SOME REACTION PATHWAYS OF DOUBLE BONDS

PETER SYKES

Peter Sykes was born in 1923 in Manchester and studied at the Universities of Manchester (BSc, MSc) and Cambridge (PhD). He is at present Fellow and Director of Studies, Christ's College, Cambridge and is University Lecturer in Organic Chemistry.

His principal research interests are in the field of organic sulphur chemistry and he has a general interest in organic reaction mechanisms. He is the author of two highly successful books: 'A Guidebook to Mechanism in Organic Chemistry' (Longman, 4th edition, 1975) and 'The Search for Organic Reaction Pathways' (Longman, 1972). The first has been translated into seven, and the second into six, other languages.

He has visited most European countries, North and South America, South Africa and the East lecturing and advising on the teaching of chemistry at secondary and tertiary levels. He has been a member of the EUPAR Commission on the Teaching of Chemistry, of the Nuffield Joint Committee for A-level Chemistry, Physics and Physical Science, and of the British Committee on Chemical Education. He is currently a member of the Nuffield Continuing Committee, is Chairman of the Chemistry Subject Committee and of the GCE Awarding Committee of the Cambridge Local Examinations Syndicate, and is on the editorial board of the 'School Science Review'. He has contributed to a great many educational programmes on BBC radio.

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Please read this carefully before you start.

USING THE CHEMISTRY CASSETTE

This Chemistry Cassette learning programme has two components, the audio-cassette and this book. The two are designed to be used together and you should always have the book with you as you work through the cassette. As you listen to the cassette you will, from time to time, be asked to switch off the player and answer some questions. You should, therefore, have pen and paper ready before you start.

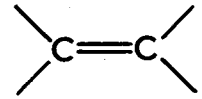
The material in the book consists of reaction schemes, figures and equations, each of which is clearly numbered. Dr Sykes refers to these by section numbers and you should locate the relevant section, and study its contents, whenever it is referred to. Because some of the questions asked are answered in subsequent reaction schemes you are advised to use a piece of card or paper to cover any schemes beyond the last one mentioned.

Tape recorded material has the important feature of being self-pacing, which means that you can work through it at a pace related to your own needs and understanding. You can switch off the player whenever you want to think, to write some notes or to answer a question. You can use the rewind control to revise or to repeat material that you may not have fully understood on a first hearing. To gain the greatest benefit from this programme you should make full use of these features. You should also, whenever appropriate, make notes to supplement the material contained in the book. You will thereby build up a detailed set of personal notes which will serve as an authoritative guide to the subject.

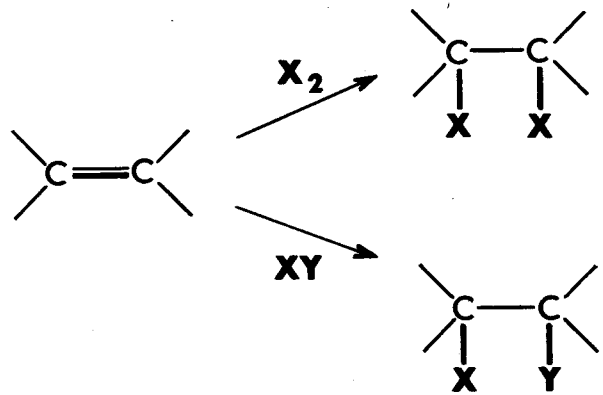
Side A

C = C

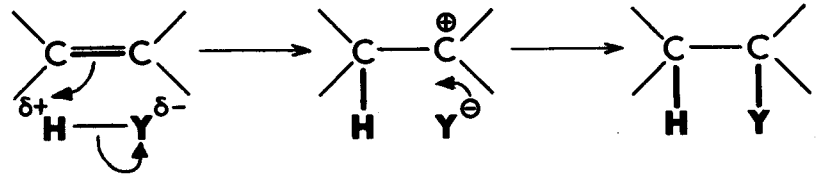
REACTIONS OF C=C



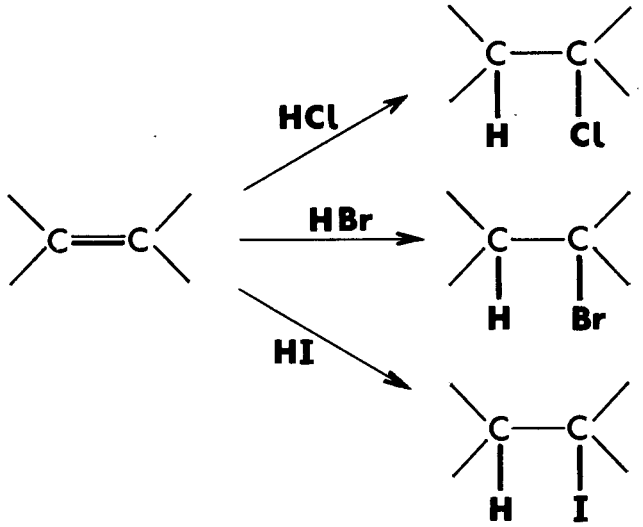
① CARBON-CARBON DOUBLE BOND : REPRESENTATION



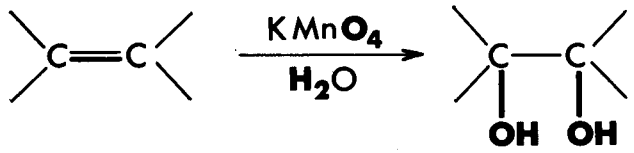
② C=C : ADDITION REACTIONS



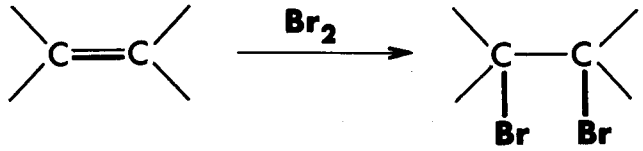
③ C=C : ELECTROPHILIC ATTACK



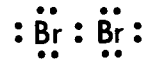
④ C=C : HCl, HBr, HI ADDITION



⑤ C=C : $KMnO_4$ REACTION

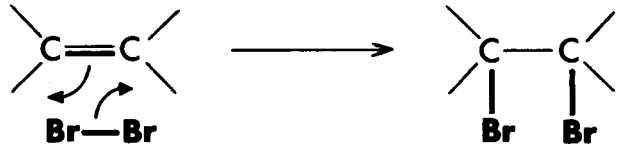


⑥ C=C : Br_2 ADDITION

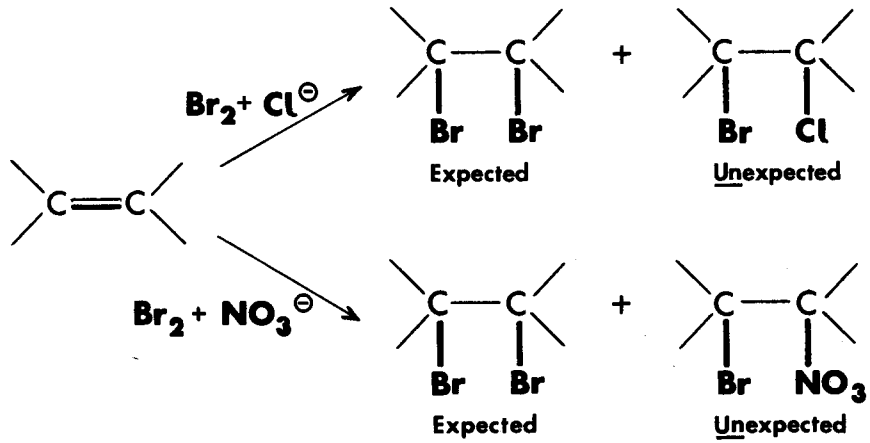


⑦ Br_2 MOLECULE : ELECTRON DISTRIBUTION

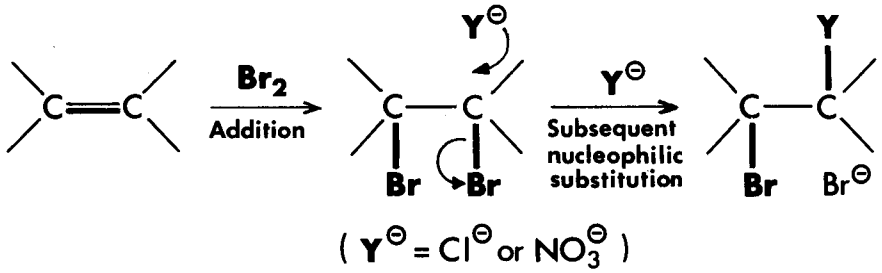
⑧ $Br_2 \longrightarrow 2\,Br^{\ominus}$: $Fe^{II} \longrightarrow Fe^{III}$ OXIDATION



⑨ Br_2 ADDITION : ONE-STEP PATHWAY

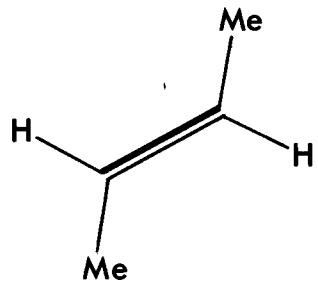


⑩ Br_2 ADDITION : UNEXPECTED PRODUCTS IN PRESENCE OF $Y^{\ominus}$

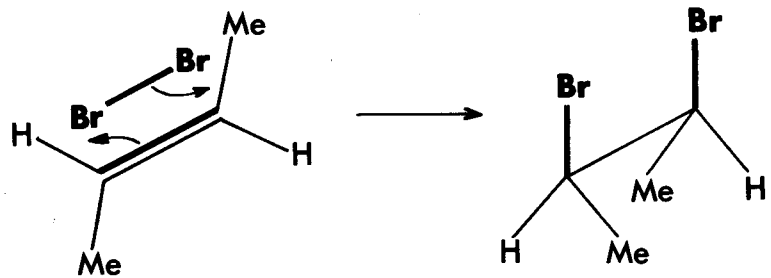


($Y^{\ominus} = Cl^{\ominus}$ or $NO_3^{\ominus}$)

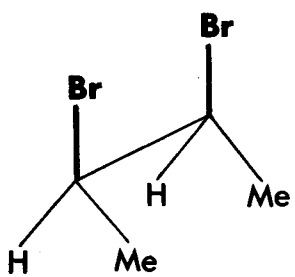
⑪ Br_2 ADDITION : SUBSEQUENT ATTACK BY $Y^{\ominus}$ ON FIRST FORMED DIBROMIDE ?



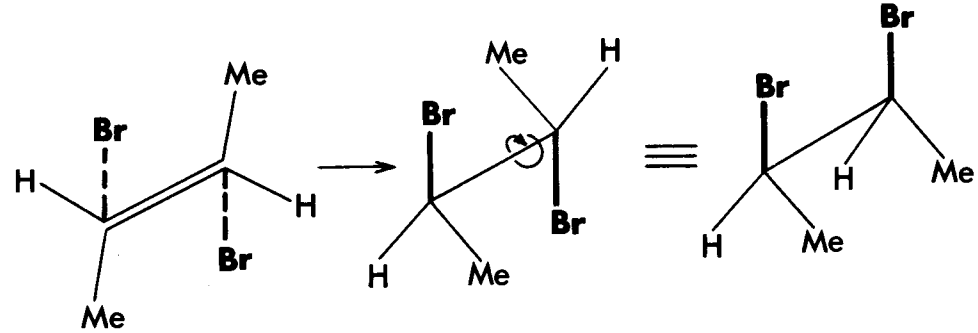
⑫ *Trans* BUT-2-ENE



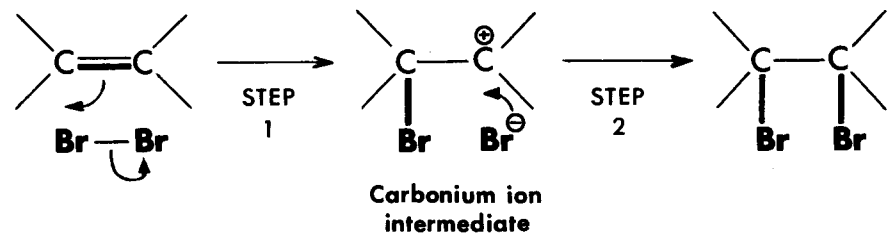
⑬ *Trans* BUT-2-ENE / Br_2 : PRODUCT OF "SAME SIDE" ADDITION



⑭ *Trans* BUT-2-ENE / Br_2 : PRODUCT ACTUALLY OBTAINED

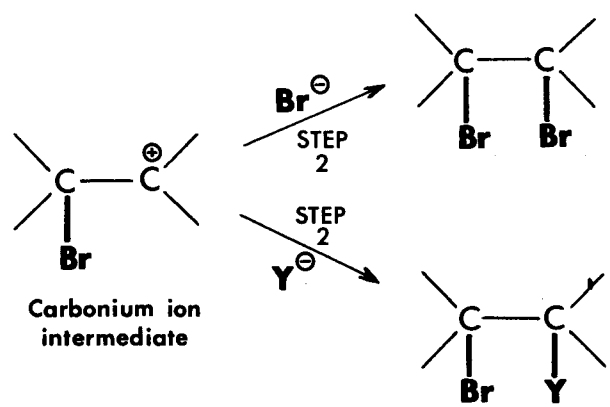


⑮ *Trans* BUT-2-ENE / Br_2 : PRODUCT OF "OPPOSITE SIDE" ADDITION



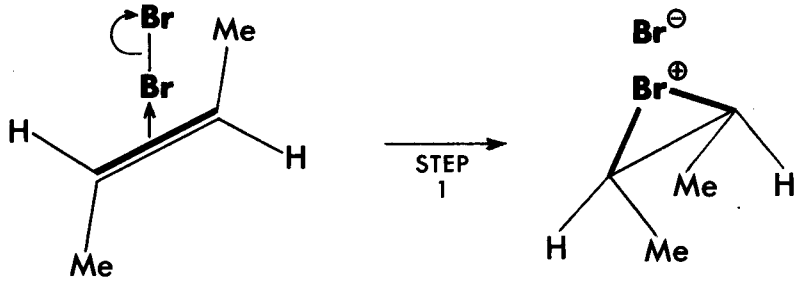
Carbonium ion intermediate

⑯ Br_2 ADDITION : TWO-STEP – CARBONIUM ION – PATHWAY



Carbonium ion intermediate

⑰ Br_2 ADDITION : PRODUCTS FROM CARBONIUM ION INTERMEDIATE



Cyclic bromonium ion intermediate

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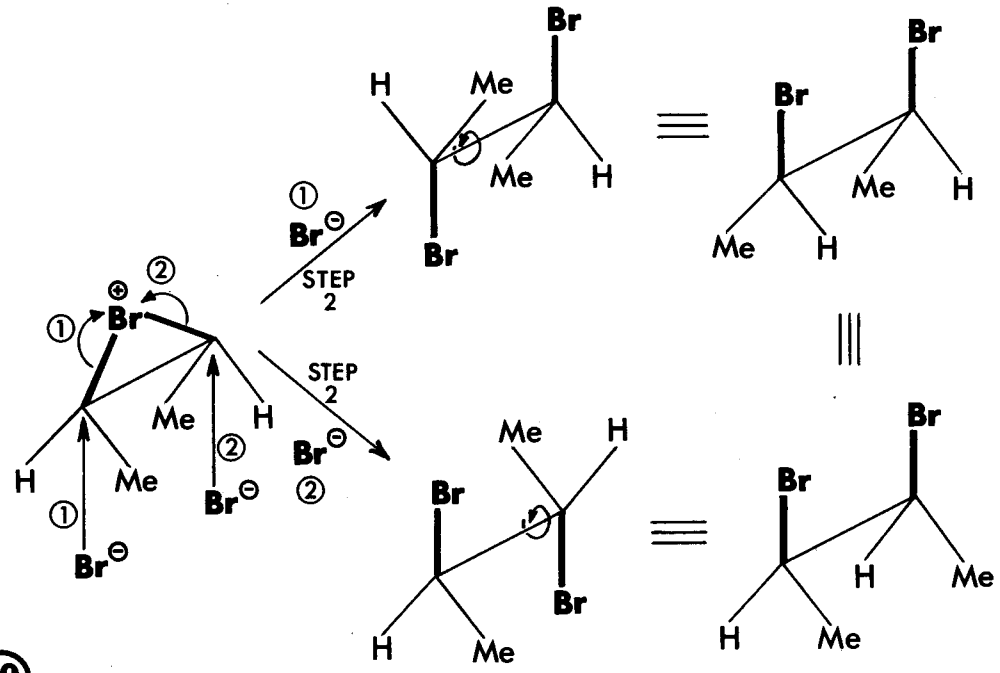
Trans BUT-2-ENE / Br_2 : BROMONIUM ION PATHWAY — STEP 1



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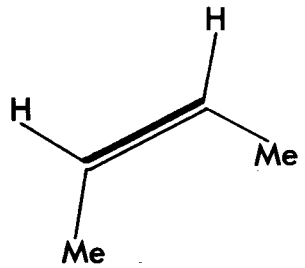
Trans BUT-2-ENE / Br_2 : BROMONIUM ION PATHWAY — STEP 2



Cis BUT-2-ENE

20

Bromonium ion

Carbonium ion

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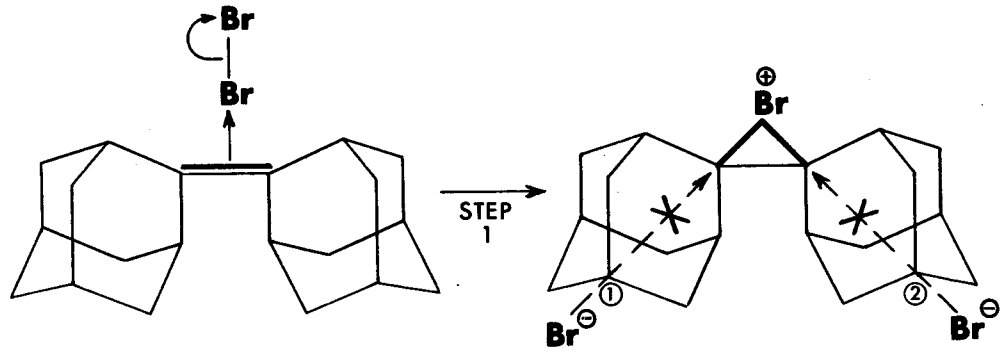
BROMONIUM / CARBONIUM IONS : INTER-RELATION



Bromonium ion

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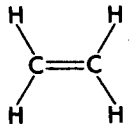
BROMONIUM ION INTERMEDIATES : ISOLATION



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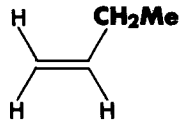
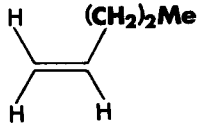
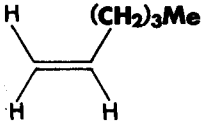


$9{\cdot}6 \times 10$



$6{\cdot}9 \times 10$



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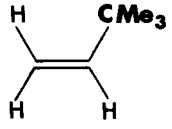
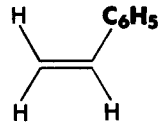
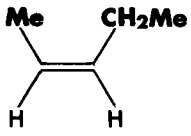


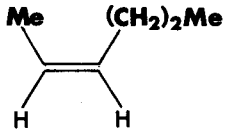
$1{\cdot}1 \times 10$



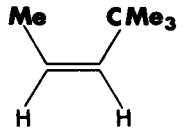
$3{\cdot}96 \times 10^3$



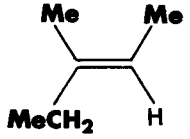
$4{\cdot}16 \times 10^3$



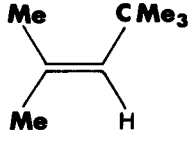
$2{\cdot}89 \times 10^3$



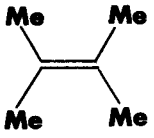
$1{\cdot}29 \times 10^3$



$1{\cdot}19 \times 10^5$

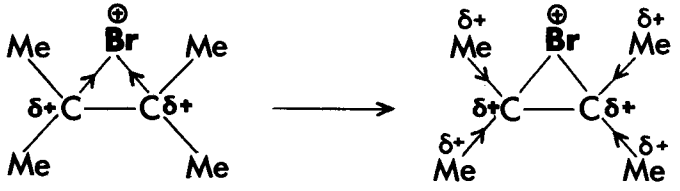


$2{\cdot}72 \times 10^4$

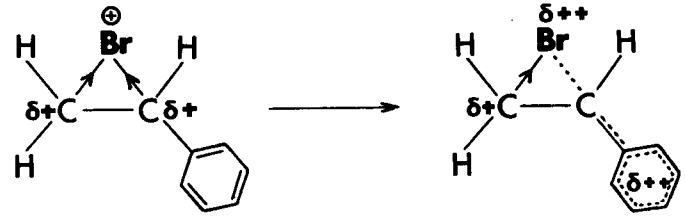


$9{\cdot}25 \times 10^5$

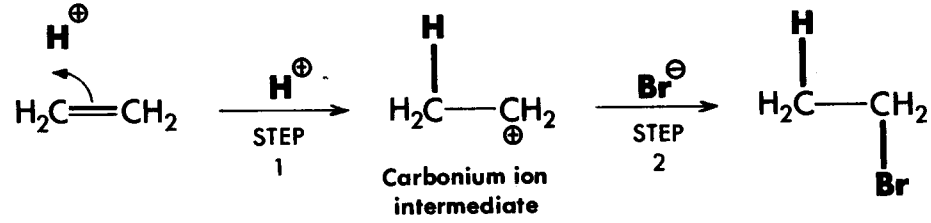
23 Br_2 ADDITION TO ALKENES : RELATIVE RATES



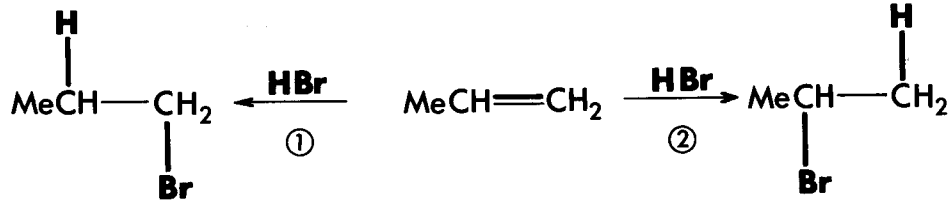
24 BROMONIUM ION INTERMEDIATES : ALKYL STABILISATION



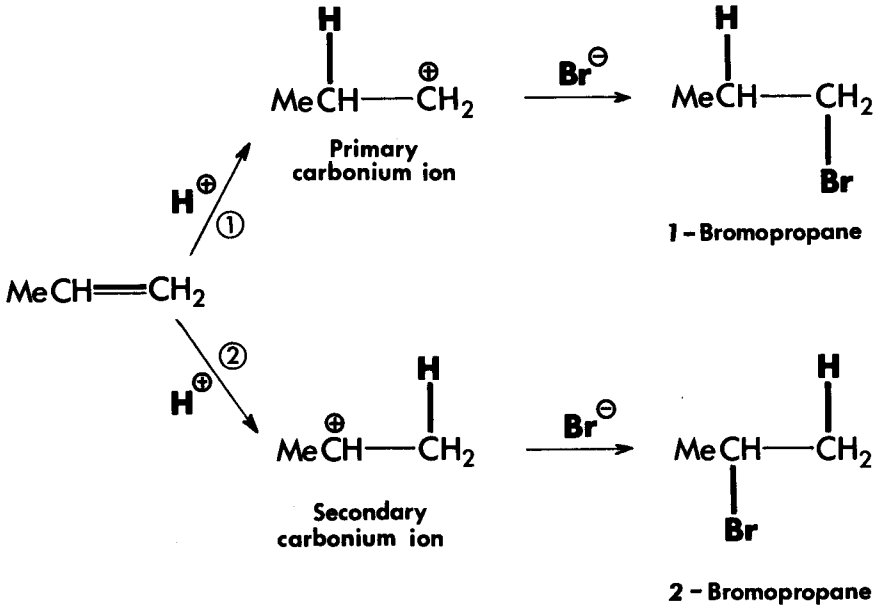
25 BROMONIUM ION INTERMEDIATES : PHENYL STABILISATION



26 HBr ADDITION : CARBONIUM ION PATHWAY



27 HBr ADDITION : ORIENTATION



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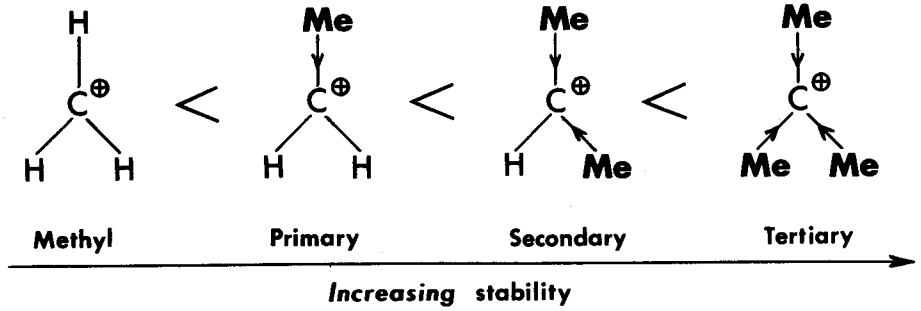
HBr ADDITION : CONTROL OF ORIENTATION



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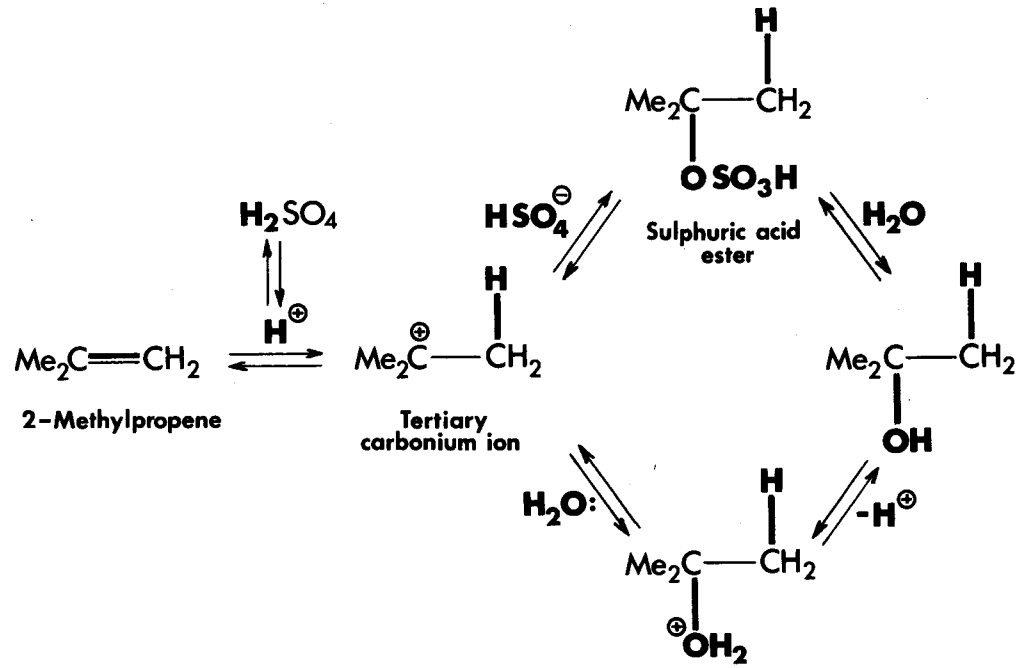
CARBONIUM IONS : RELATIVE STABILITY



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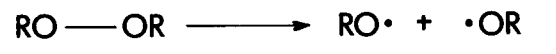
DILUTE H_2SO_4 ADDITION : NETT HYDRATION



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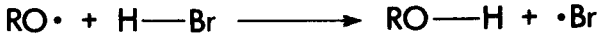
PEROXIDE CLEAVAGE



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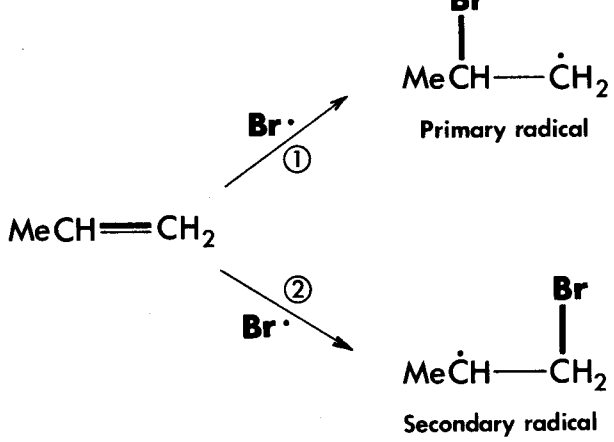
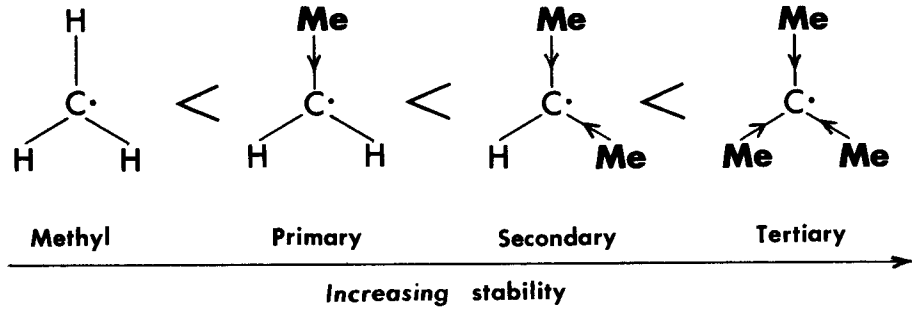
HBr : H ABSTRACTION BY RO·



33

HBr ADDITION : INITIAL ATTACK BY Br·



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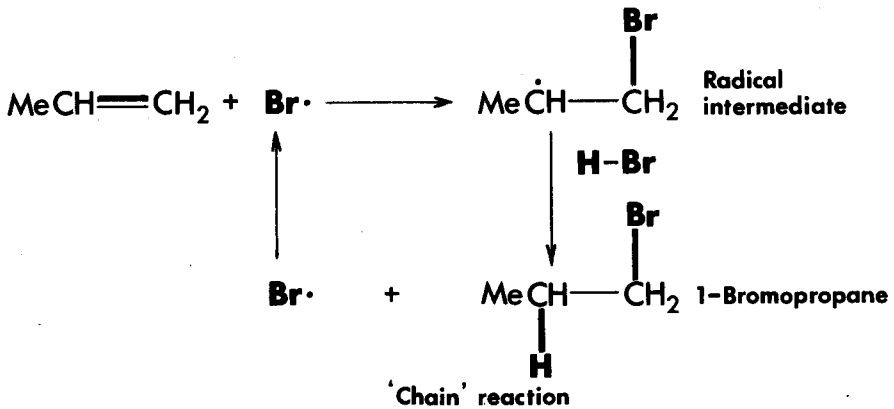
RADICALS : RELATIVE STABILITY



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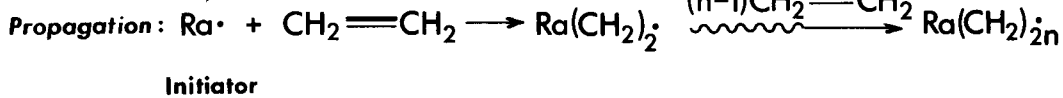
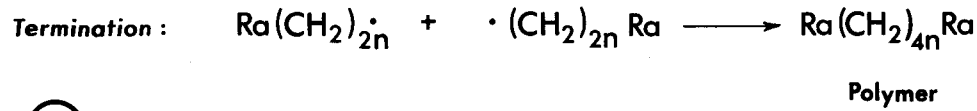
HBr ADDITION : RADICAL CHAIN PATHWAY





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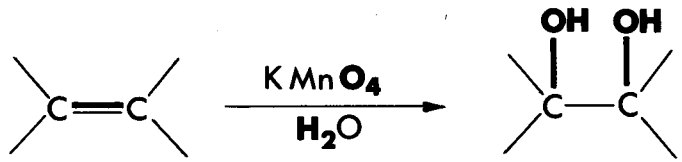
RADICAL INDUCED POLYMERISATION



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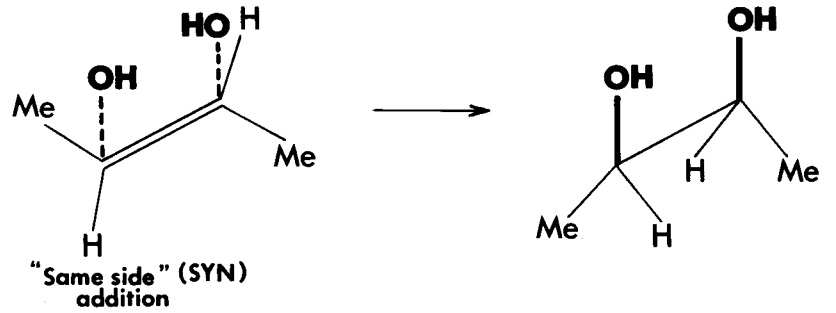
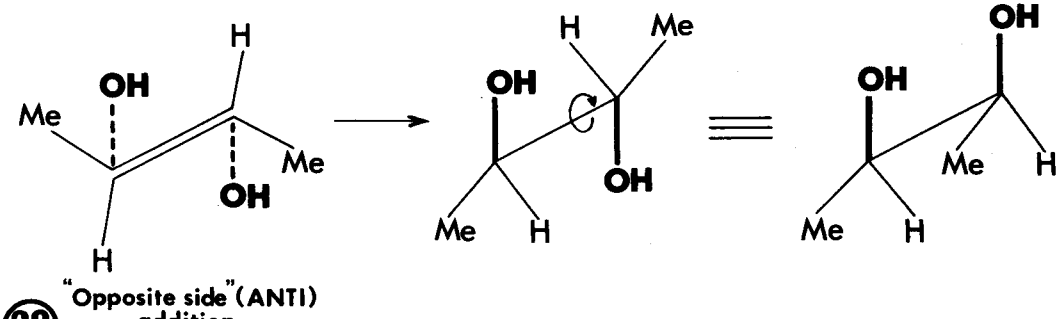
HYDROXYLATION : $KMnO_4$





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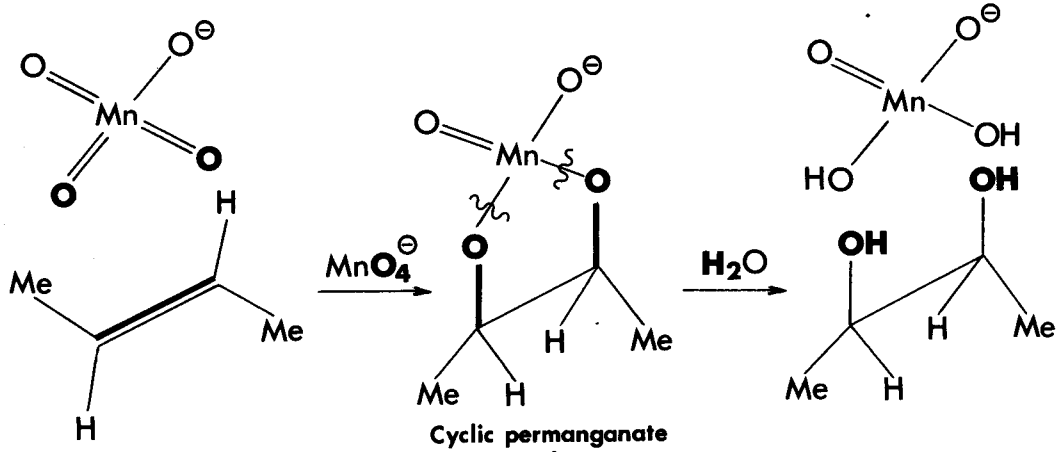
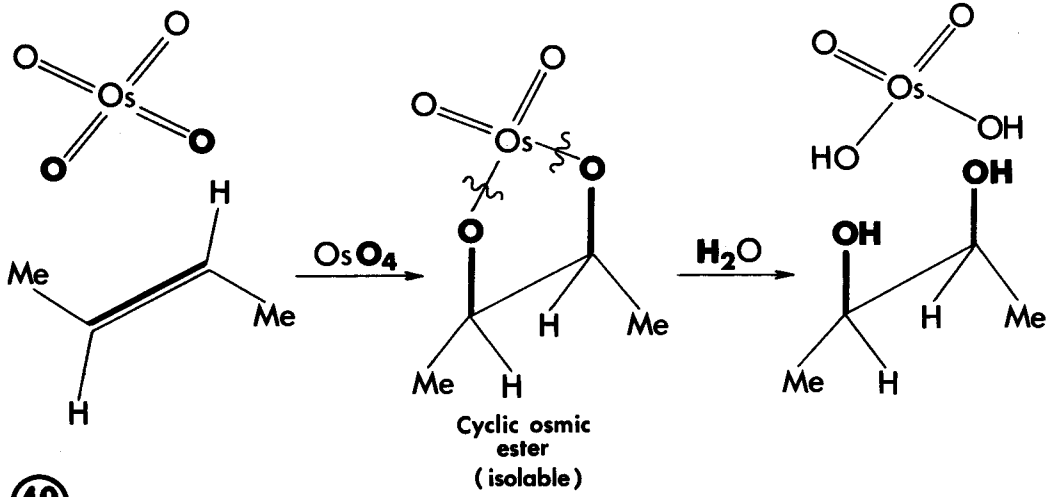
HYDROXYLATION : SYN / ANTI ADDITION



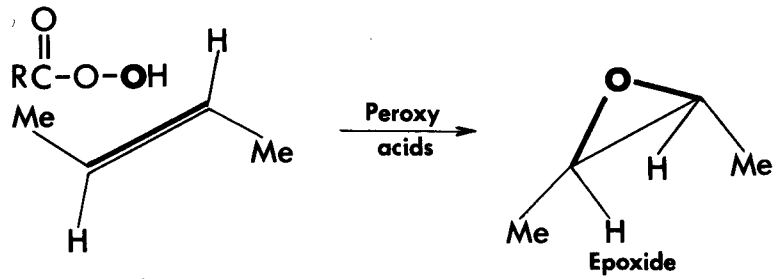
39

HYDROXYLATION : $KMnO_4$ – SYN PATHWAY



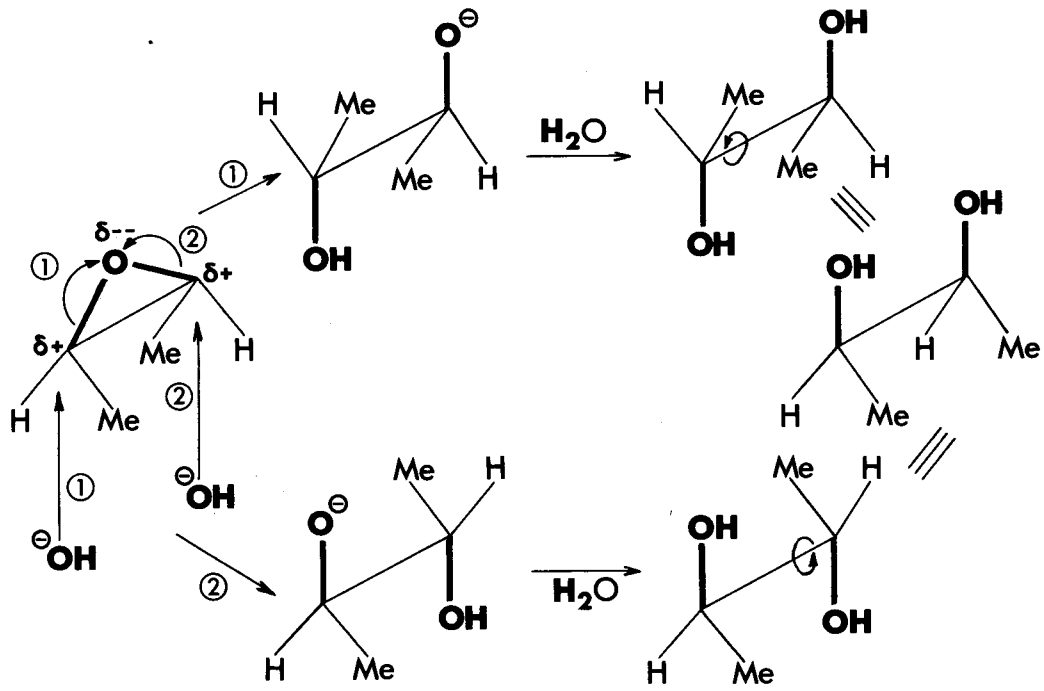
40

HYDROXYLATION : OsO_4 – SYN PATHWAY



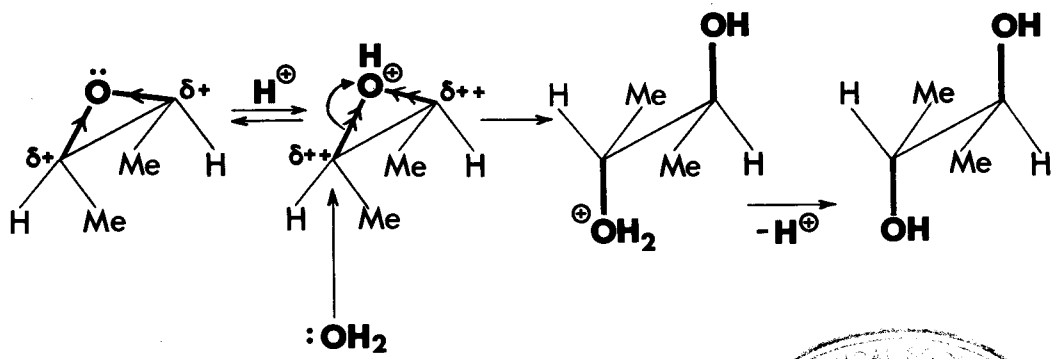
41

HYDROXYLATION : EPOXIDE FORMATION



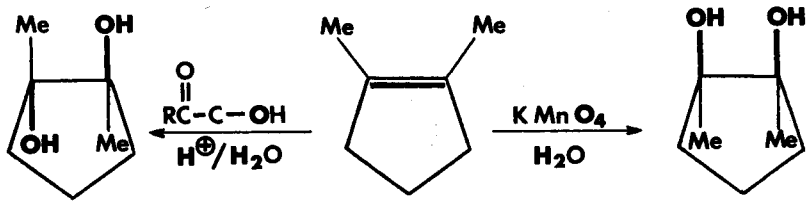
42

HYDROXYLATION : EPOXIDE HYDROLYSIS (BASE)



43

HYDROXYLATION : EPOXIDE HYDROLYSIS (ACID)

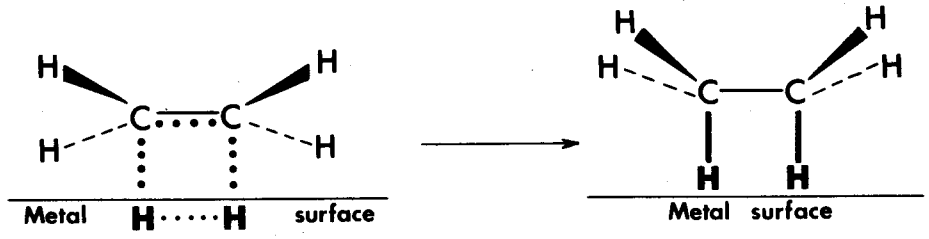


ANTI hydroxylation

SYN hydroxylation

(44)

HYDROXYLATION : STEREOSELECTIVE CONTROL



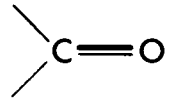
(45)

CATALYTIC HYDROGENATION : SYN ADDITION

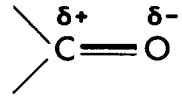
Side B

C = O

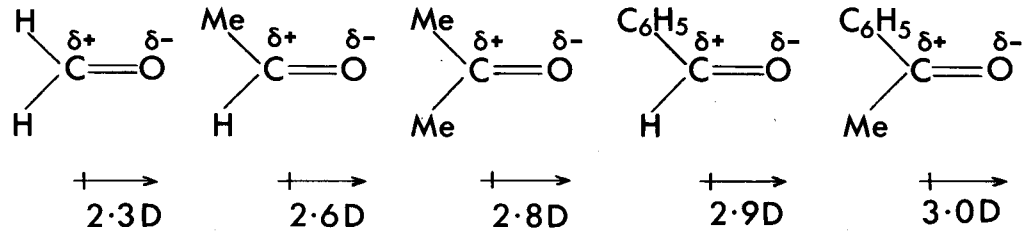
REACTIONS OF C=O



① CARBONYL GROUP: REPRESENTATION



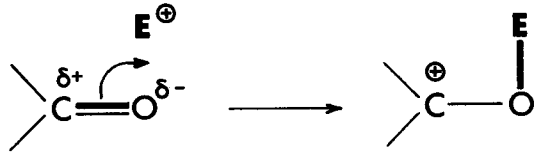
② CARBONYL GROUP: POLARITY



The crossed tail of the arrow indicates the +ve end of the dipole. The common units of dipole moment are Debyes (D): $1D = 3{\cdot}335640 \times 10^{-30}$ Curie metres

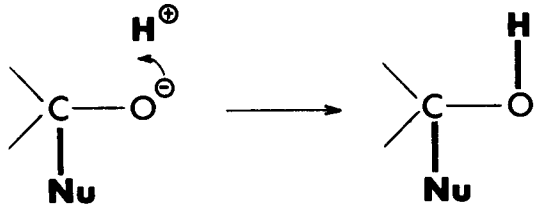
③ CARBONYL COMPOUNDS: DIPOLE MOMENTS

④ C=O: NUCLEOPHILIC ATTACK



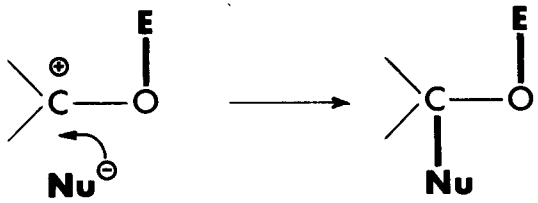
5

C=O:ELECTROPHILIC ATTACK



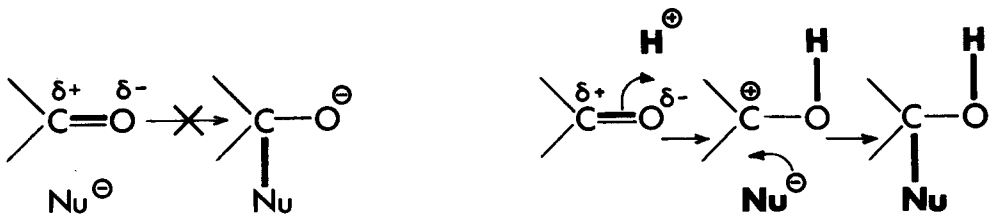
4a

NUCLEOPHILIC ATTACK:COMPLETION OF ADDITION (BY ELECTROPHILE)



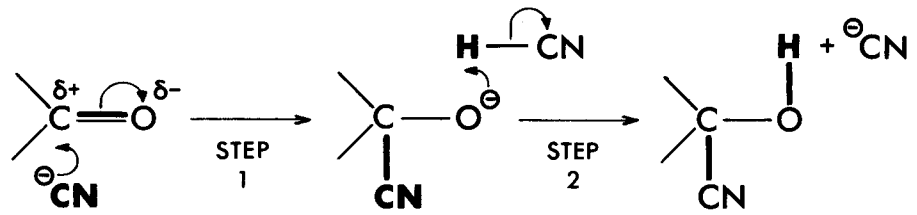
5a

ELECTROPHILIC ATTACK:COMPLETION OF ADDITION (BY NUCLEOPHILE)



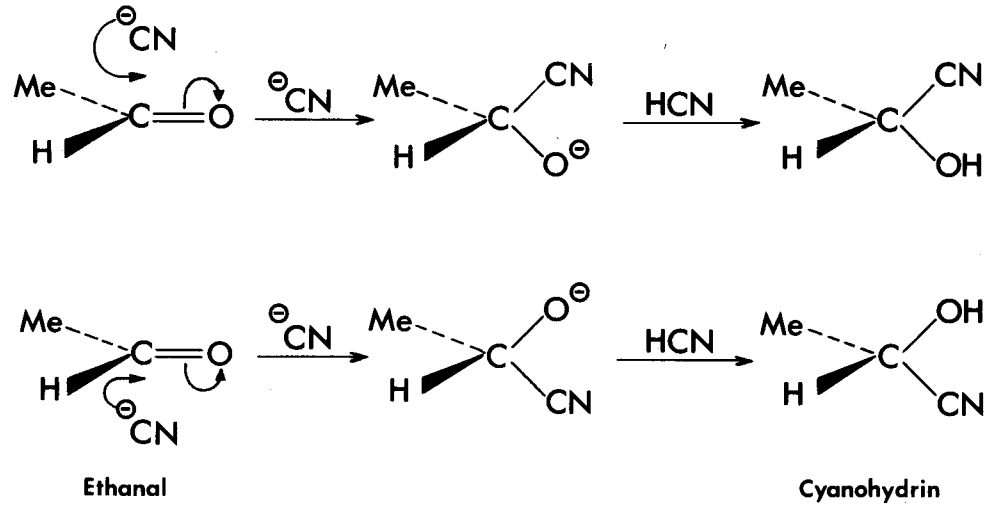
6

NUCLEOPHILIC ADDITION:ACID-CATALYSIS



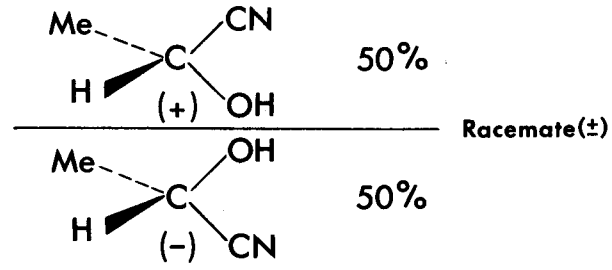
7

HCN ADDITION:CYANOHYDRIN FORMATION



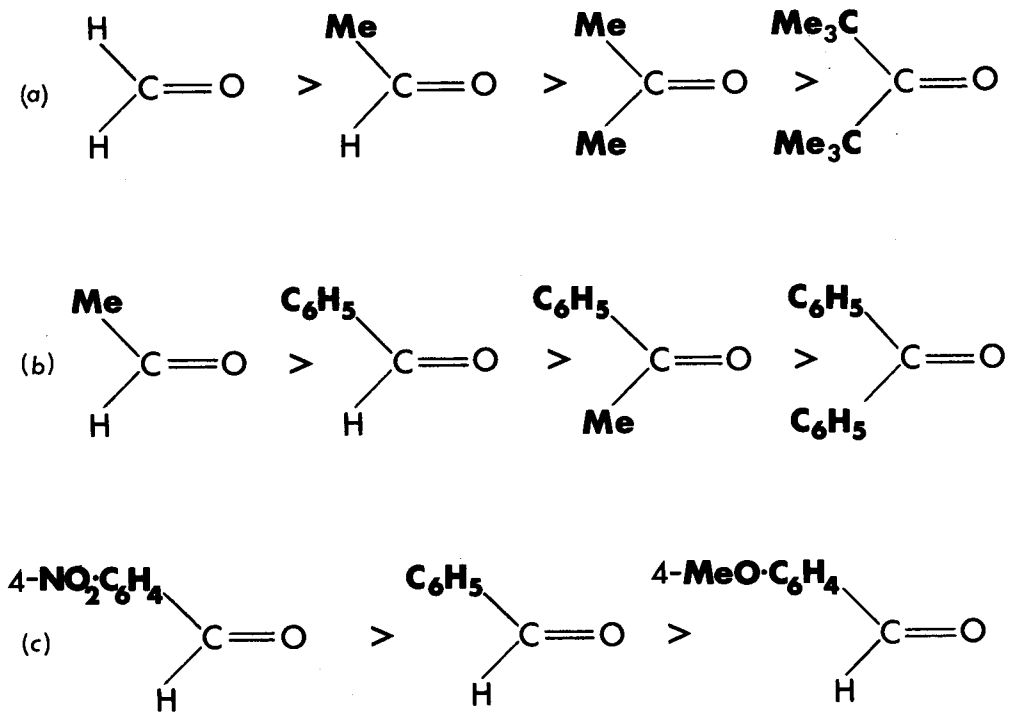
8

HCN ADDITION: $^{\ominus}$CN ATTACK FROM ABOVE AND BELOW



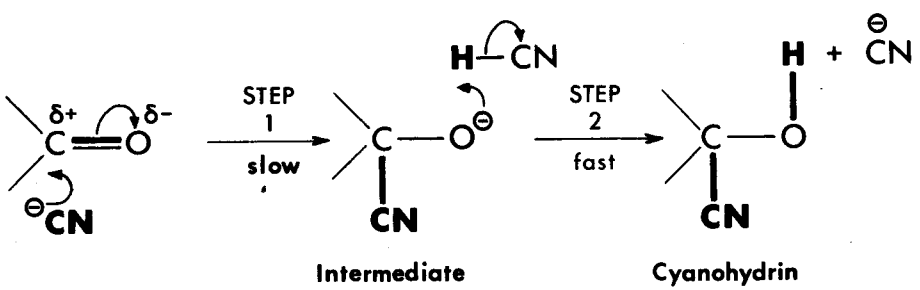
9

HCN ADDITION:FORMATION OF A RACEMATE (±)



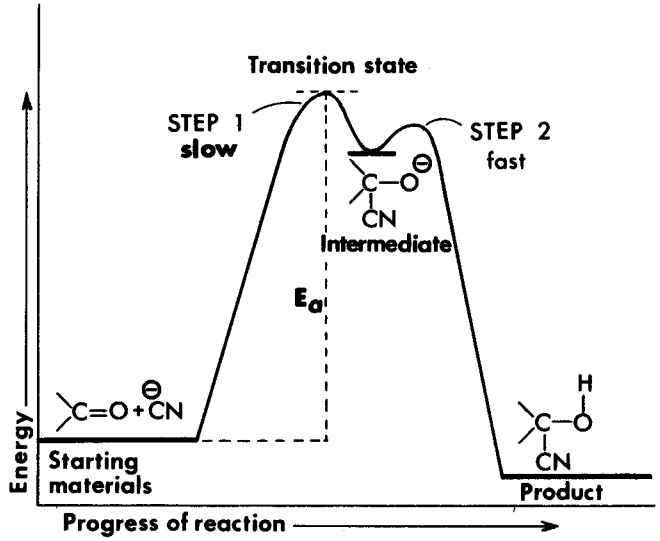
10

ADDITION TO C=O: RELATIVE RATES



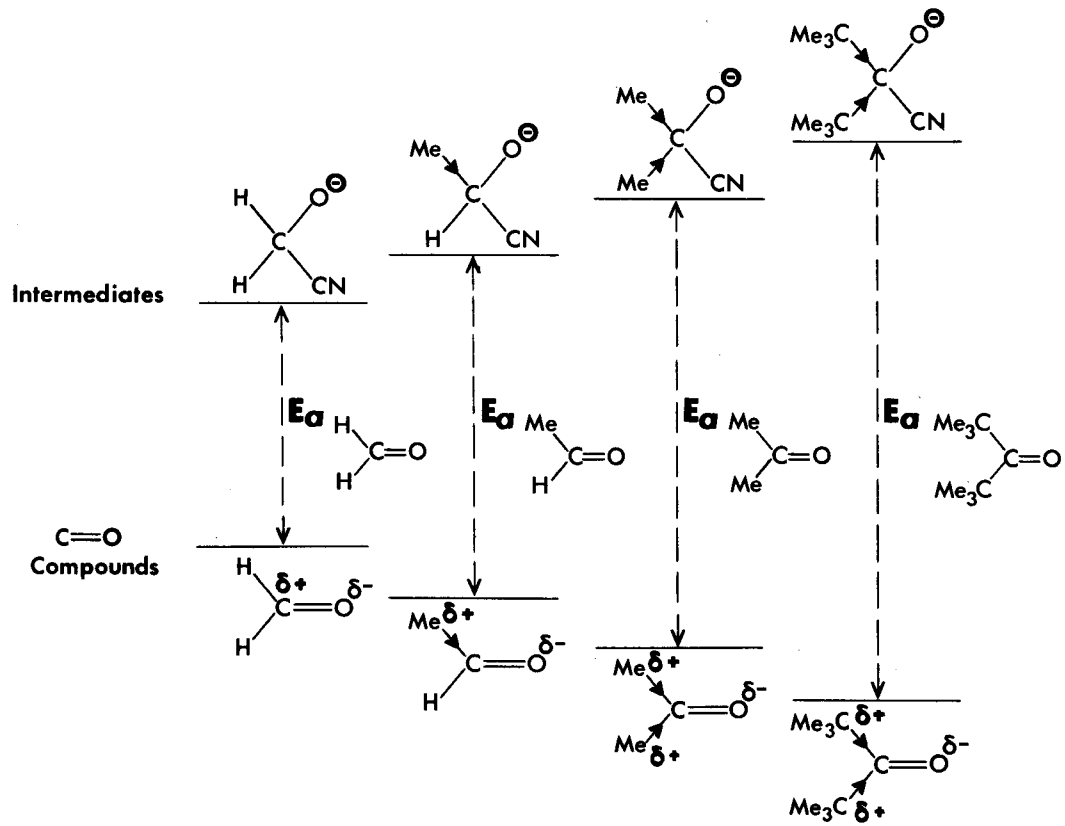
11

HCN ADDITION: TWO-STEP PATHWAY



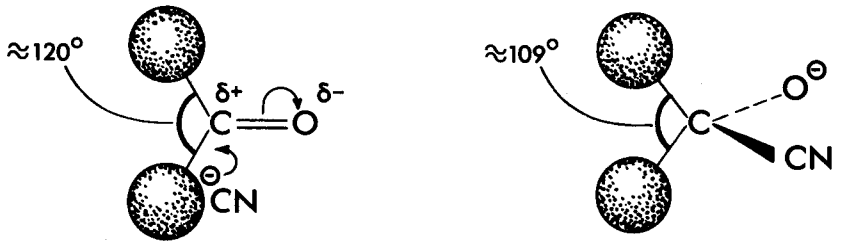
12

HCN ADDITION: ENERGY PROFILE



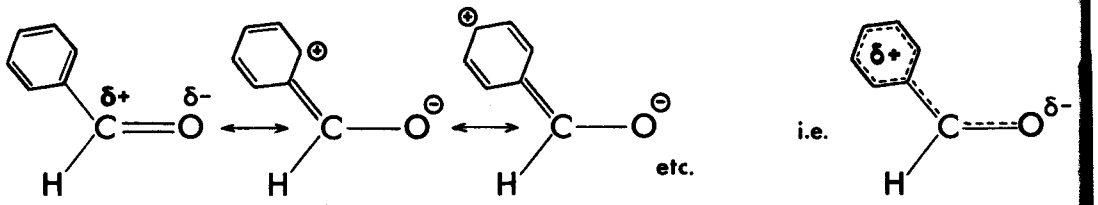
13

NUCLEOPHILIC ATTACK: ELECTRONIC (INDUCTIVE) EFFECT



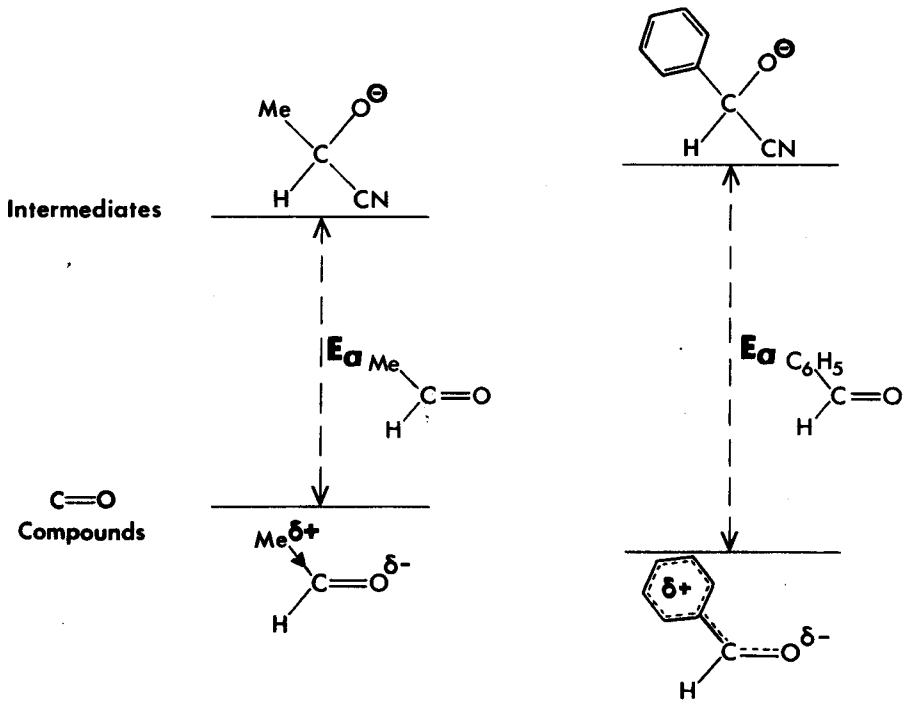
14

NUCLEOPHILIC ATTACK: STERIC EFFECT



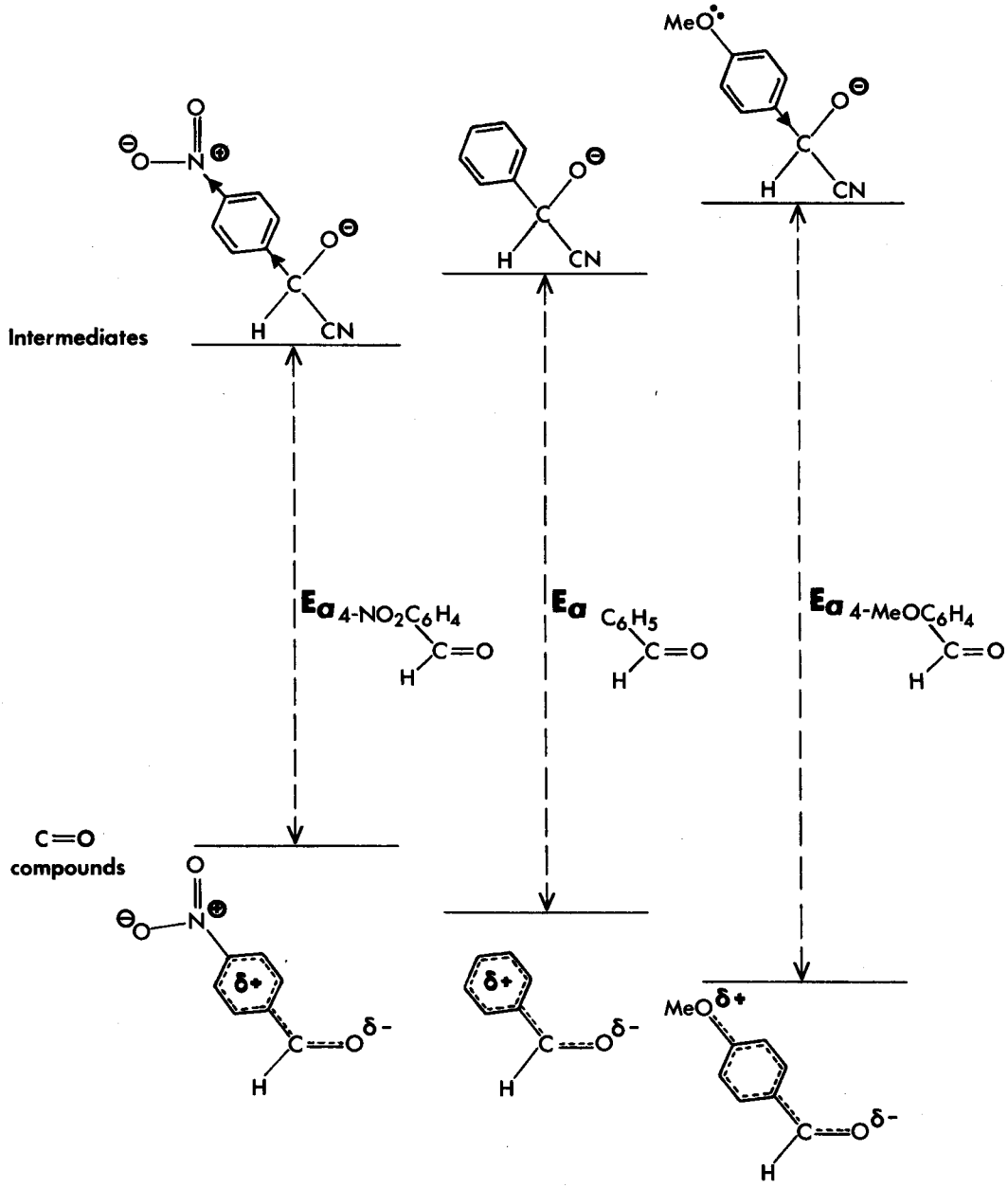
15

BENZALDEHYDE: STABILISATION BY CHARGE-SPREADING



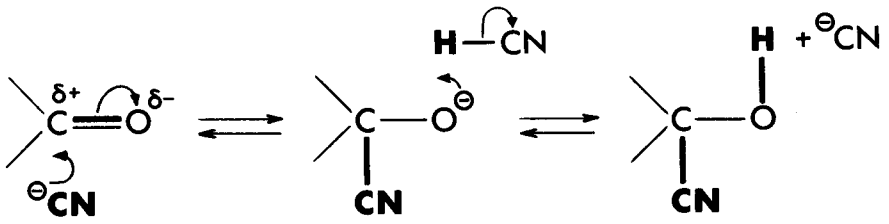
16

NUCLEOPHILIC ATTACK: MeCHO *v.* C_6H_5CHO



17

NUCLEOPHILIC ATTACK: 4-SUBSTITUTED BENZALDEHYDES

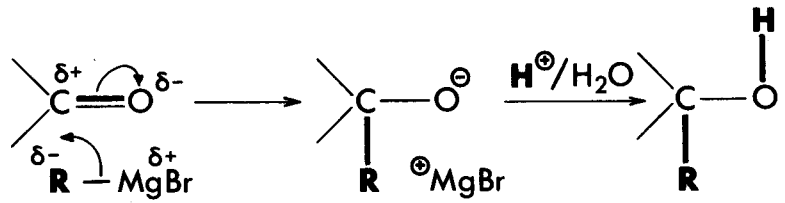


Carbonyl compound	K
MeCHO	very large
4-$NO_2C_6H_4CHO$	1420
C_6H_5CHO	210
4-$MeOC_6H_4CHO$	32
MeCOMe	294
$MeCH_2COMe$	38
C_6H_5COMe	0·8
$C_6H_5COC_6H_5$	very small indeed

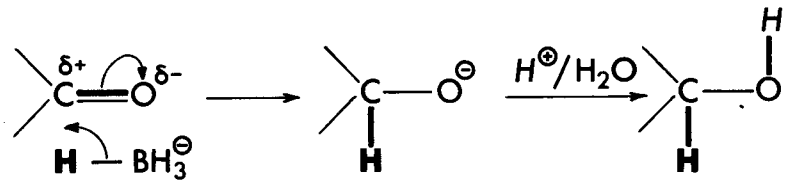
18

HCN ADDITION: SOME K VALUES

(a) GRIGNARD REAGENTS, RMg Br:

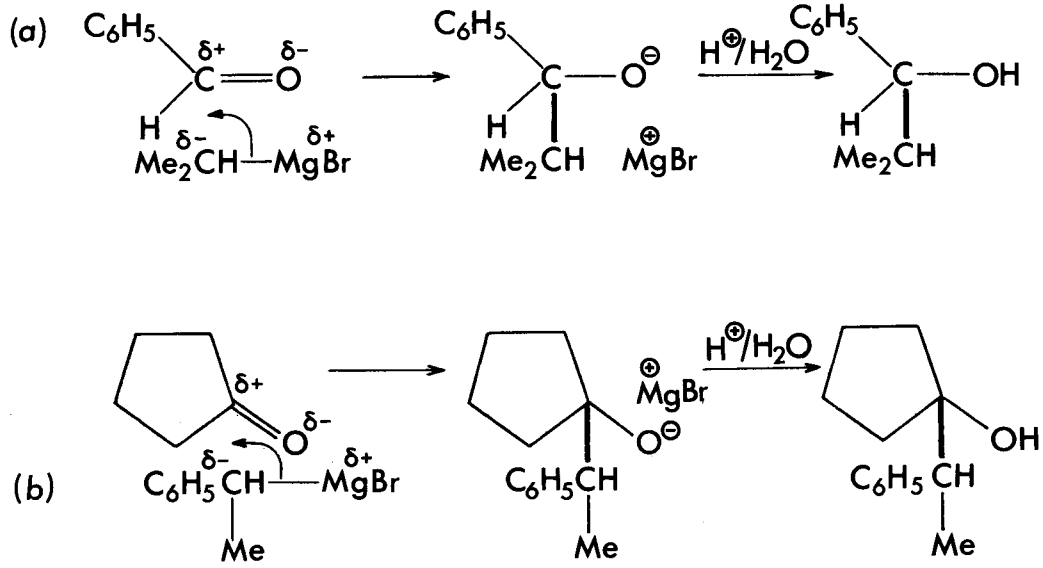


(b) BOROHYDRIDE ION, $BH_4^{\ominus}$:



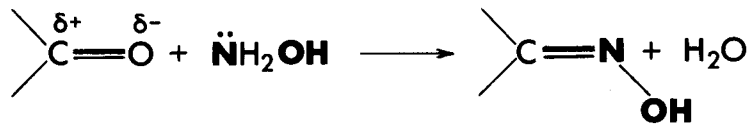
19

NUCLEOPHILIC ADDITION: IRREVERSIBLE



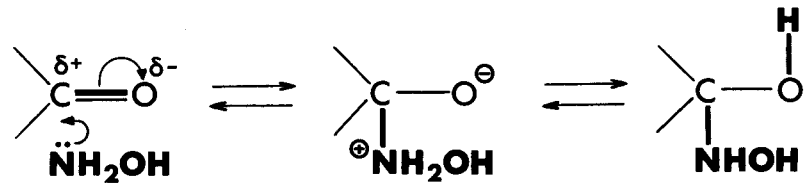
20

SYNTHESES: C=O/GRIGNARD REAGENT



21

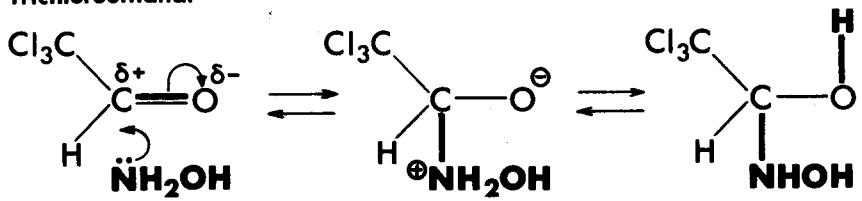
HYDROXYLAMINE (NH_2OH): OXIME FORMATION



22

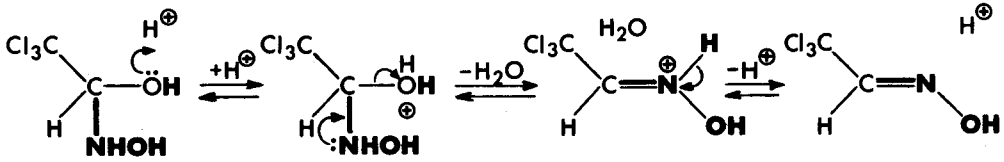
NH_2OH: ADDITION

Trichloroethanal



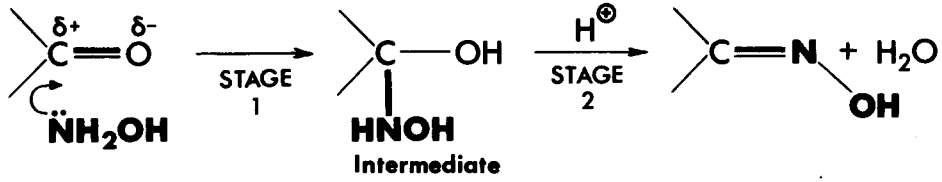
23

NH$_2$OH : STABLE ADDITION PRODUCT



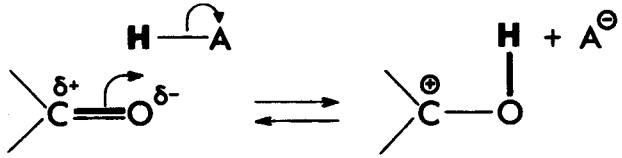
24

NH$_2$OH : DEHYDRATION OF ADDITION PRODUCT



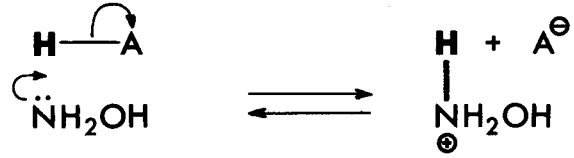
25

OXIME FORMATION : TWO-STAGE PATHWAY



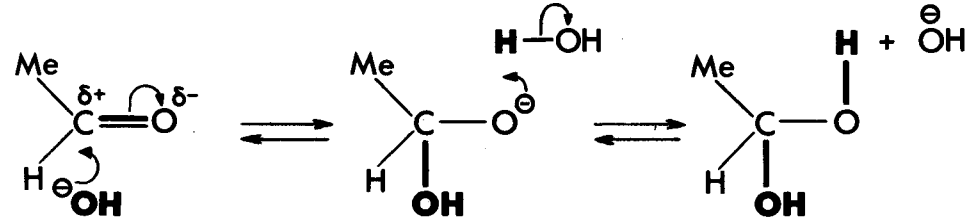
26

C=O : PROTONATION



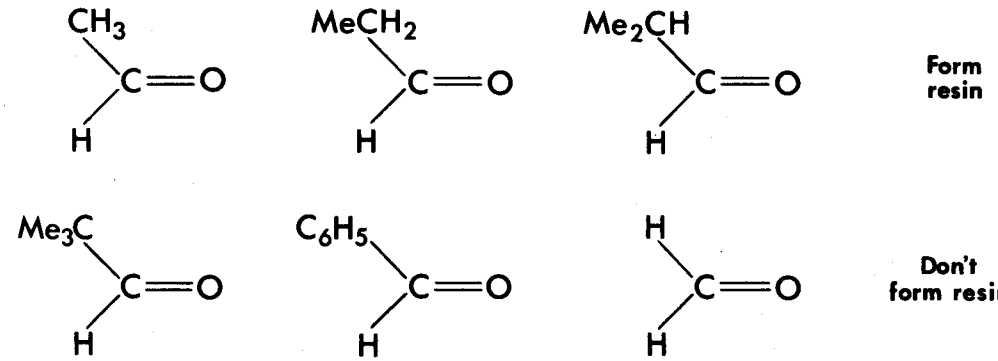
27

NH$_2$OH : PROTONATION



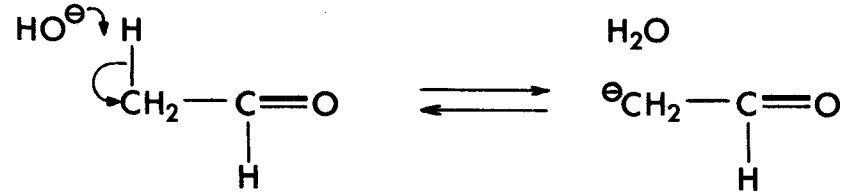
28

C=O : HYDRATION



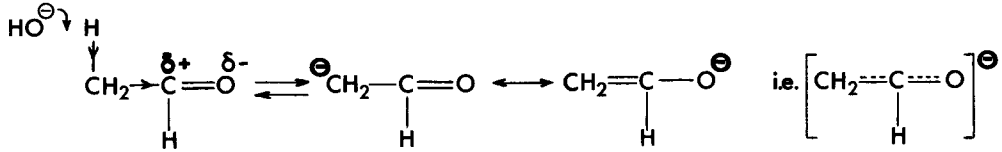
29

STRUCTURE v. RESIN-FORMATION



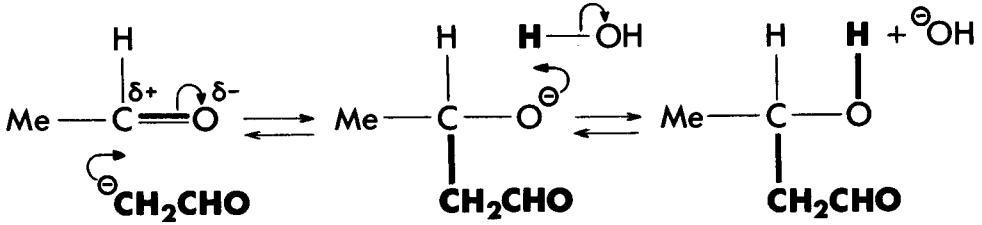
30

PROTON REMOVAL



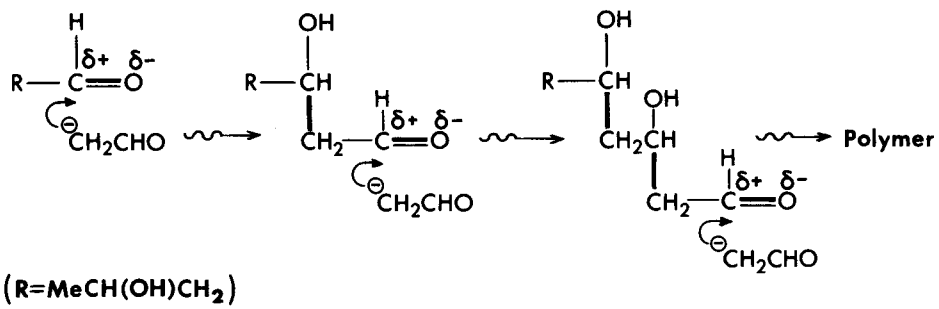
31

EFFECTS PROMOTING ACIDITY



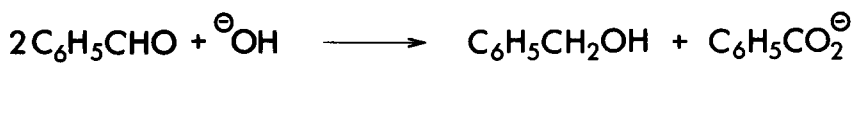
32

C=O:CARBANION ADDITION



33

C=O:RESIN-FORMATION



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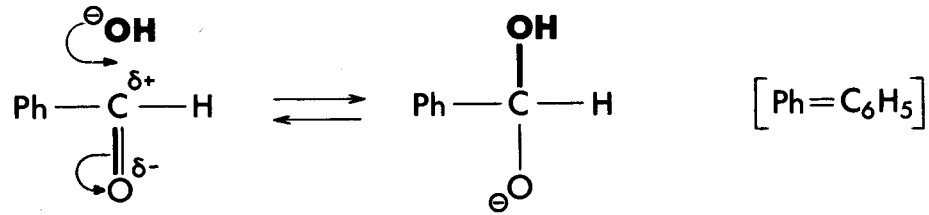
BENZALDEHYDE: $^{\ominus}$OH REACTION



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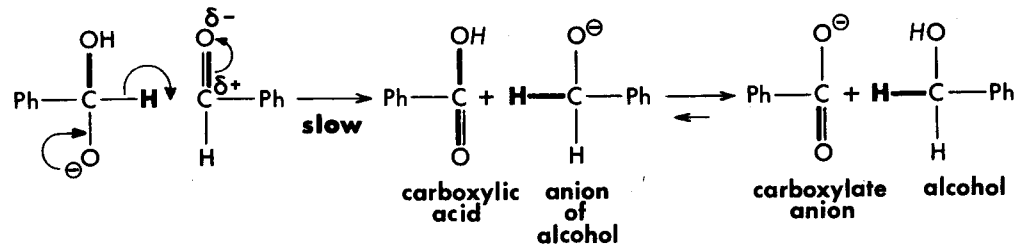
BENZALDEHYDE: $^{\ominus}$OH ADDITION



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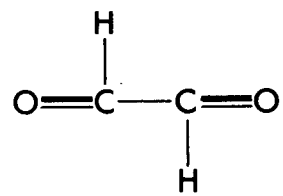
BENZALDEHYDE: CANNIZZARO REACTION

$$\text{Rate} = k\,[C_6H_5CHO]^2\,[^{\ominus}OH]$$

37

CANNIZZARO REACTION: RATE EQUATION



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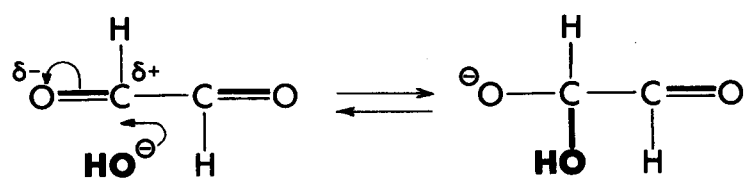
ETHANEDIAL (GLYOXAL)



39

ETHANEDIAL: $^{\ominus}$OH ADDITION