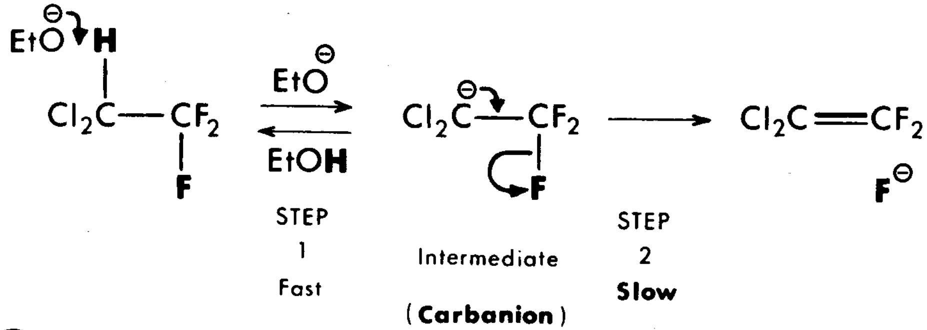
E2 PATHWAY



$$\text{RATE} = k\,[\mathbf{B:}]\,[\mathbf{X_2CH-CH_2Y}]$$

⑮

E1cB PATHWAY



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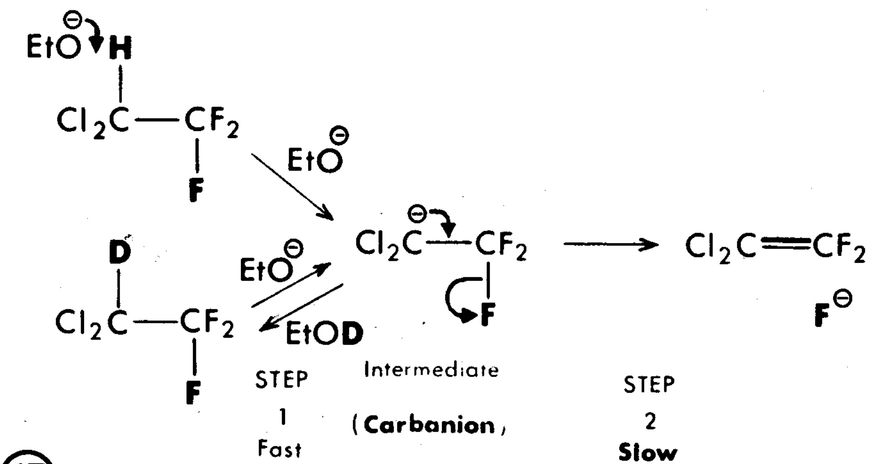
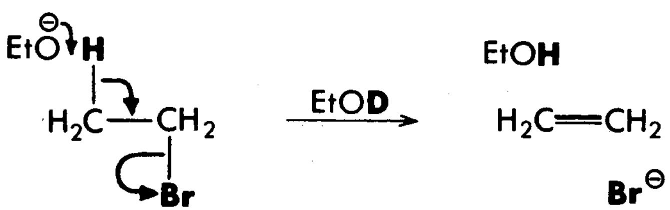
ElcB PATHWAY



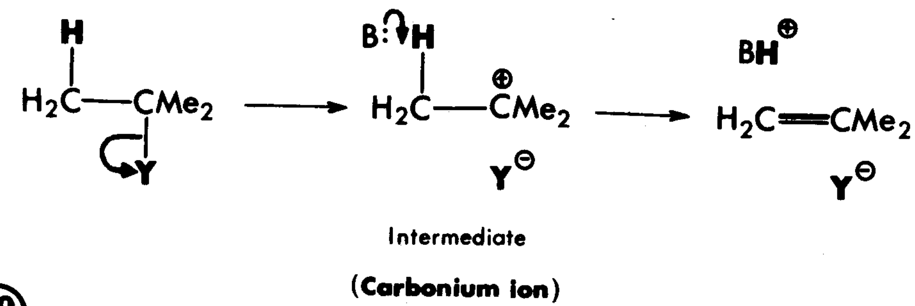
17

DEUTERIUM INCORPORATION IN ElcB PATHWAY



18

NO DEUTERIUM INCORPORATION IN E2 PATHWAY



19

E1 PATHWAY

$$CH_3^{\oplus} < \mathbf{Me}CH_2^{\oplus} < \mathbf{Me_2}CH^{\oplus} < \mathbf{Me_3}C^{\oplus}$$

Increasing stability →

20

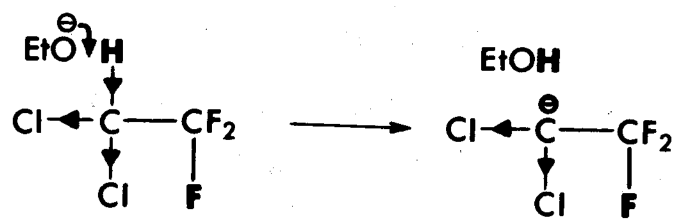
RELATIVE CARBONIUM ION STABILITY

$$CH_3{-}CH_2Br < CH_3{-}CH\mathbf{Me}Br < CH_3{-}C\mathbf{Me_2}Br$$

Increasing E1 elimination →

21

RELATIVE ELIMINATION BY E1 PATHWAY



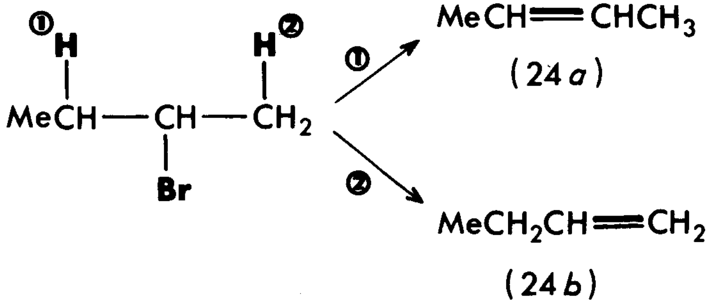
22

ACIDITY OF H AND CARBANION STABILISATION IN ElcB PATHWAY

$MeCH_2CH(Br)CH_3$

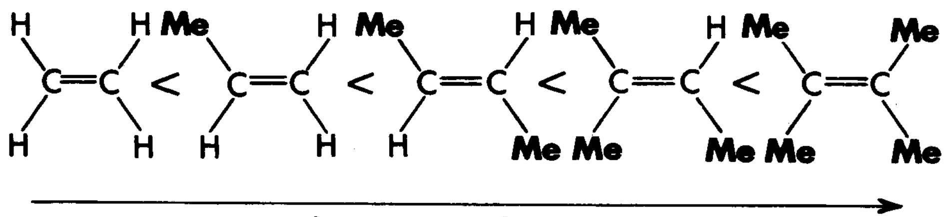
(23)

ALTERNATIVE ELIMINATIONS FROM A BROMOALKANE ?



(24)

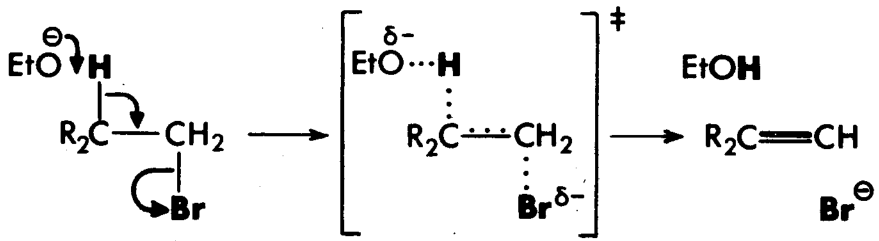
ALTERNATIVE ELIMINATIONS FROM A BROMOALKANE



Increasing stability

(25)

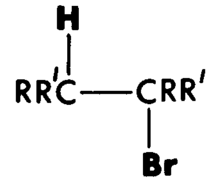
RELATIVE ALKENE STABILITY



Transition state

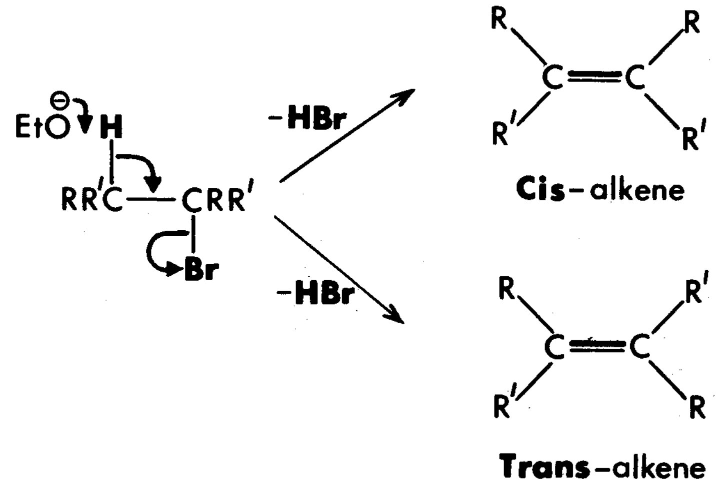
(26)

E2 PATHWAY



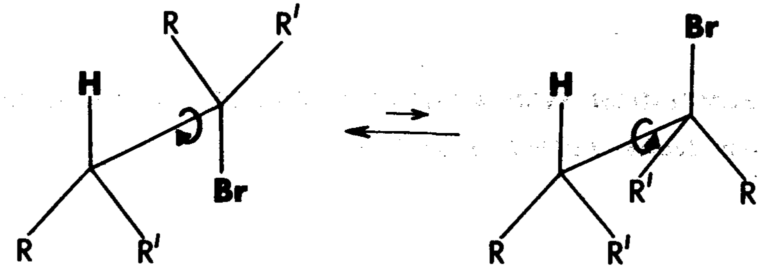
(27)

ALTERNATIVE ELIMINATION PRODUCTS FROM A BROMOALKANE ?



(28)

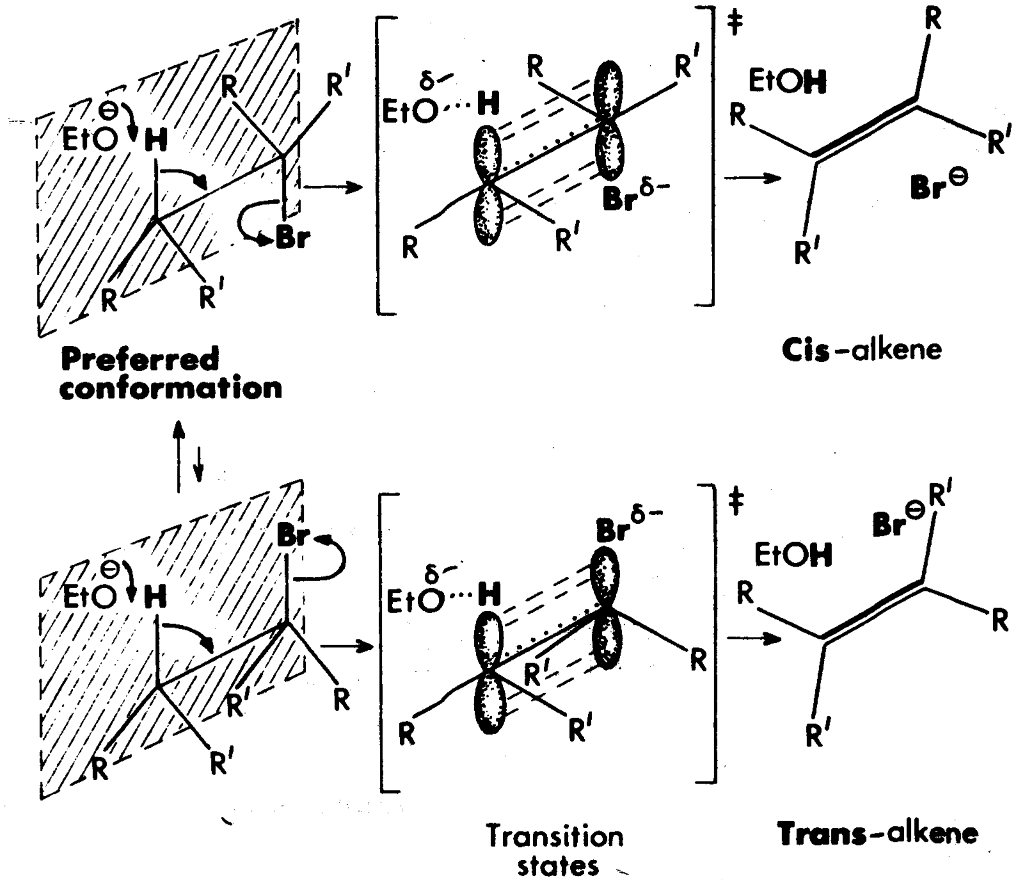
CIS- AND TRANS-ALKENES FROM E2 ELIMINATION



(29a) (29b)

(29)

ALTERNATIVE CONFORMATIONS OF A BROMOALKANE



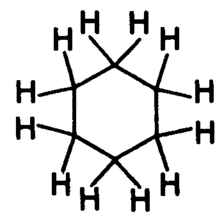
(Note overlap of the developing p orbitals forming partial double bond)

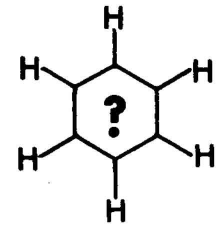
E2 ELIMINATION FROM ALTERNATIVE CONFORMATIONS TO YIELD Cis- OR Trans-ALKENE, RESPECTIVELY

Side B

AROMATIC SUBSTITUTION

AROMATIC SUBSTITUTION





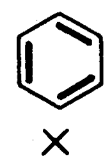
Cyclohexane

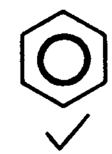
C_6H_{12}

Benzene

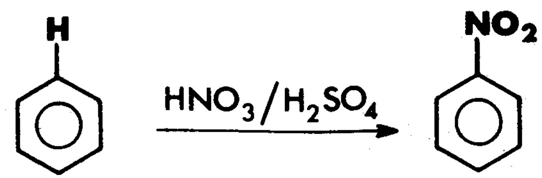
C_6H_6

(1) CYCLOHEXANE v. BENZENE

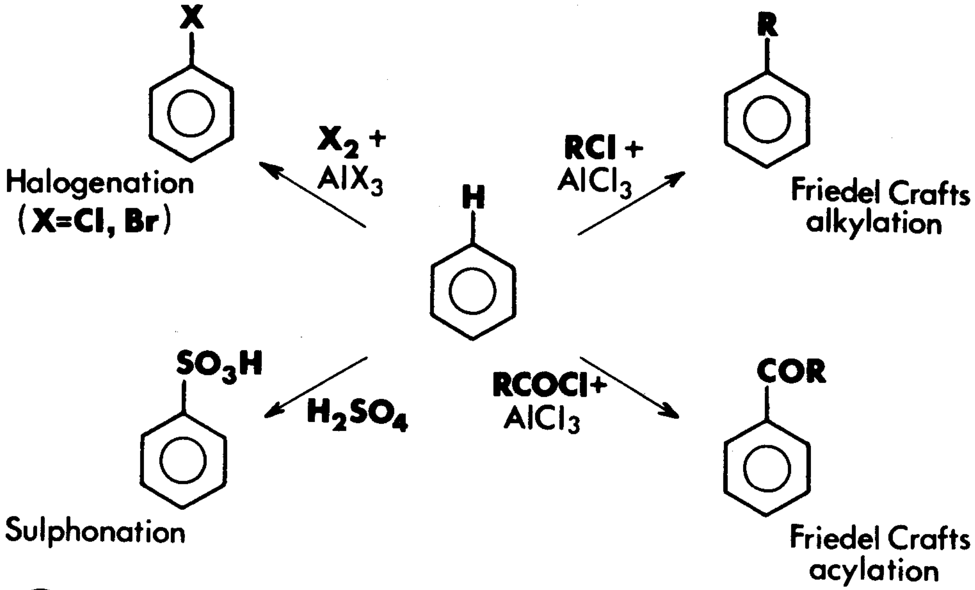




(2) REPRESENTATIONS OF BENZENE



(3) NITRATION OF BENZENE

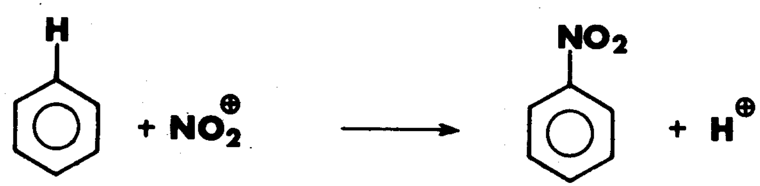


④ OTHER AROMATIC SUBSTITUTION REACTIONS

$$H\ddot{O}-NO_2 \overset{H_2SO_4}{\rightleftharpoons} H\overset{H}{\underset{\oplus}{O}}-NO_2 \overset{H_2SO_4}{\rightleftharpoons} H_3O^{\oplus} + NO_2^{\oplus}$$

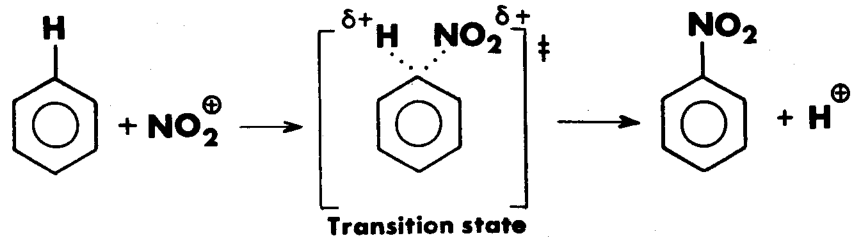
i.e. $HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^{\oplus} + H_3O^{\oplus} + 2HSO_4^{\ominus}$

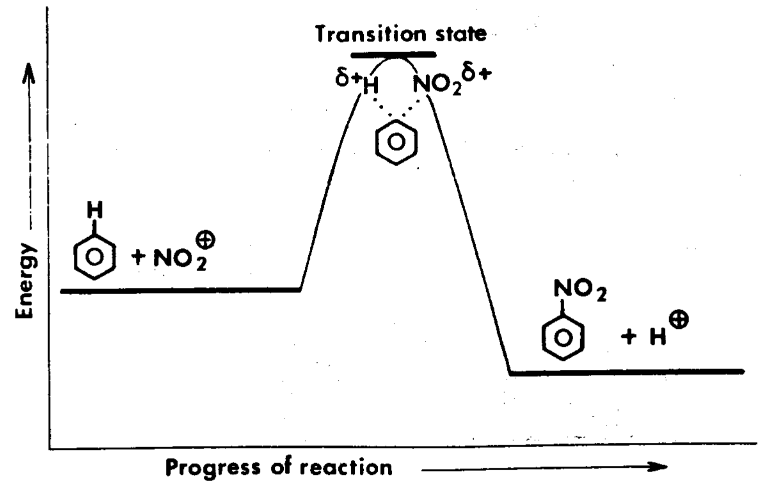
⑤ $NO_2^{\oplus}$ FROM NITRATING MIXTURE



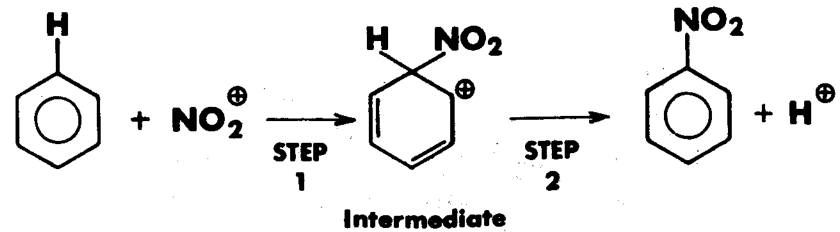
⑥ NITRATION OF BENZENE BY $NO_2^{\oplus}$

⑦ GENERALISED RATE LAW FOR NITRATION OF BENZENE

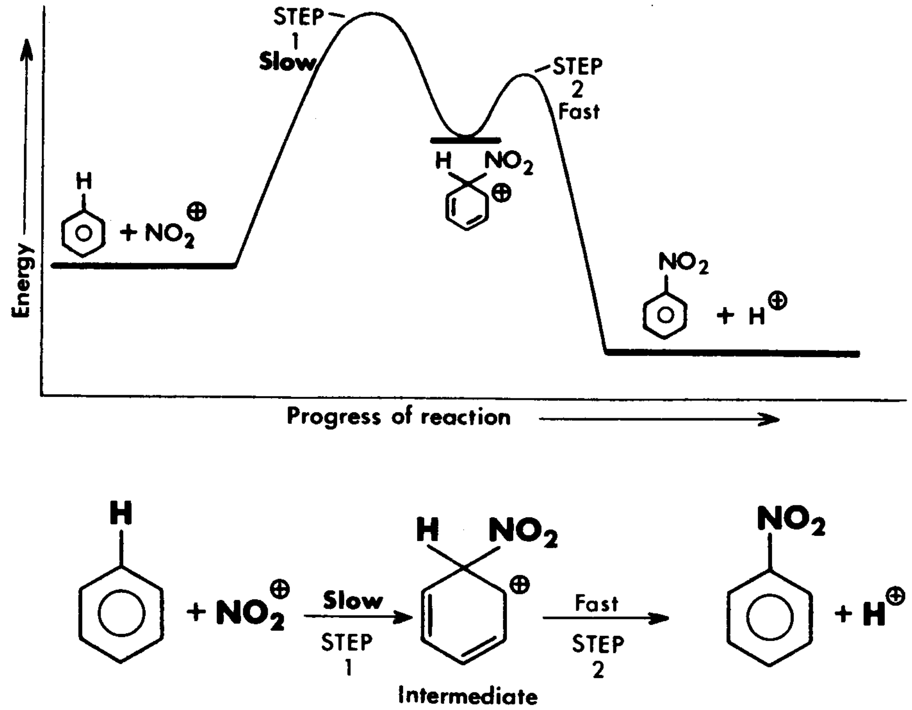




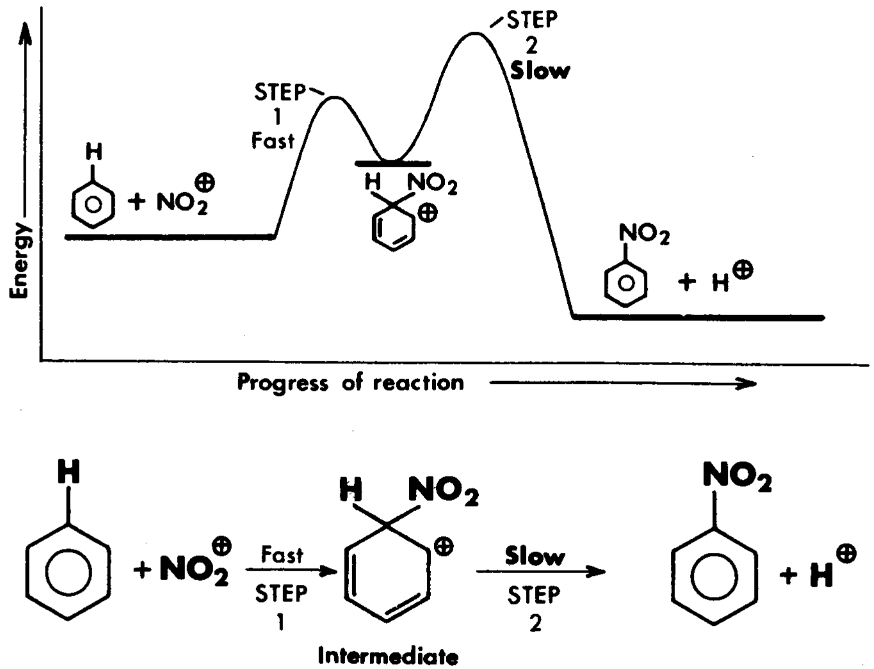
⑧ NITRATION: ONE-STEP PATHWAY AND ENERGY PROFILE



⑨ NITRATION: TWO-STEP PATHWAY

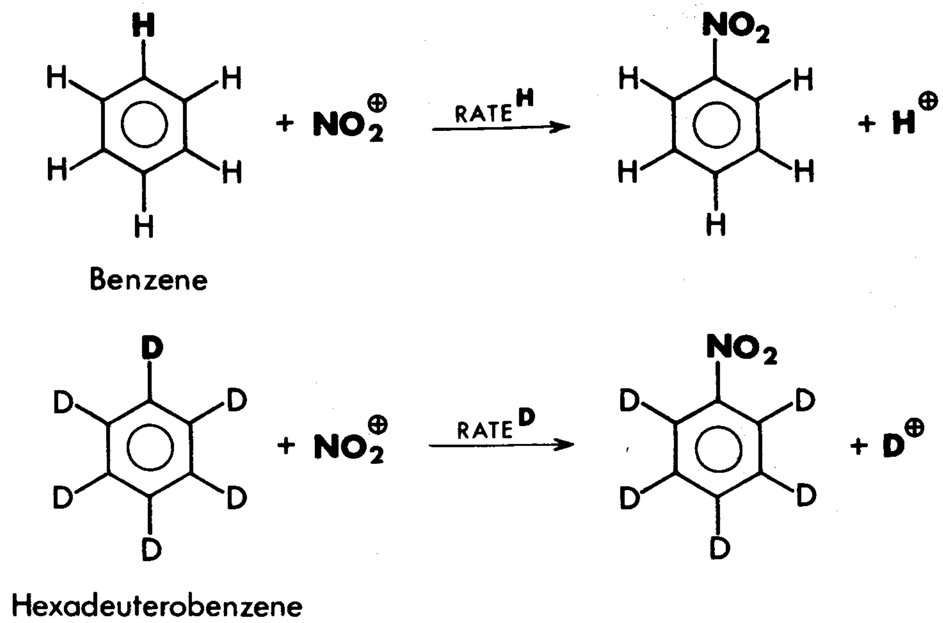


NITRATION: TWO-STEP PATHWAY (*a*) – **STEP 1 SLOW**

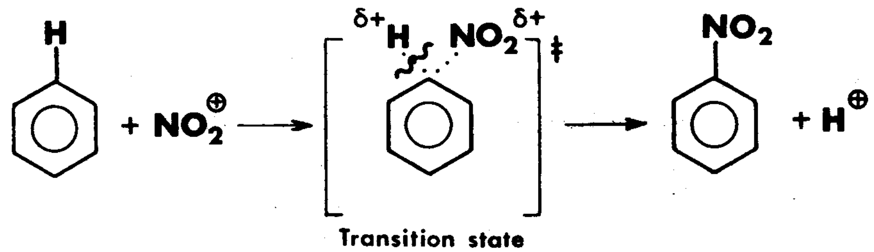


(10)

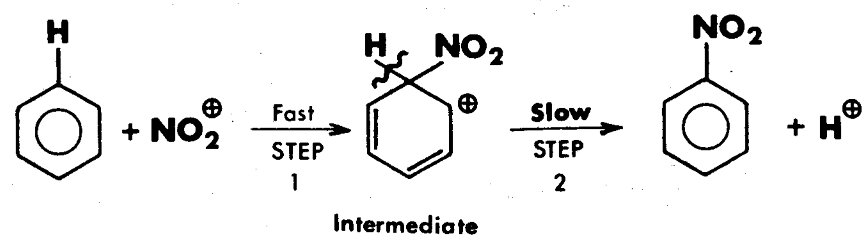
NITRATION: TWO-STEP PATHWAY (*b*) – **STEP 2 SLOW**



(11) NITRATION OF BENZENE AND HEXADEUTEROBENZENE

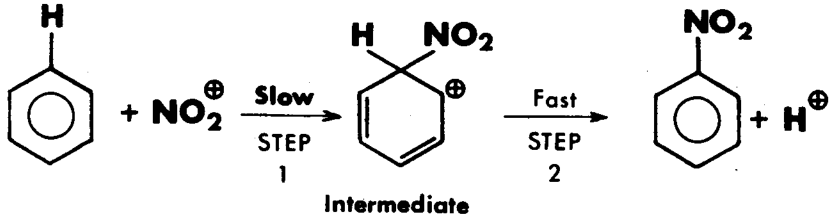


NITRATION: ONE-STEP PATHWAY



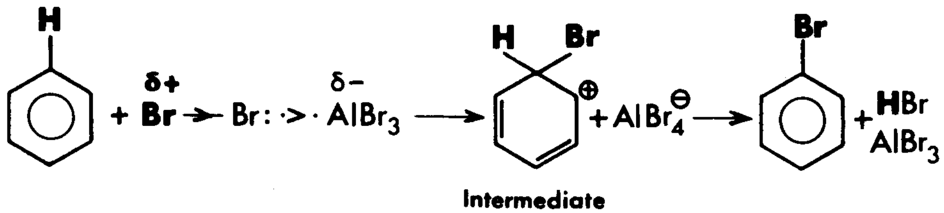
(12)

NITRATION: TWO-STEP PATHWAY (*b*)



(13)

NITRATION: TWO-STEP PATHWAY (a)

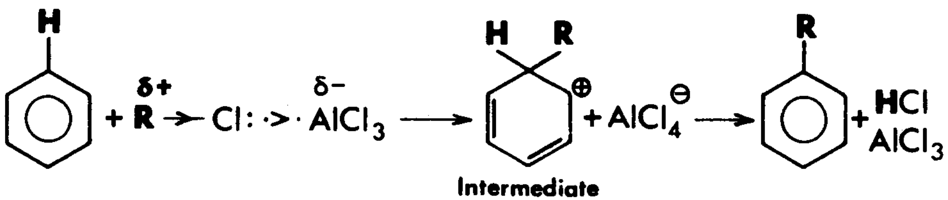


(14)

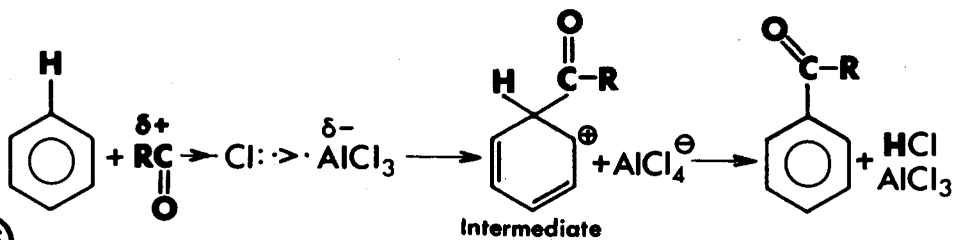
BROMINATION

(15)

POLARISATION IN ALKYL AND ACYL HALIDES

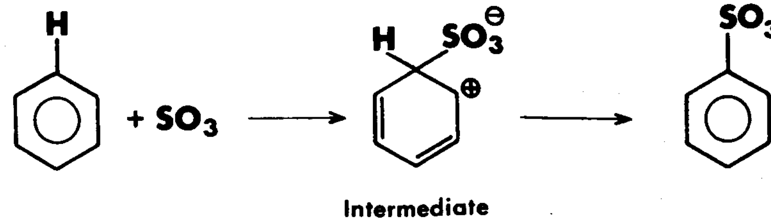


FREIDEL CRAFTS: ALKYLATION



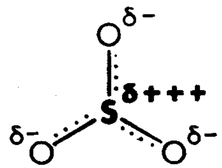
(16)

FRIEDEL CRAFTS: ACYLATION



(17)

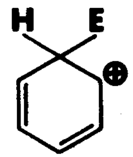
SULPHONATION



$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$$

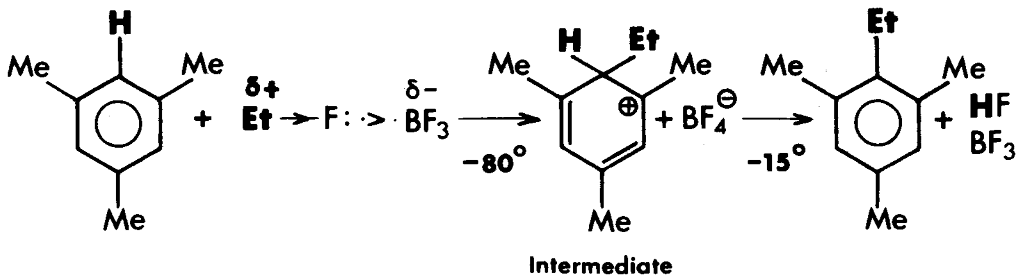
(18)

SO_3 AS ELECTROPHILE; AND ITS FORMATION

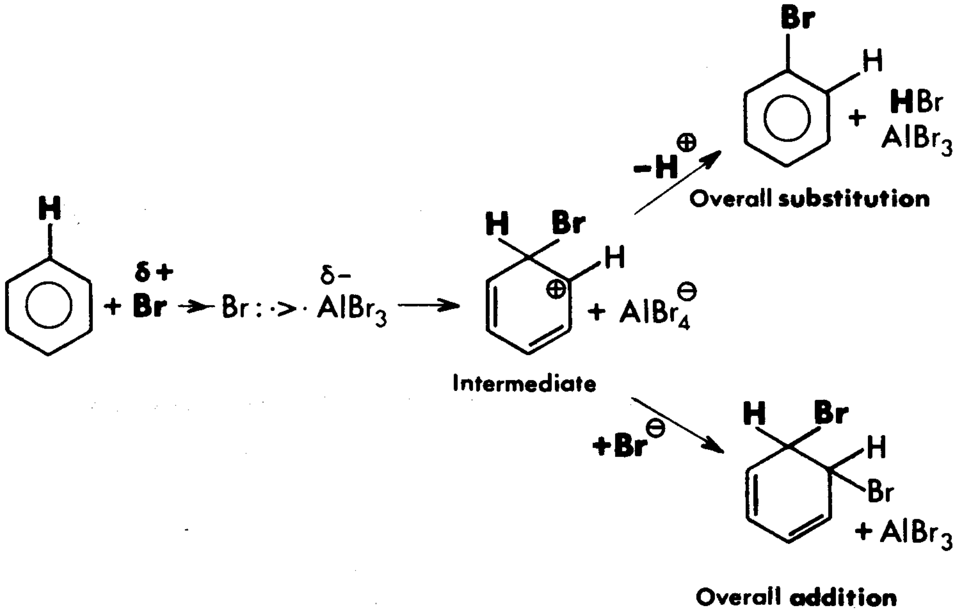


GENERALISED FORM OF INTERMEDIATE

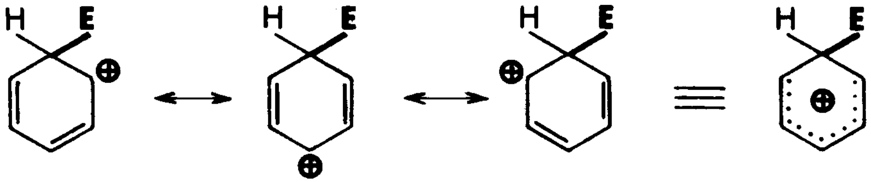
(19)



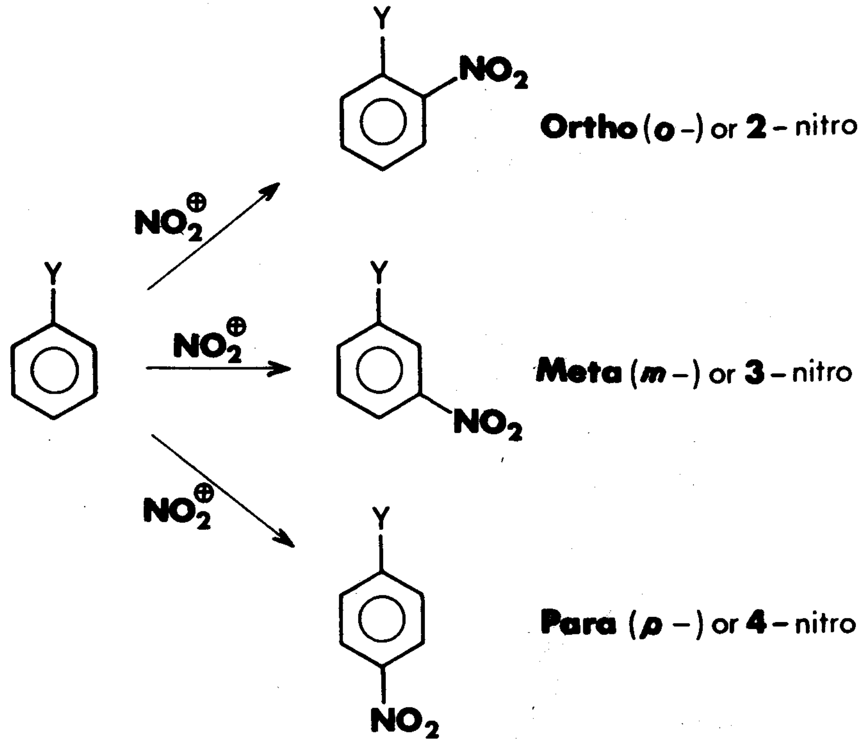
(20) ETHYLATION OF 1,3,5 – TRIMETHYLBENZENE



(21) BROMINATION : SUBSTITUTION *v.* ADDITION



(22) STABILISATION OF INTERMEDIATES: DELOCALISATION

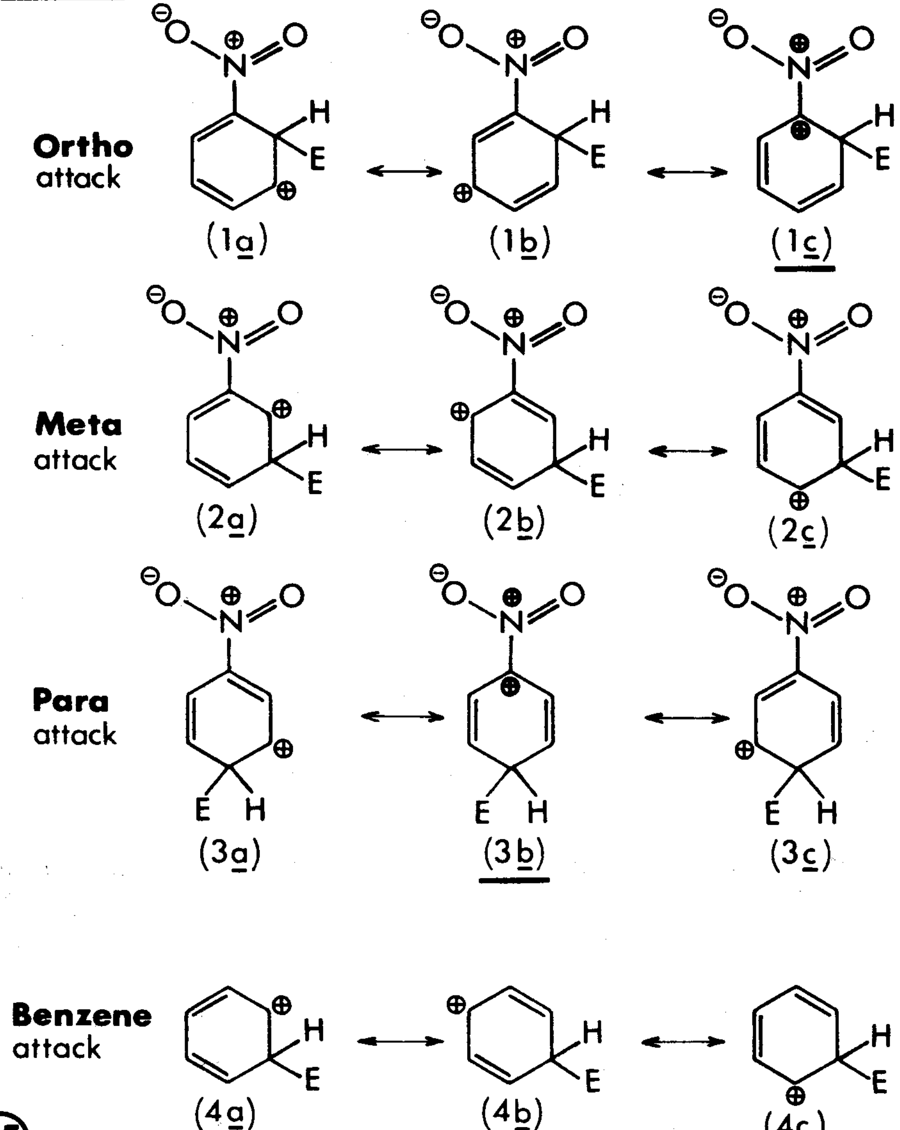


(23) NITRATION OF C_6H_5Y

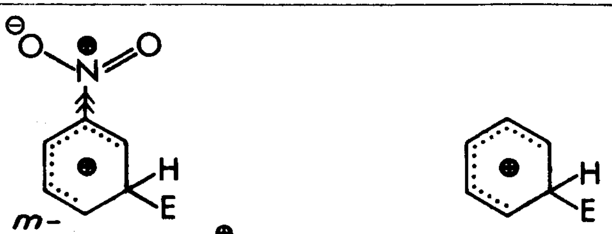
m – Directing groups		*o-/p*–Directing groups	
NO_2	(–)	OH	(+)
SO_3H	(–)	OMe	(+)
CO_2H	(–)	OCOMe	(+)
CO_2Et	(–)	NH_2	(+)
$CONH_2$	(–)	NMe_2	(+)
CN	(–)	NHCOMe	(+)
CHO	(–)	Me	(+)
COMe	(–)		

(24) LIST OF *m* – AND *o-/p* – DIRECTING GROUPS

Y = NO_2

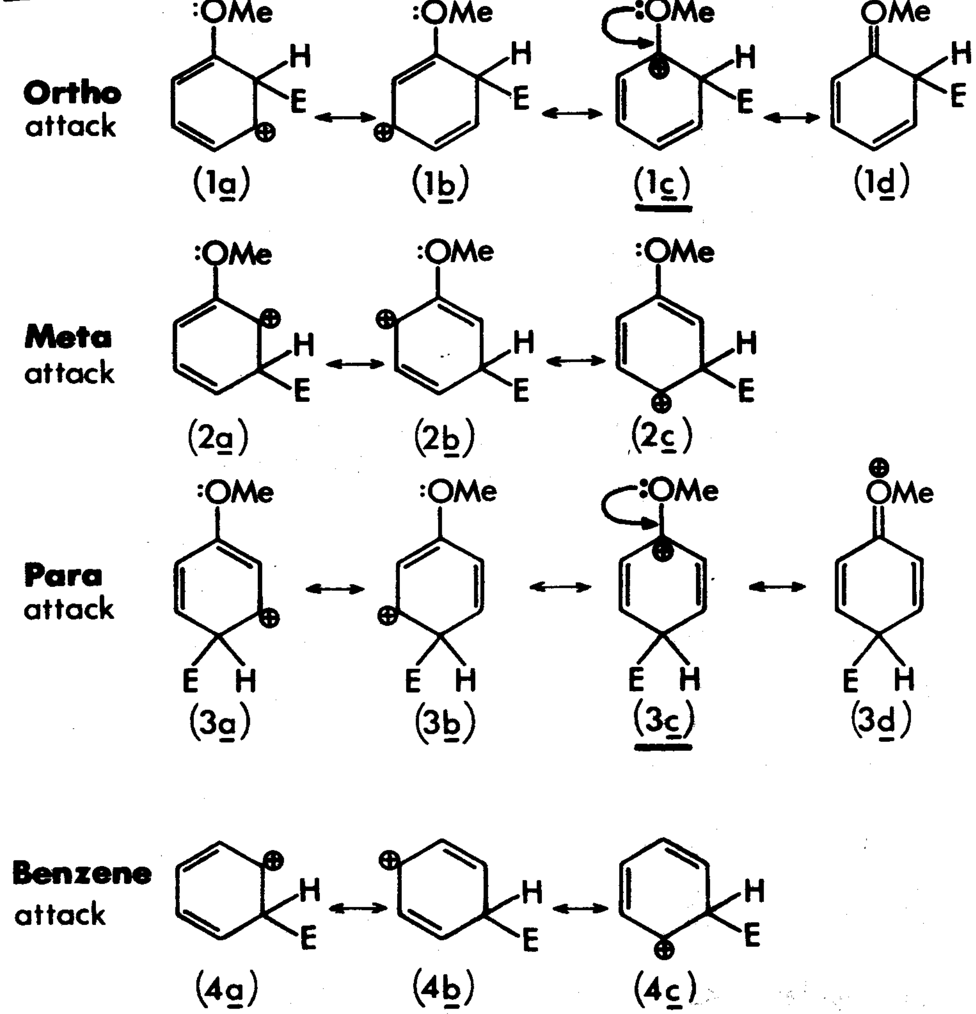


(25) ATTACK OF $E^{\oplus}$ ON C_6H_5Y ($Y = NO_2$) AND ON C_6H_6

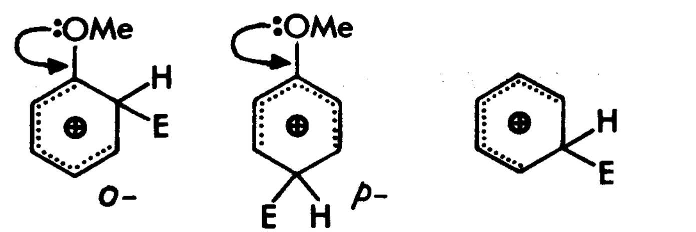


(26) ATTACK OF $E^{\oplus}$ ON $C_6H_5NO_2$ (m-) AND ON C_6H_6

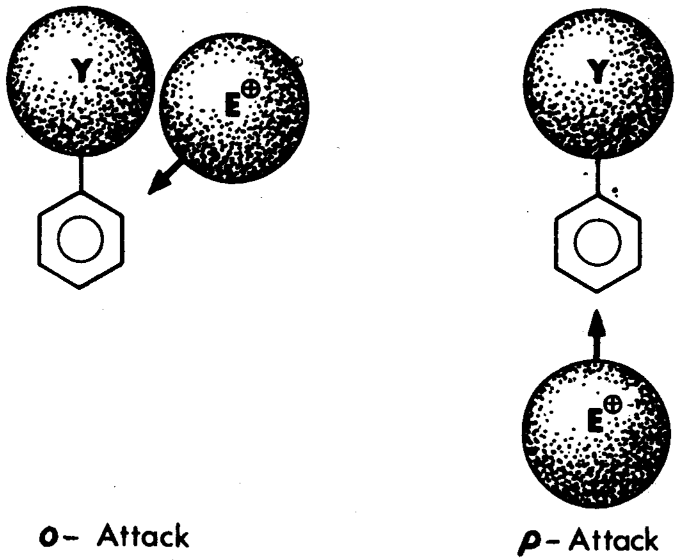
Y = OMe



(27) ATTACK OF $E^{\oplus}$ ON C_6H_5Y (Y = OMe) AND ON C_6H_6



(28) ATTACK OF $E^{\oplus}$ ON C_6H_5OMe (o- and p-) AND ON C_6H_6



(29) STERIC EFFECT IN ATTACK ON *o*- AND *p*- POSITIONS

Y (↓ Increase in size of Y)	% *o*-	% *p*-
CH_3	58	37
CH_2**Me**	45	49
CH**Me**$_2$	30	62
C**Me**$_3$	16	73

E (↓ Increase in size of E)	% *o*-	% *p*-
Chlorination	39	55
Nitration	30	70
Bromination	11	87
Sulphonation	1	99

(30) STERIC EFFECTS AND *o*-/*p*- PROPORTIONS