Organic Reaction Mechanisms

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Lecture Outline: Part 1

Context

Why bother with Organic Reaction Mechanisms?

What is a covalent bond?

What are curly reaction mechanism arrows and what is their physical meaning?

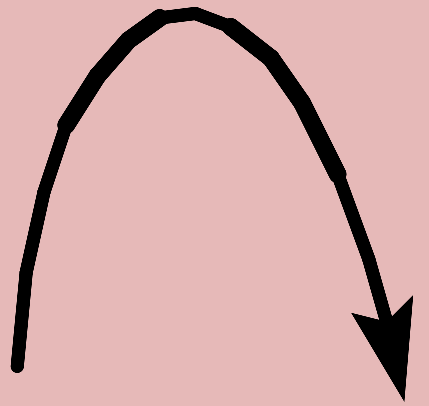
How do we form bonds with pairs of electrons (lone pairs or bonding electron pairs)?

Types of Organic Reaction Mechanisms

Organic Reaction Mechanisms

- *Nucleophilic substitution with haloalkanes*
- *Nucleophilic addition with aldehydes/ketones*
- *Nucleophilic aromatic substitution*
- *Electrophilic aromatic substitution*
- *Electrophilic addition to alkenes*
- *Elimination of HX from haloalkanes (X = halogen)*
- *Free radical chlorination of alkanes*

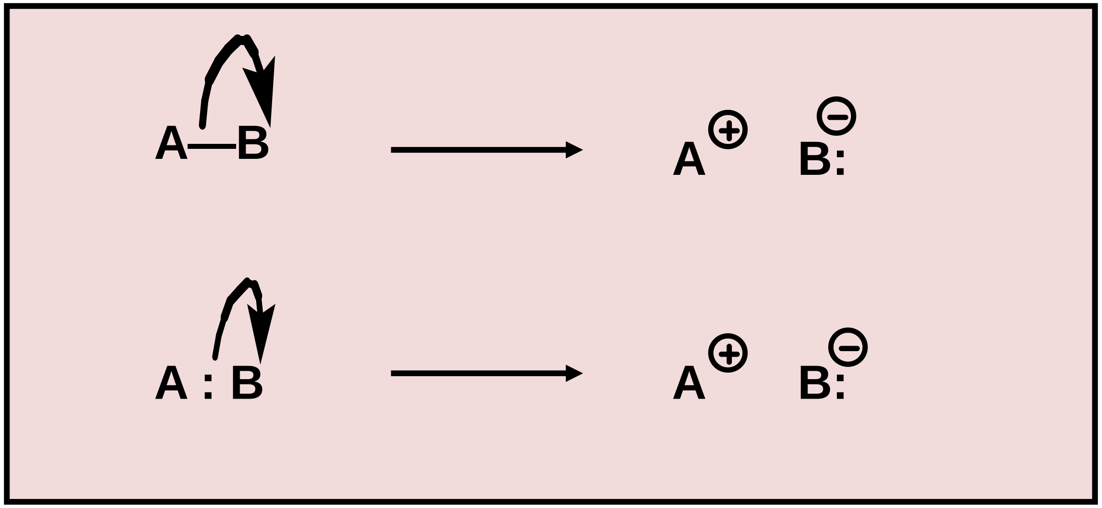
Reaction Mechanism 'Curly' Arrows



Two Electron Movement

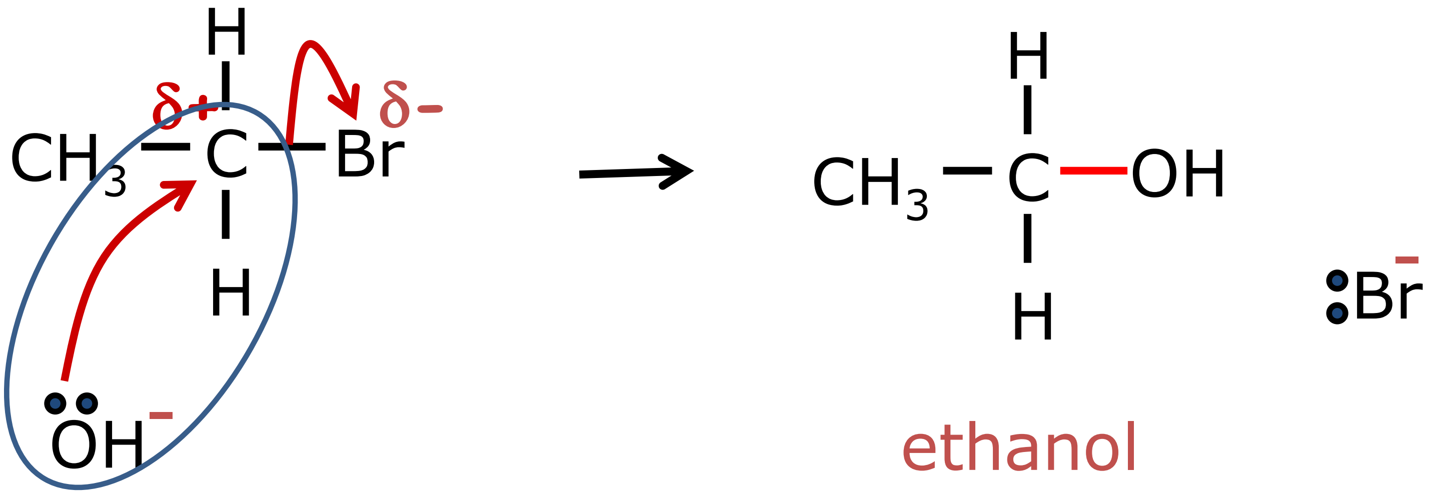
Double headed arrow

Heterolytic Bond Cleavage

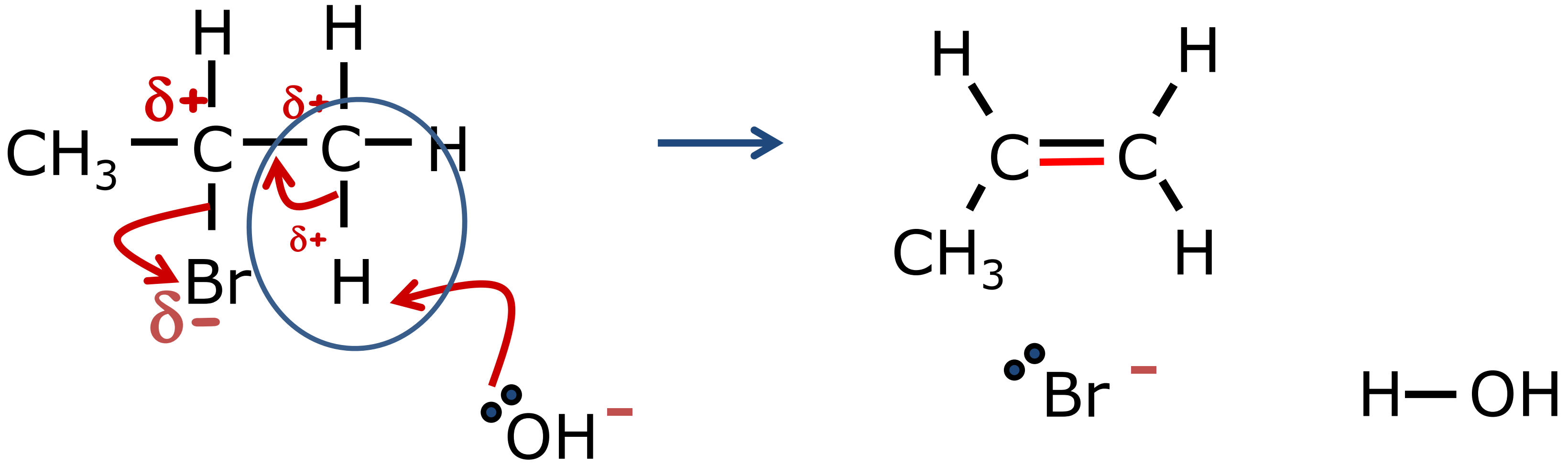


Electronegativty of atom A is less than atom B

Lone Pairs Forming Bonds

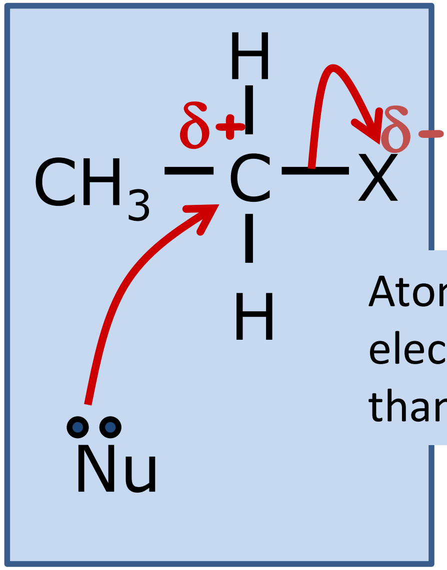


Bonding Electrons Forming Bonds



Nucleophilic Substitution on a Saturated Carbon

Electron rich Nucleophile (Nu) in search of an electron poor saturated carbon centre



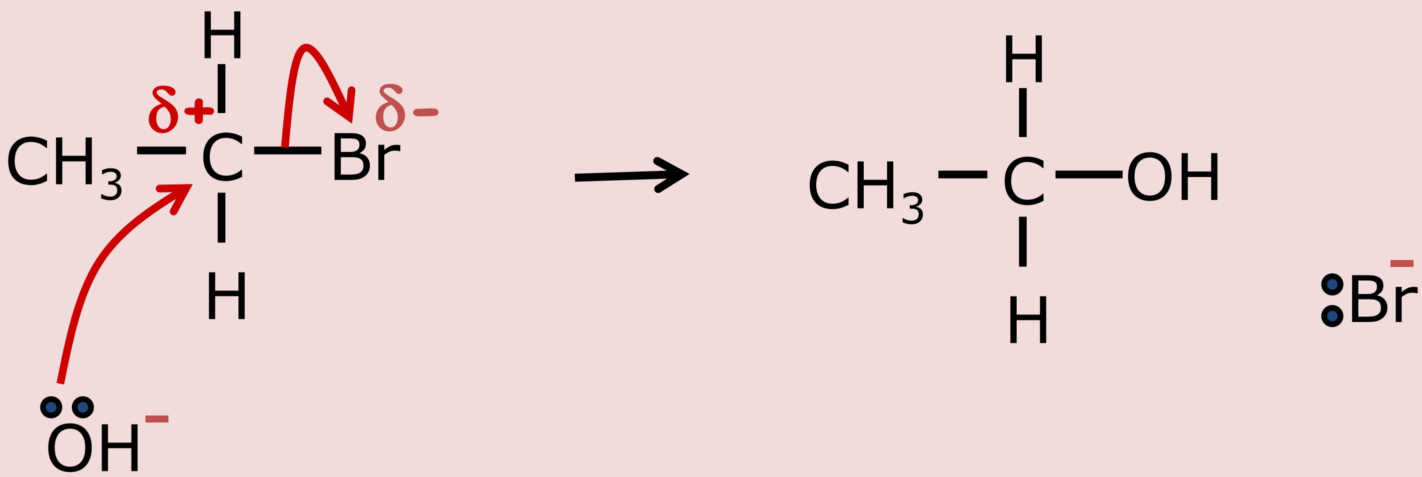
Atom X is more electronegative than C

AS Level

Nucleophilic Substitution: 1

$CH_3CH_2Br + OH^-$ (aqueous) $\longrightarrow$ $CH_3CH_2OH + Br^-$

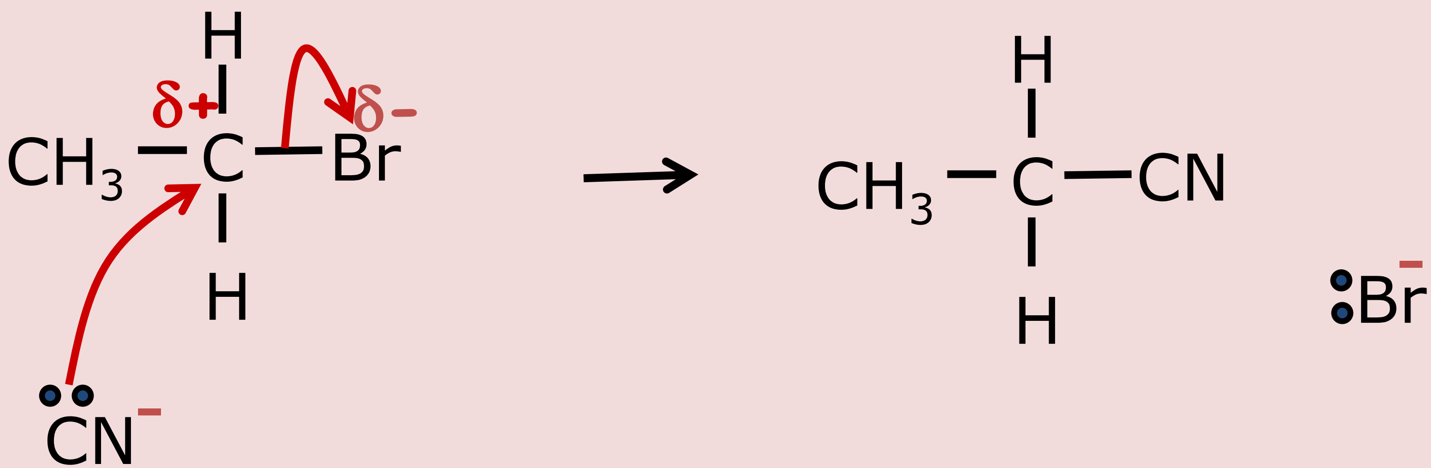
ethanol



Nucleophilic Substitution: 2

CH_3CH_2I (ethanol) + CN^-(aq) ⟶ $CH_3CH_2CN + I^-$

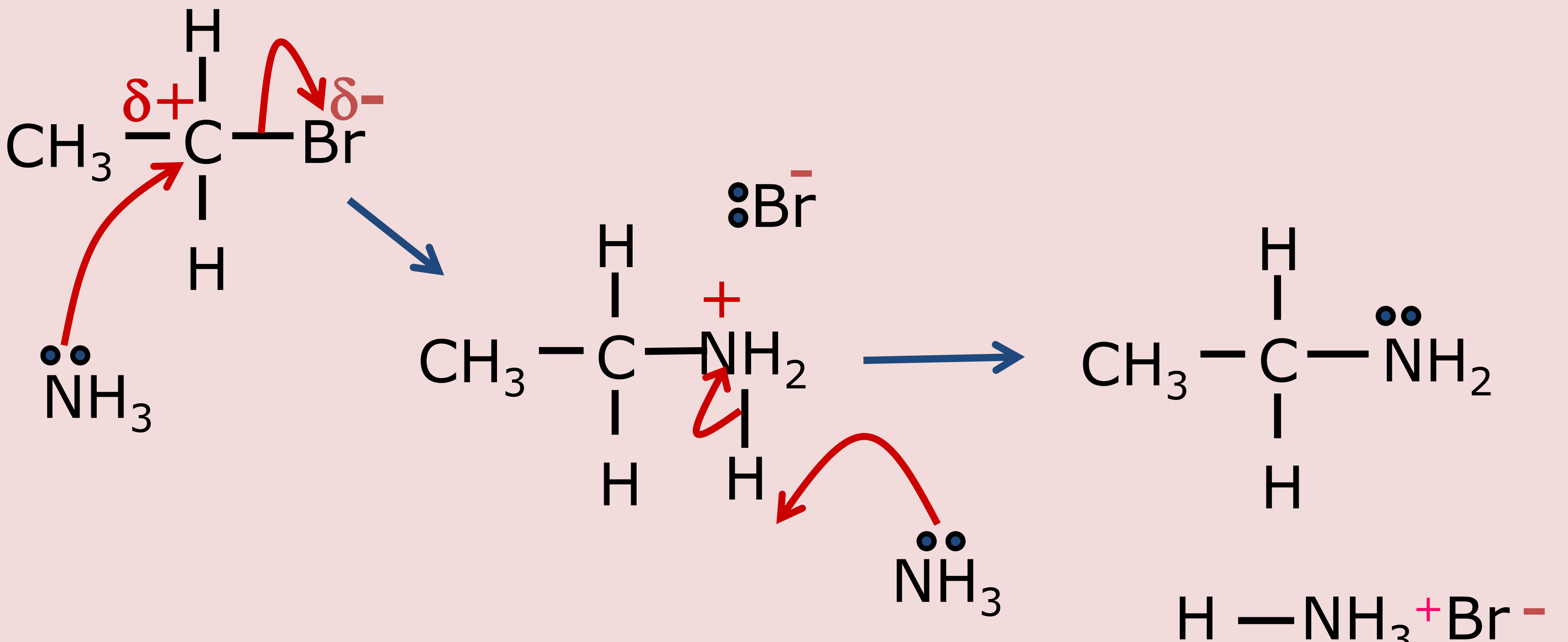
propanenitrile



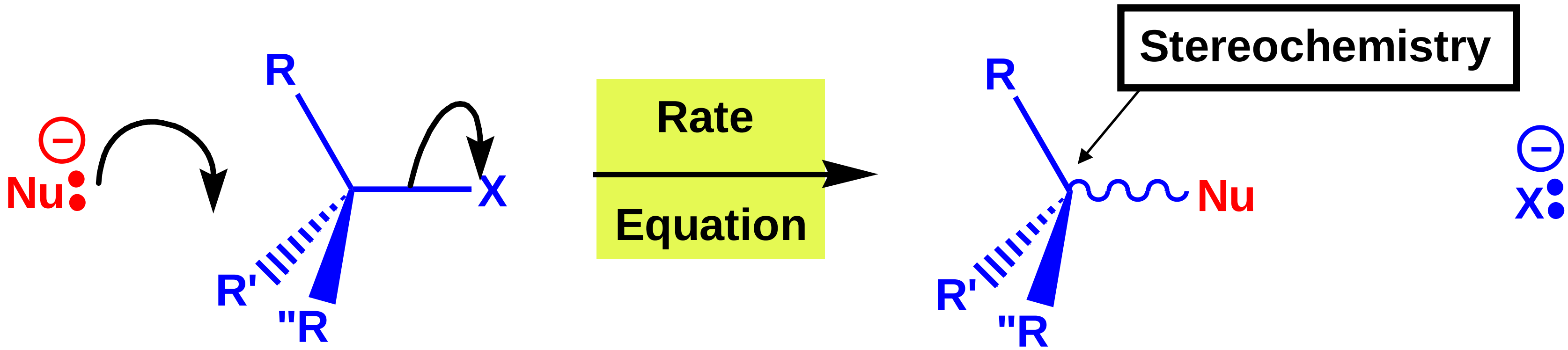
Nucleophilic Substitution: 3

$$CH_3CH_2Br + 2\,NH_3 \longrightarrow CH_3CH_2NH_2 + NH_4^{+}Br^{-}$$

aminoethane



Nothing is Black and White: 1

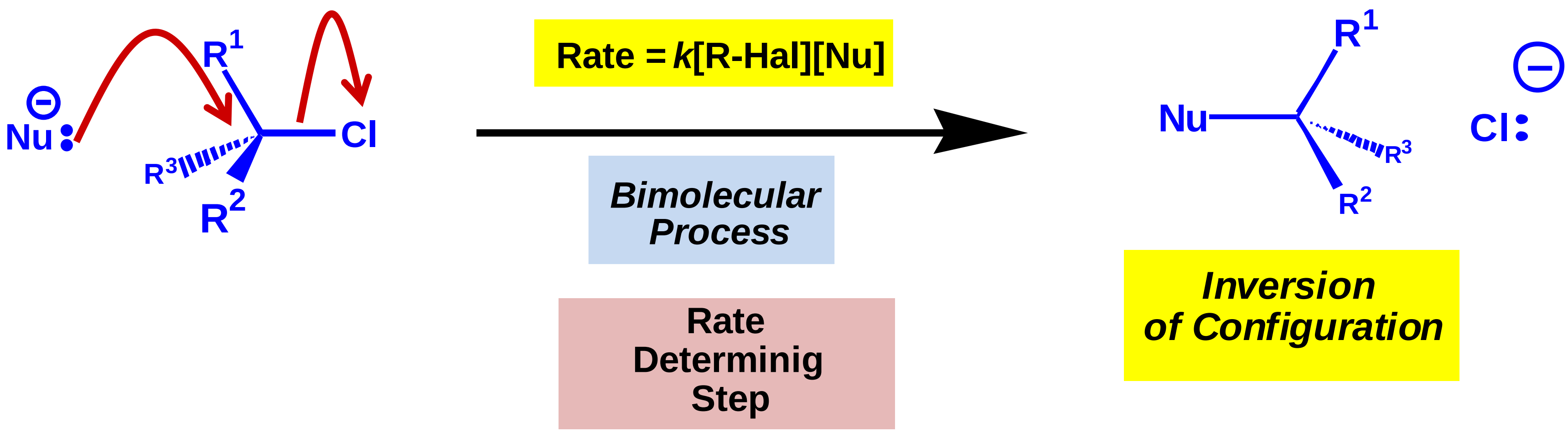


It is found that there are two possible stereochemical outcomes, each described by a different rate equation, and different stereochemical outcomes.

Descriptor	Rate Equation	Stereochemical Outcome
S_N2	rate = k[R-Hal][Nu]	Inversion
S_N1	rate = k[R-Hal]	Racemisation

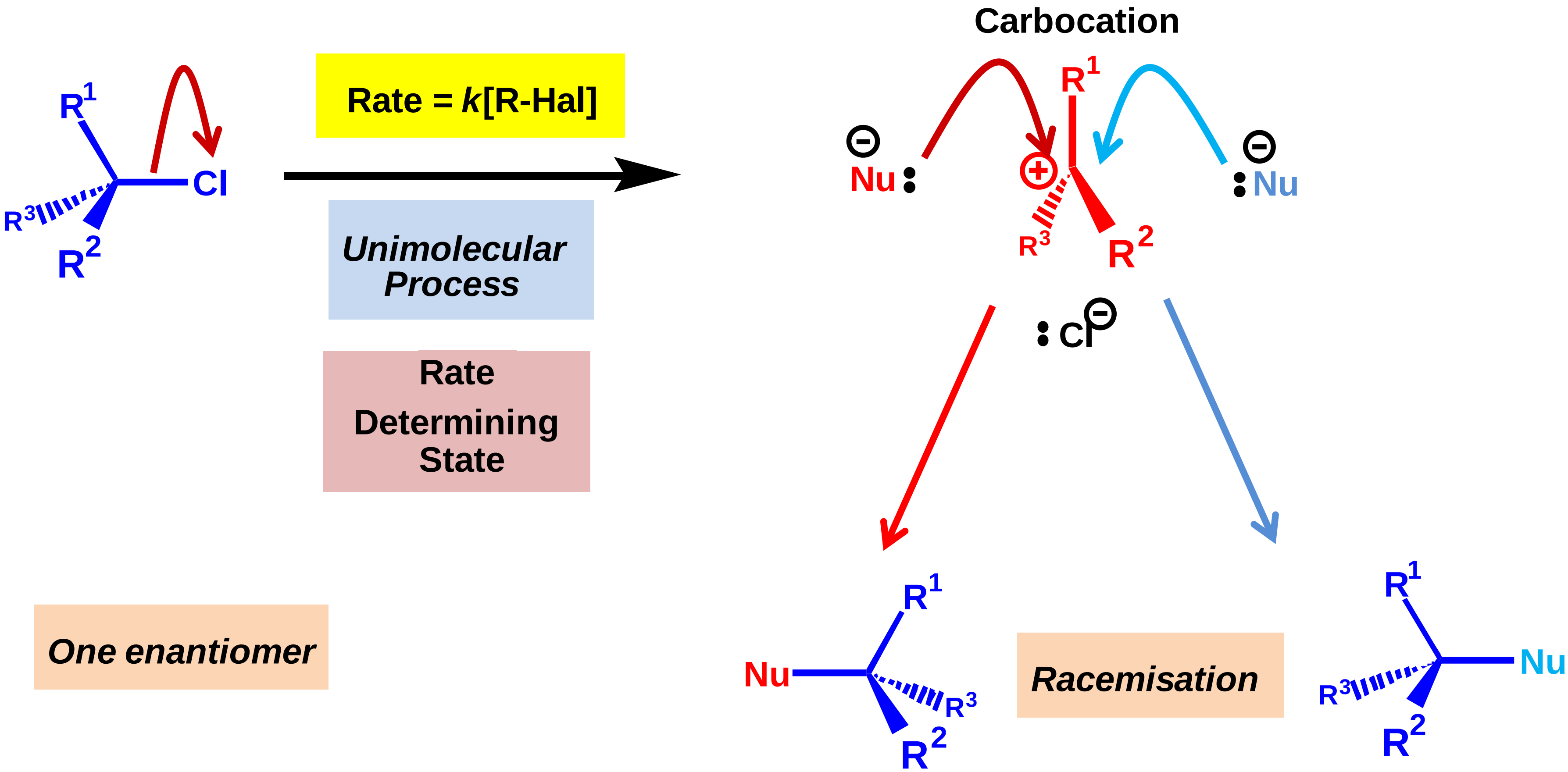
Nucleophilic Substitution: S_N2

Nucleophile can attacks from only one side of the chloroalkane



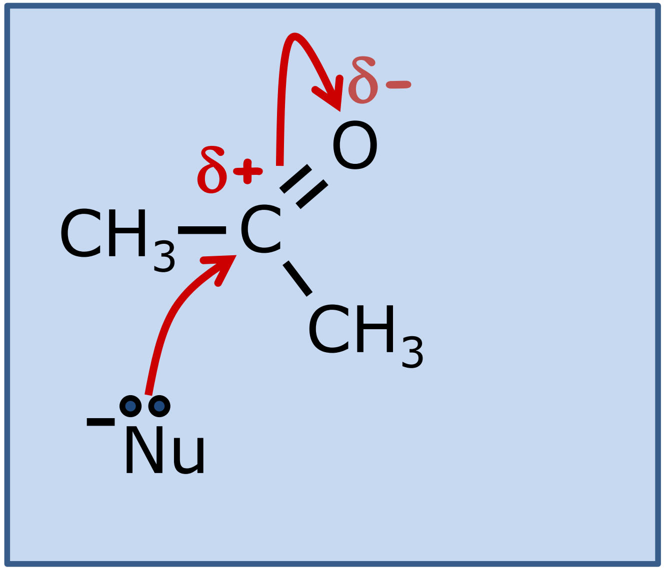
Nucleophilic Substitution: S_N1

Nucleophile attacks from either side of the carbocation with equal probability.



Nucleophilic Addition to Aldehydes/Ketones (C=O)

Electron rich Nucleophile (Nu) in search of an electron poor unsaturated carbon centre

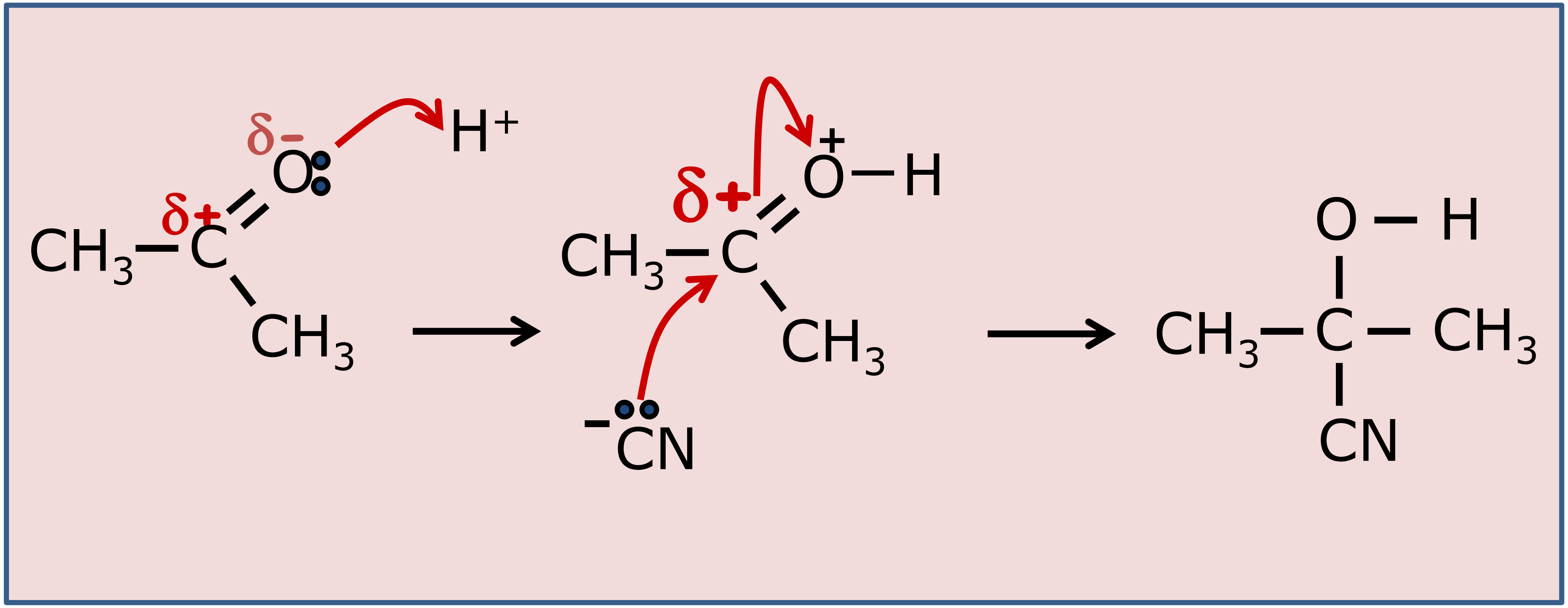


A2 Level

Nucleophilic Add'n to Aldehydes/Ketones 1

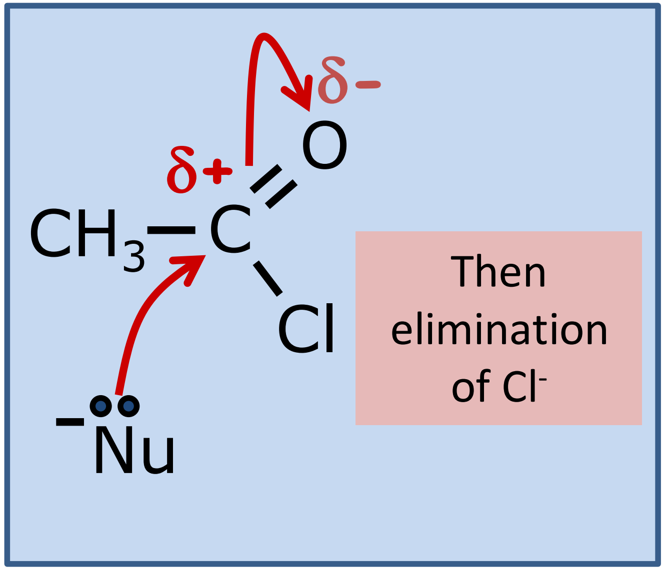
CH_3COMe + HCN ⟶ $CH_3C(OH)(CN)Me$

2-hydroxy-2-methylpropanenitrile



Nucleophilic Addition to Acid Chlorides (R(Cl)C=O) Followed by Elimination

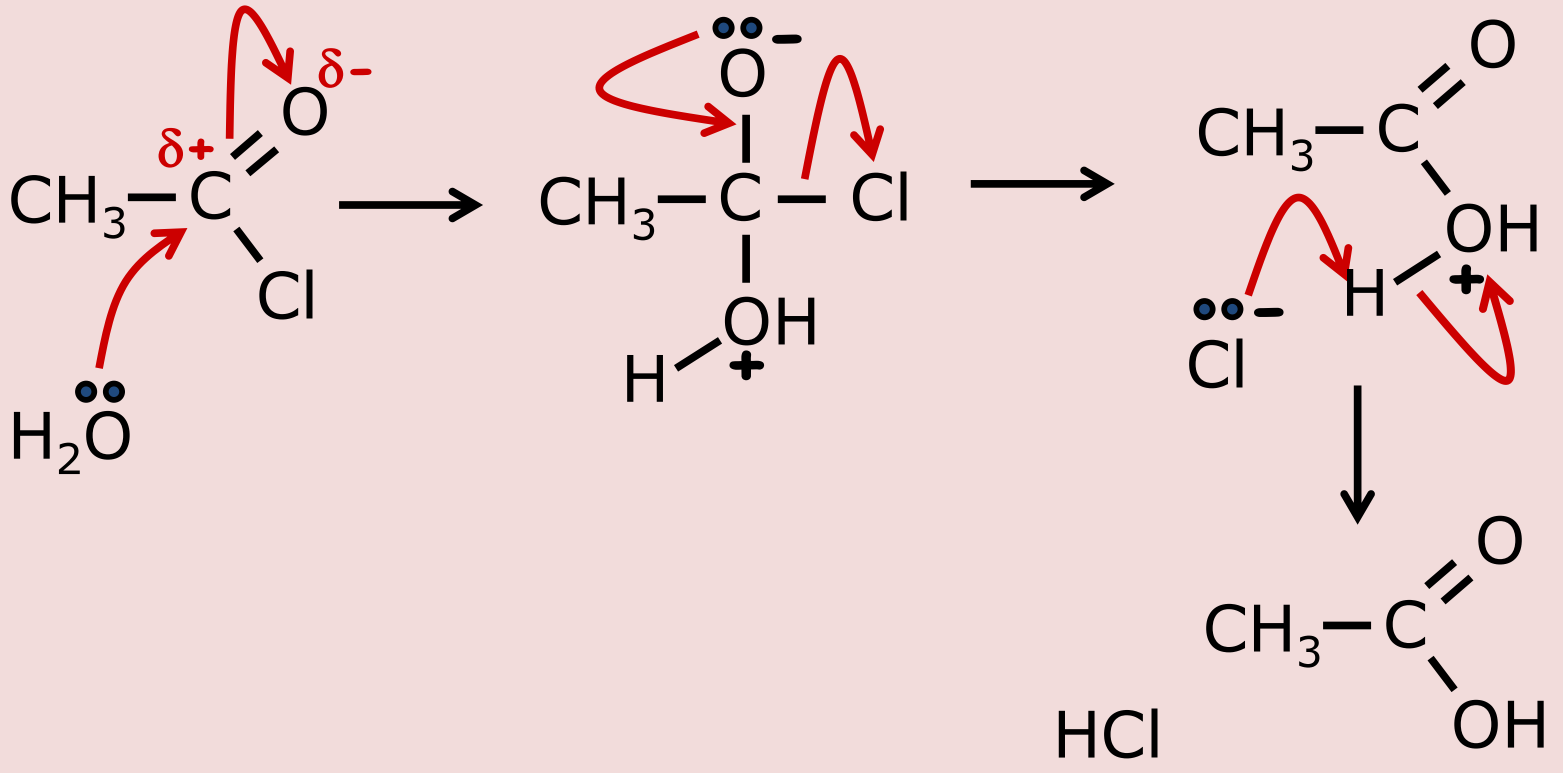
Electron rich Nucleophile (Nu) in search of an electron poor unsaturated carbon centre



AS Level

Nucleophilic Add'n to Acid Chlorides 1

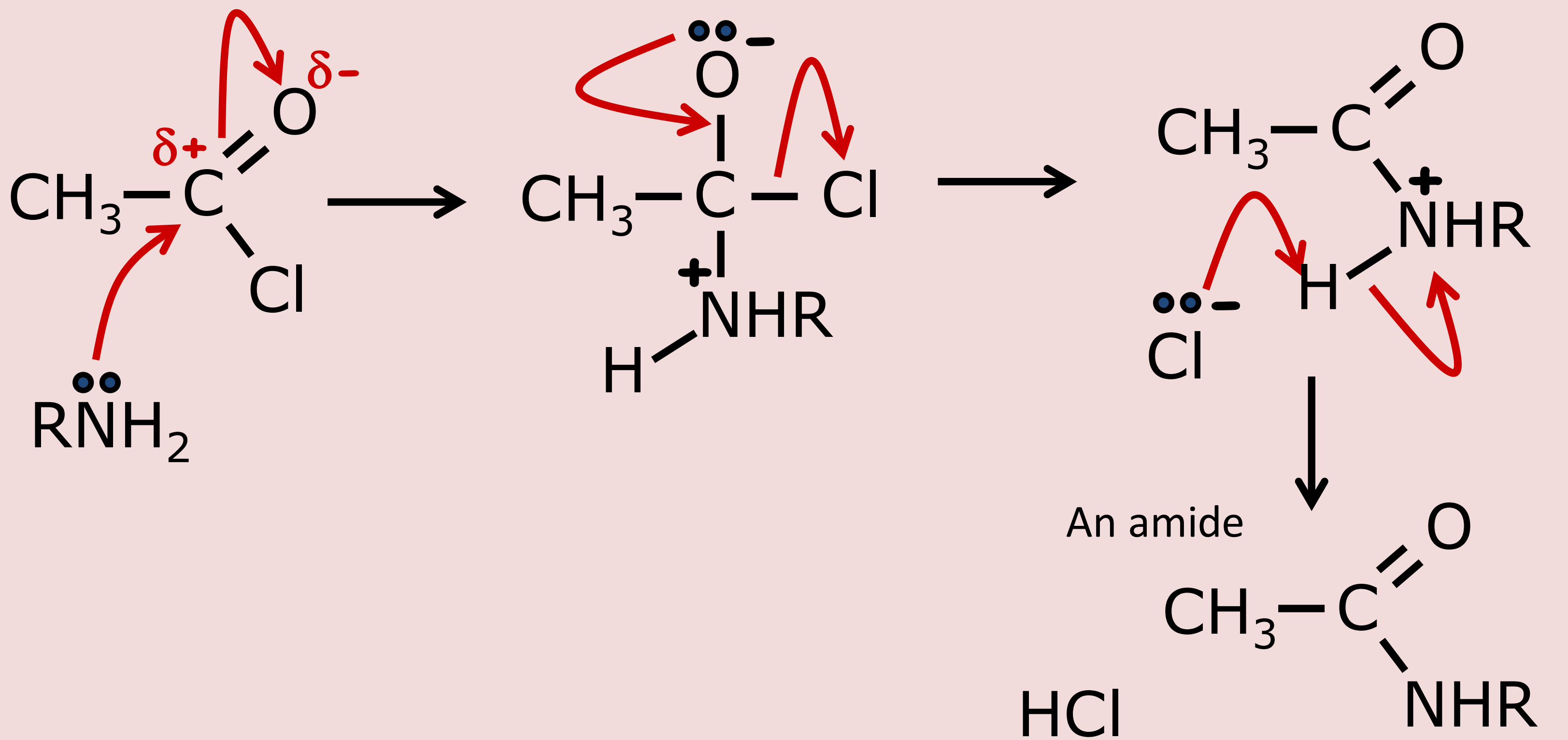
$$CH_3COCl \quad + \quad H_2O \longrightarrow CH_3COOH \quad + \quad HCl$$



Nucleophilic Add'n to Acid Chlorides 1

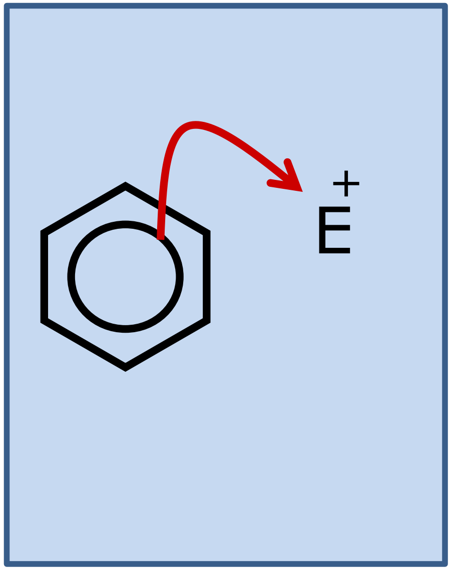
$$CH_3COCl + CH_3NH_2 \longrightarrow CH_3CONHCH_3 + HCl$$

N-methylethanamide



Electrophilic Aromatic Substitution

Electron rich aromatic unit
in search of an
electron poor electrophile (E)



A2 Level

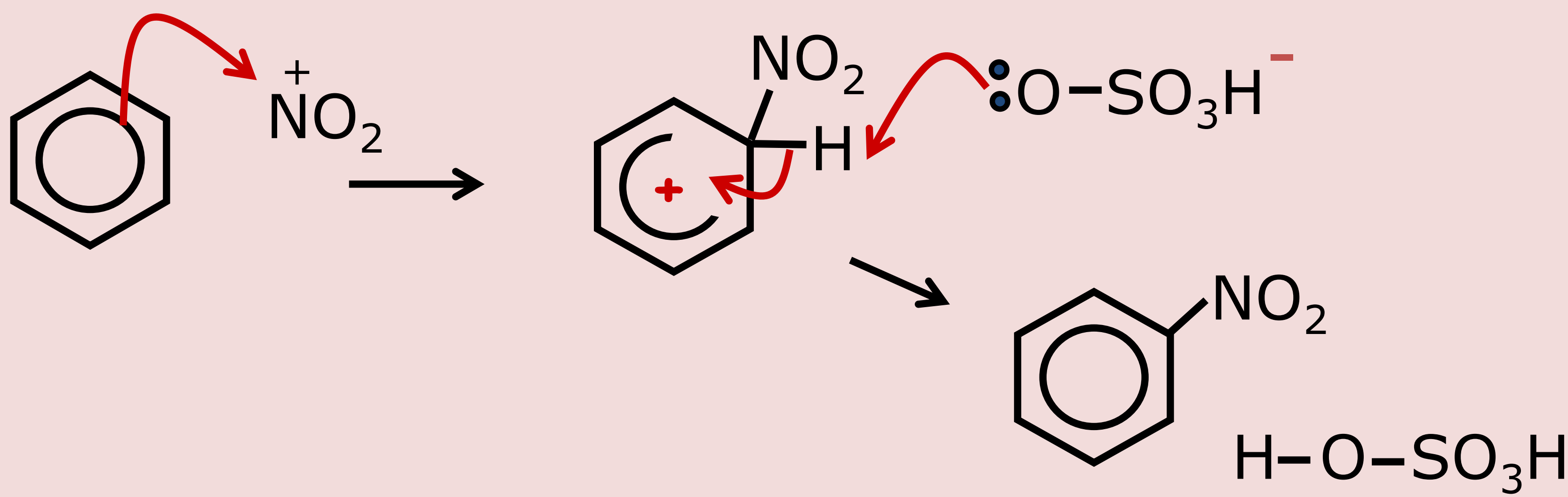
Electrophilic Aromatic Substitution 1

$$C_6H_6 + HNO_3/H_2SO_4 \longrightarrow C_6H_5NO_2 + H_2O$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{+}{N}O_2 + 2HSO_4^- + H_3O^+$$

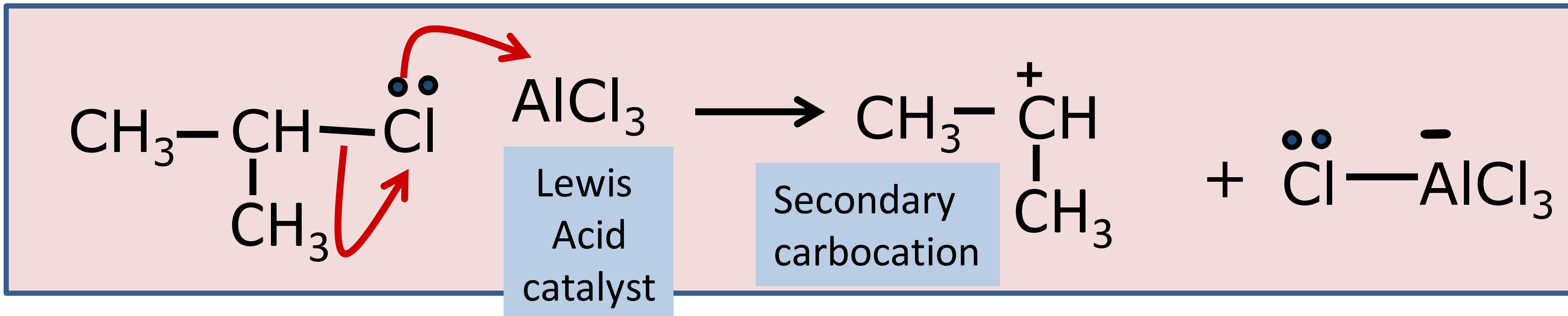
catalyst

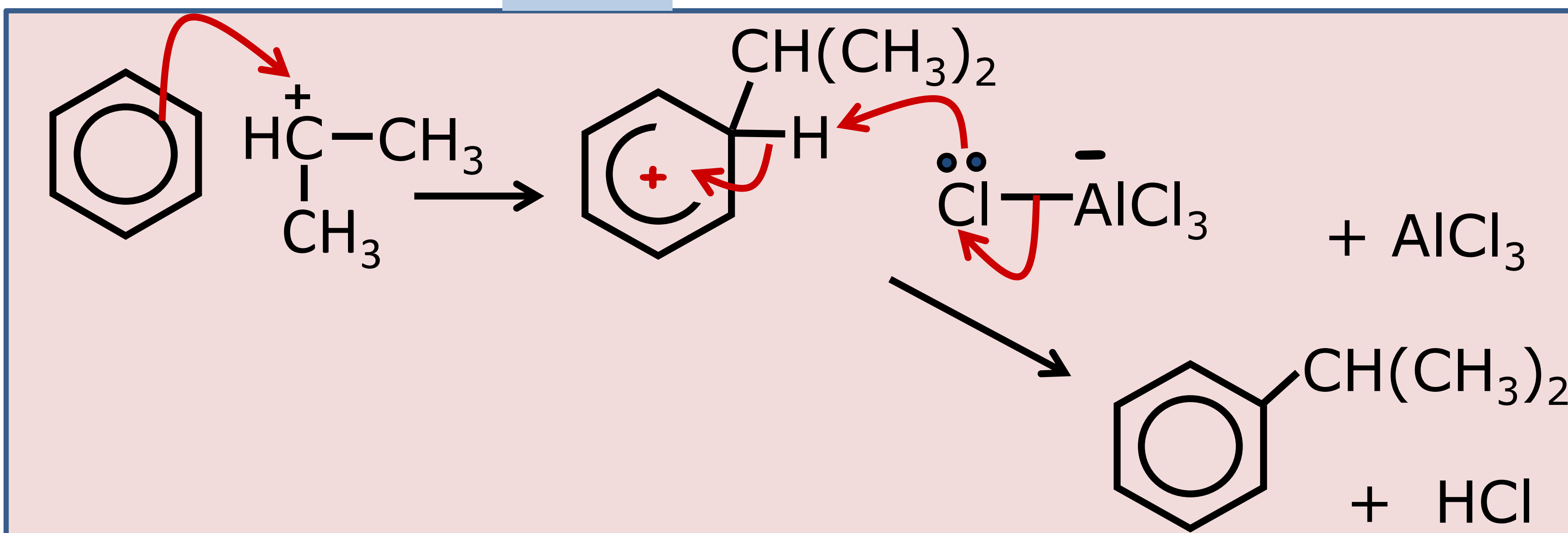
Electrophile
Nitronium Ion



Electrophilic Aromatic Substitution 2

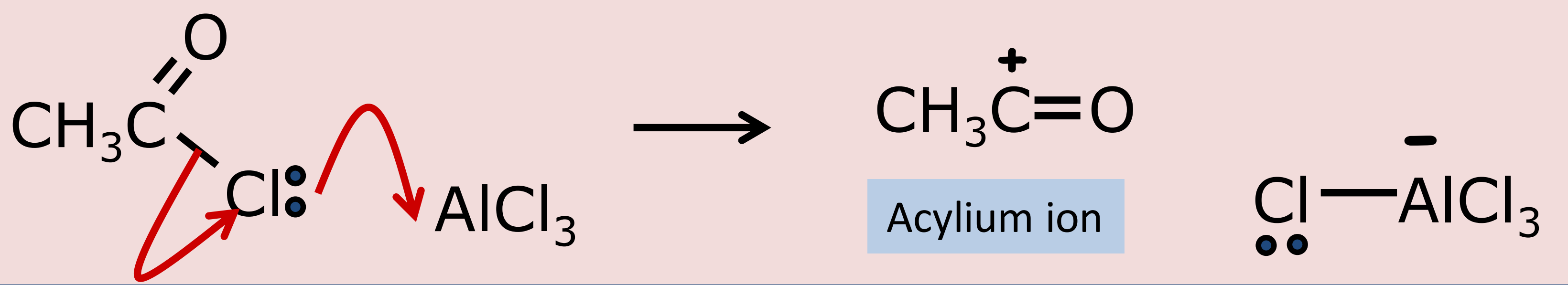
$$C_6H_6 + (CH_3)_2CHCl \xrightarrow{\text{Lewis acid}} C_6H_5CH(CH_3)_2 + HCl$$

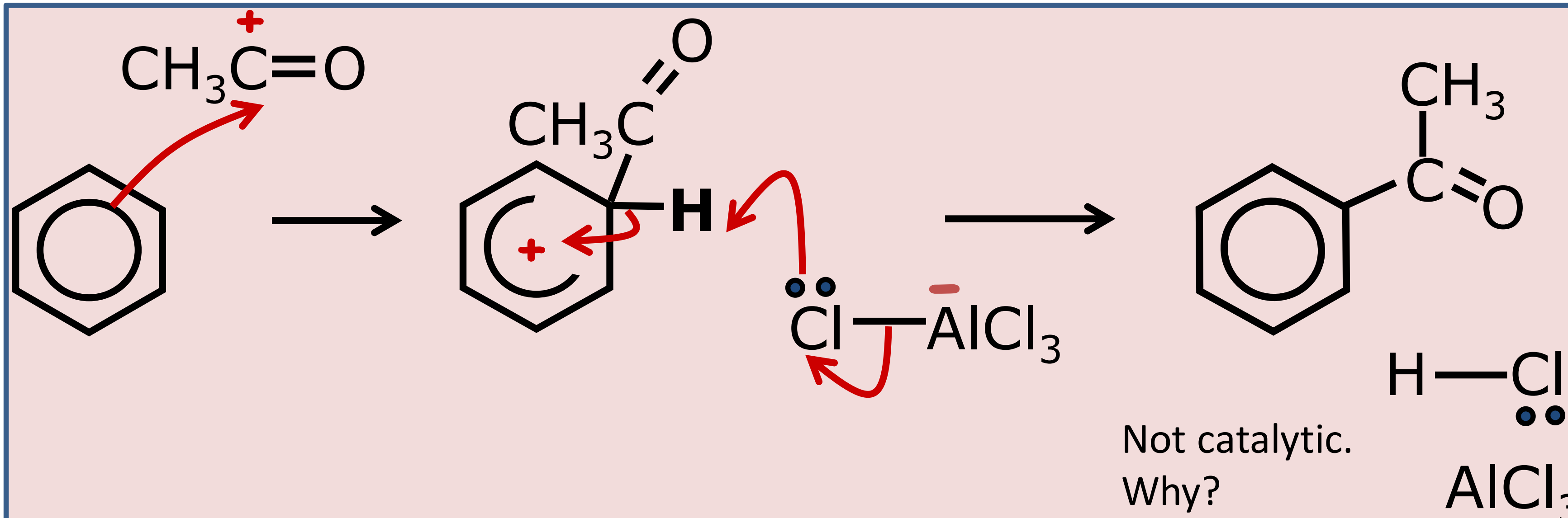




Electrophilic Aromatic Substitution 3

$$C_6H_6 + RCOCl \xrightarrow{\text{Lewis acid}} C_6H_5COR + HCl$$

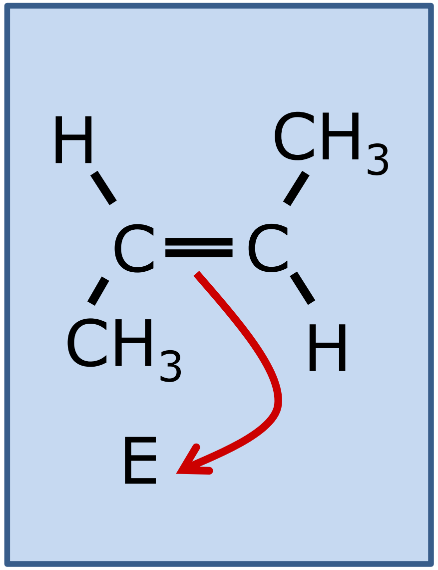




Not catalytic.
Why?

Electrophilic Addition to Alkene

Electron rich π-bond
in search of an
electron poor electrophile (E)

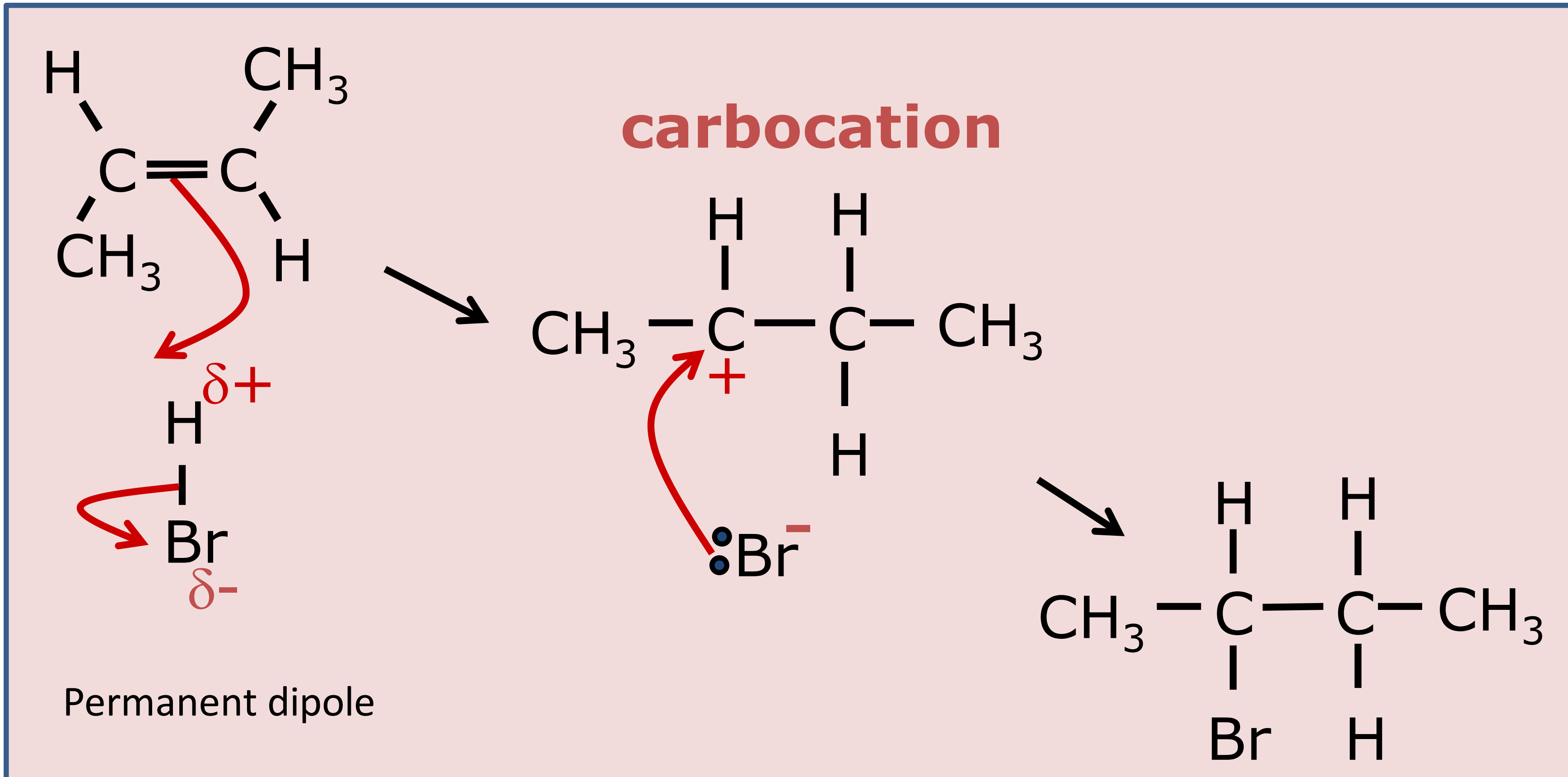


AS Level

Electrophilic Addition to an Alkene: 1

$CH_3CH{=}CHCH_3 + HBr \longrightarrow CH_3CH_2CHBrCH_3$

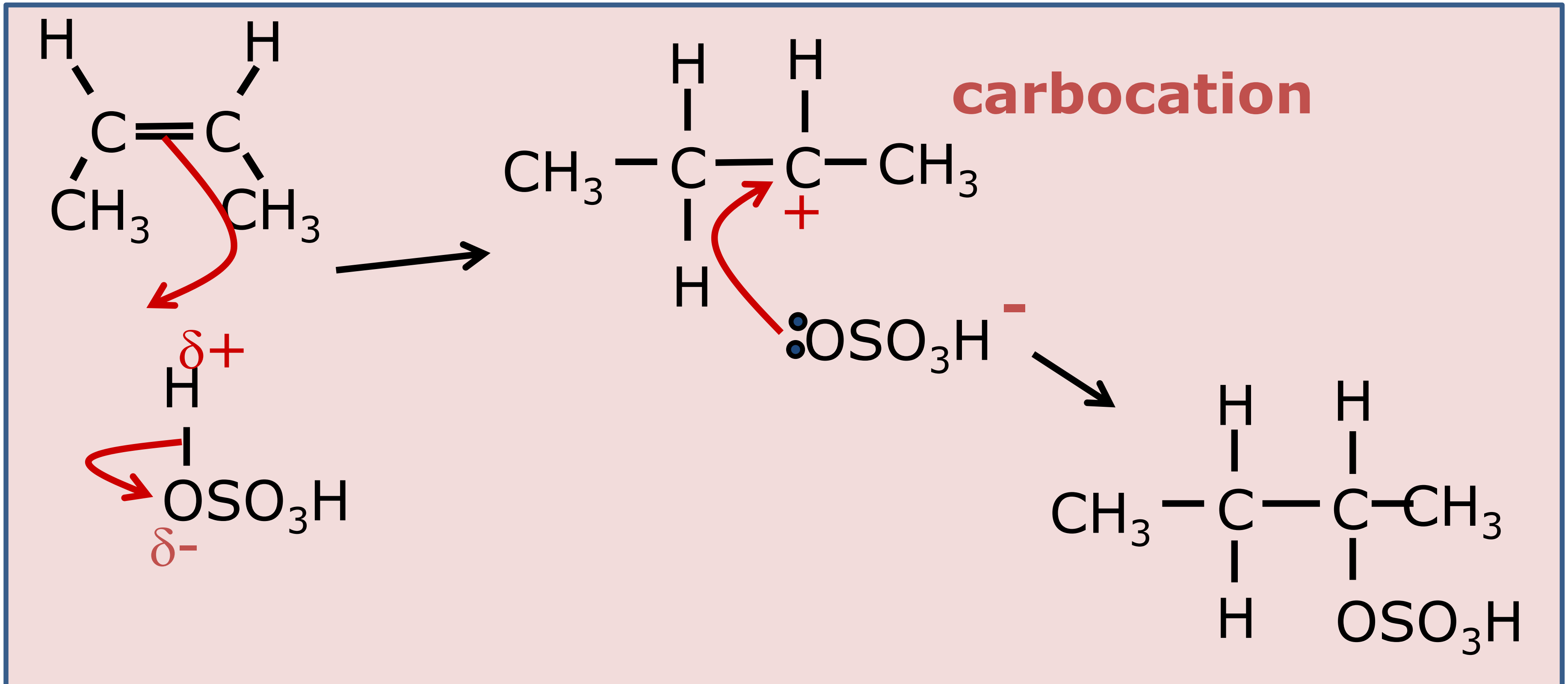
2-bromobutane



Electrophilic Addition to an Alkene: 2

$CH_3CH{=}CHCH_3 + HOSO_3H \longrightarrow CH_3CH_2CH(OSO_3H)CH_3$

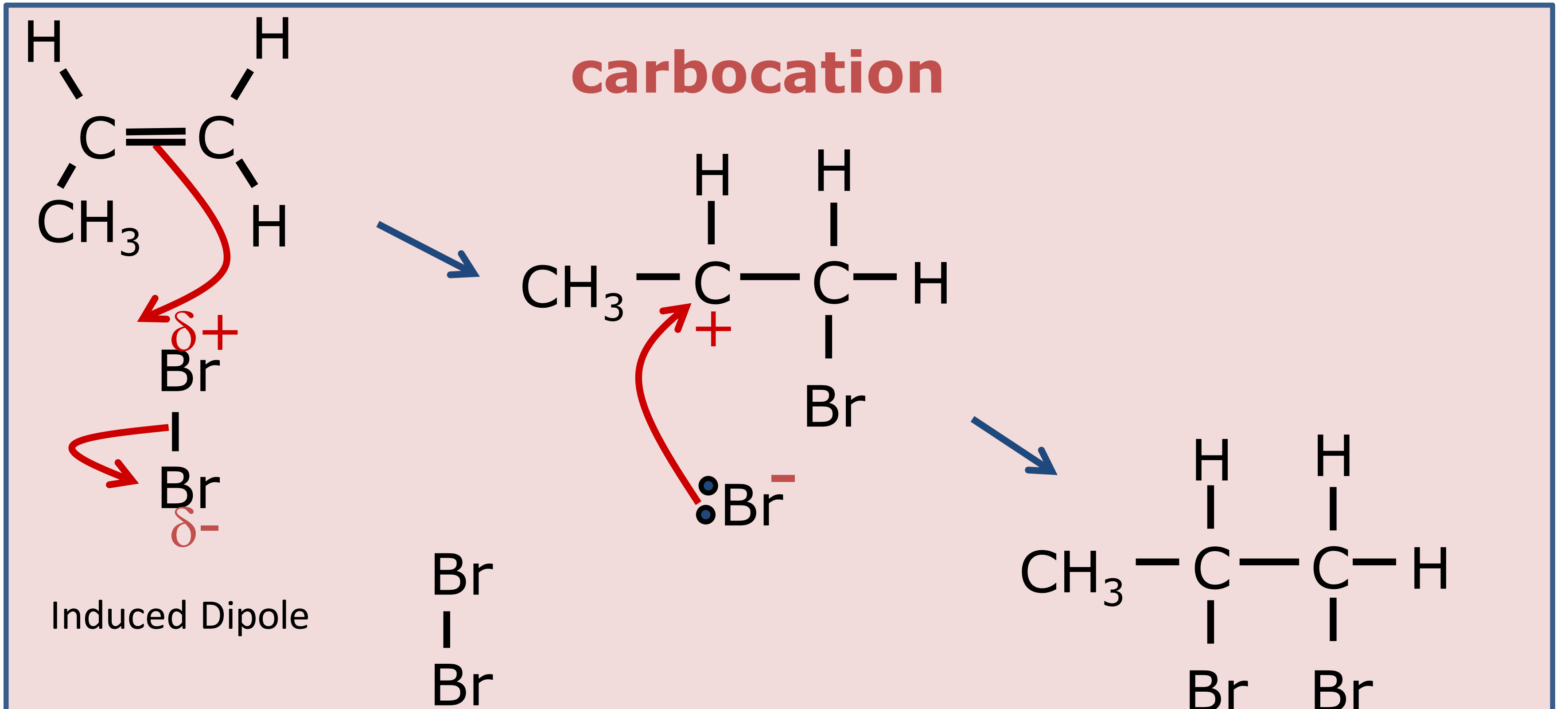
2-butylhydrogensulphate



Electrophilic Addition to an Alkene: 3

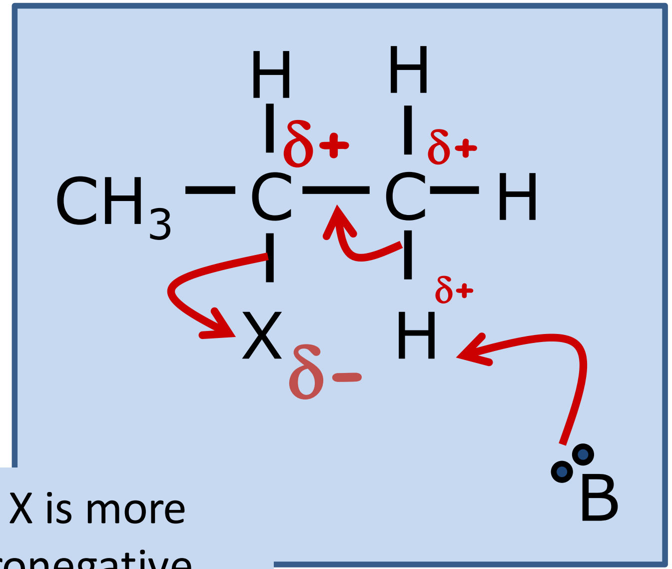
$CH_3CH{=}CH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br$

1,2-dibromopropane



Elimination of HX from Alkanes to form an alkene

Lone Pair of Electrons on Base (B:)in search of an electron poor hydrogen centre



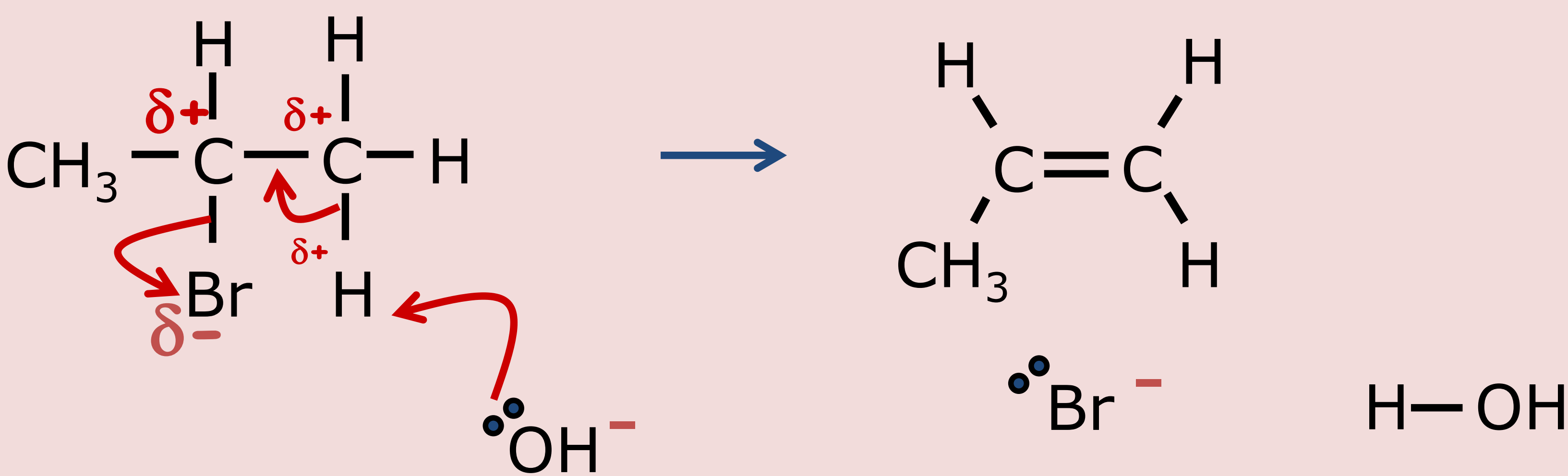
Atom X is more electronegative than C

AS Level

Elimination of HX: 1

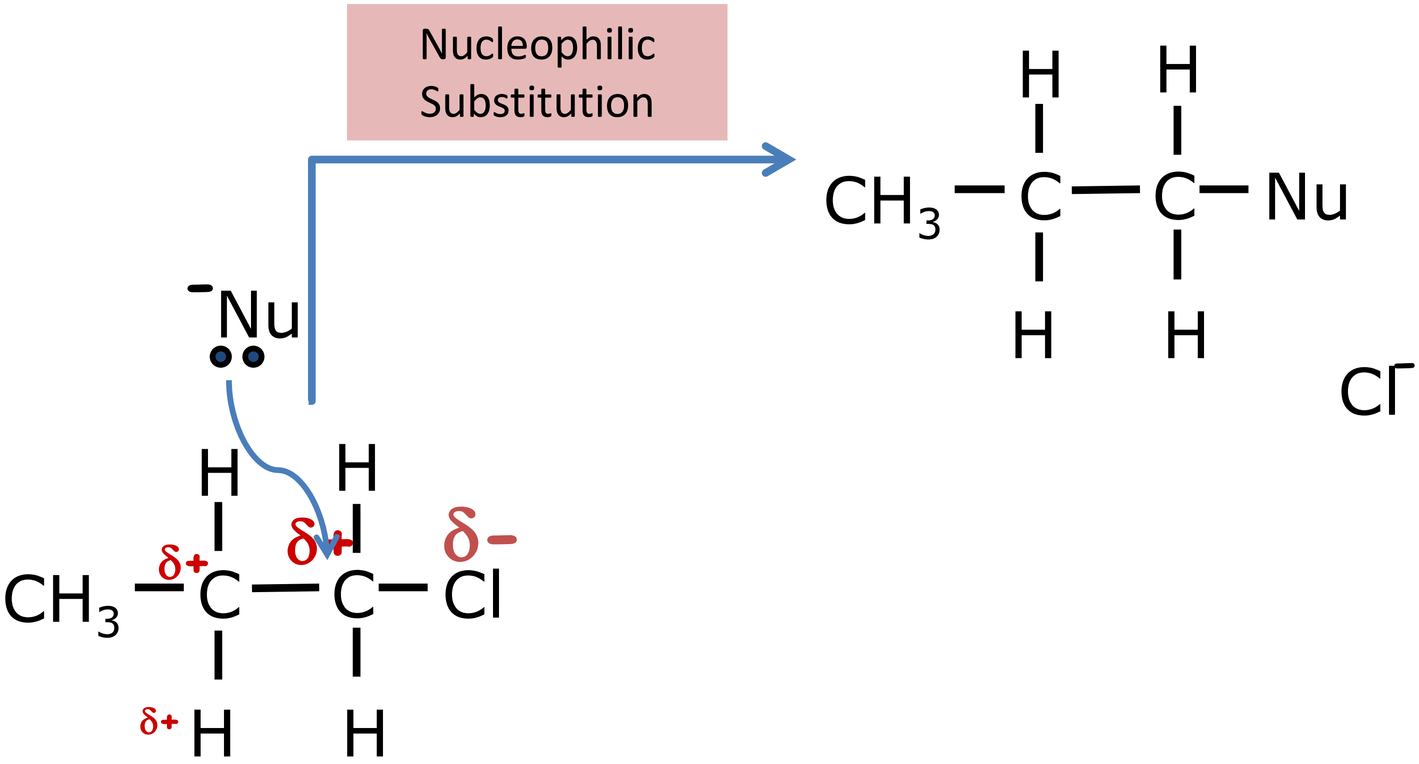
$$CH_3CHBrCH_3 + OH^- \longrightarrow CH_3CH{=}CH_2 + H_2O + Br^-$$

(in **ethanol**) propene



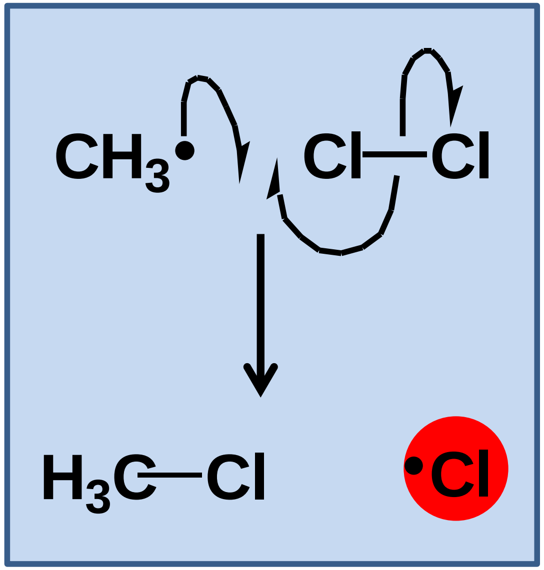
acting as a **base**
this time....

Nothing is Black and White! 2



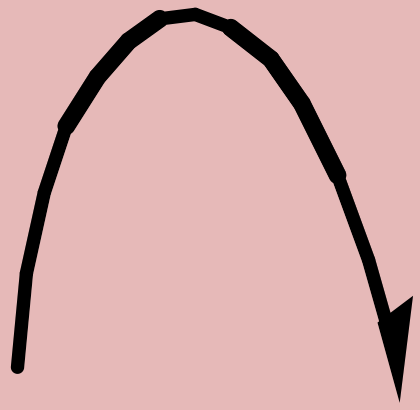
Free Radical Substitution of Alkanes

Light Induced Radical Formation and Subsequent Replacement Reactions



AS Level

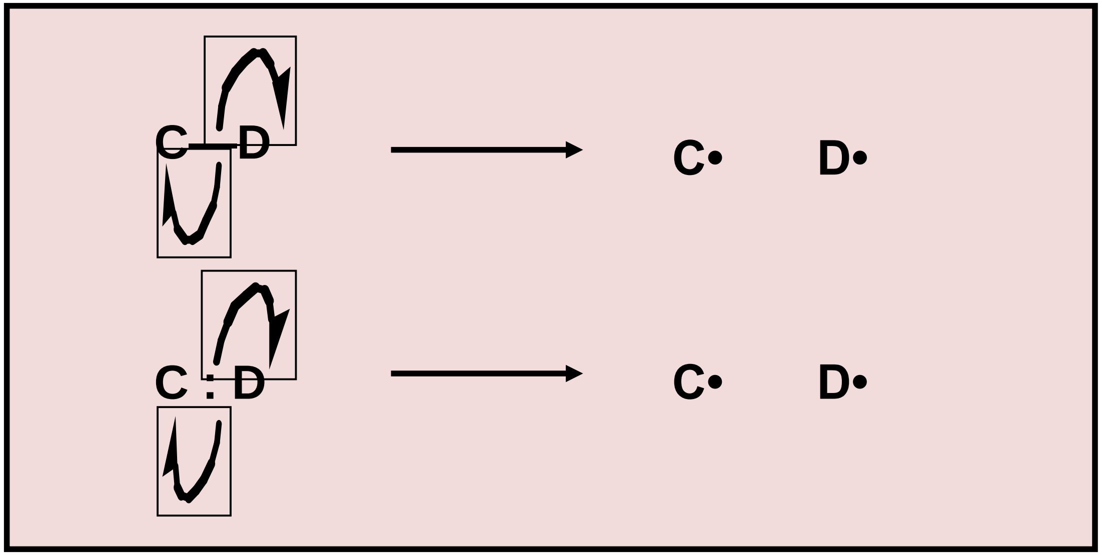
Reaction Mechanism 'Curly' Arrows



One Electron Movement

Single 'fish hook' headed arrow

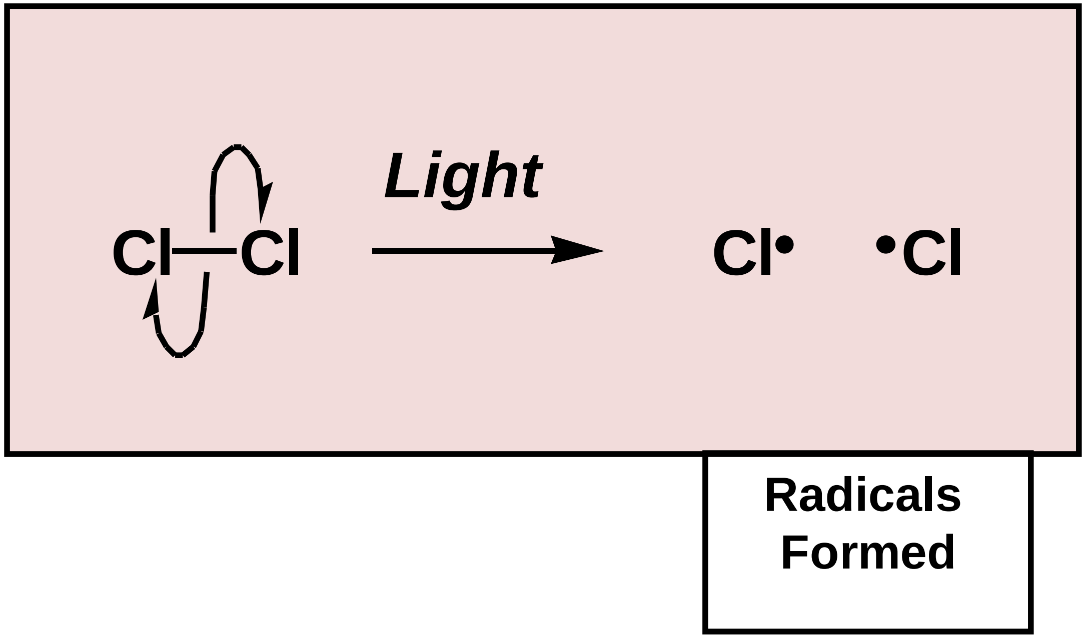
Homolytic Bond Cleavage



Electronegativty of atom A is usually similar to atom B

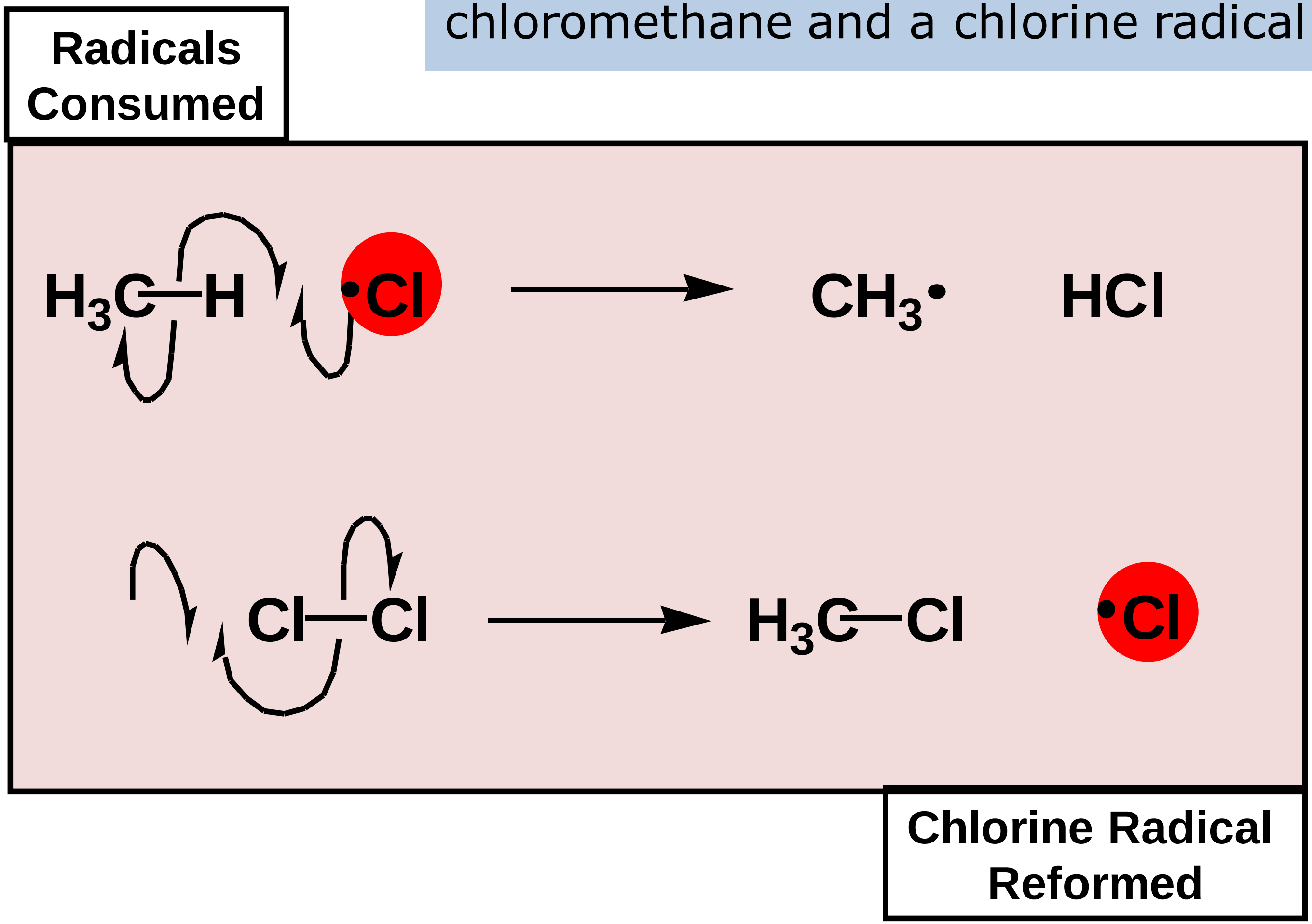
Initiation

the formation of chlorine radicals by the homolytic bond cleavage of diatomic chlorine, induced by light.



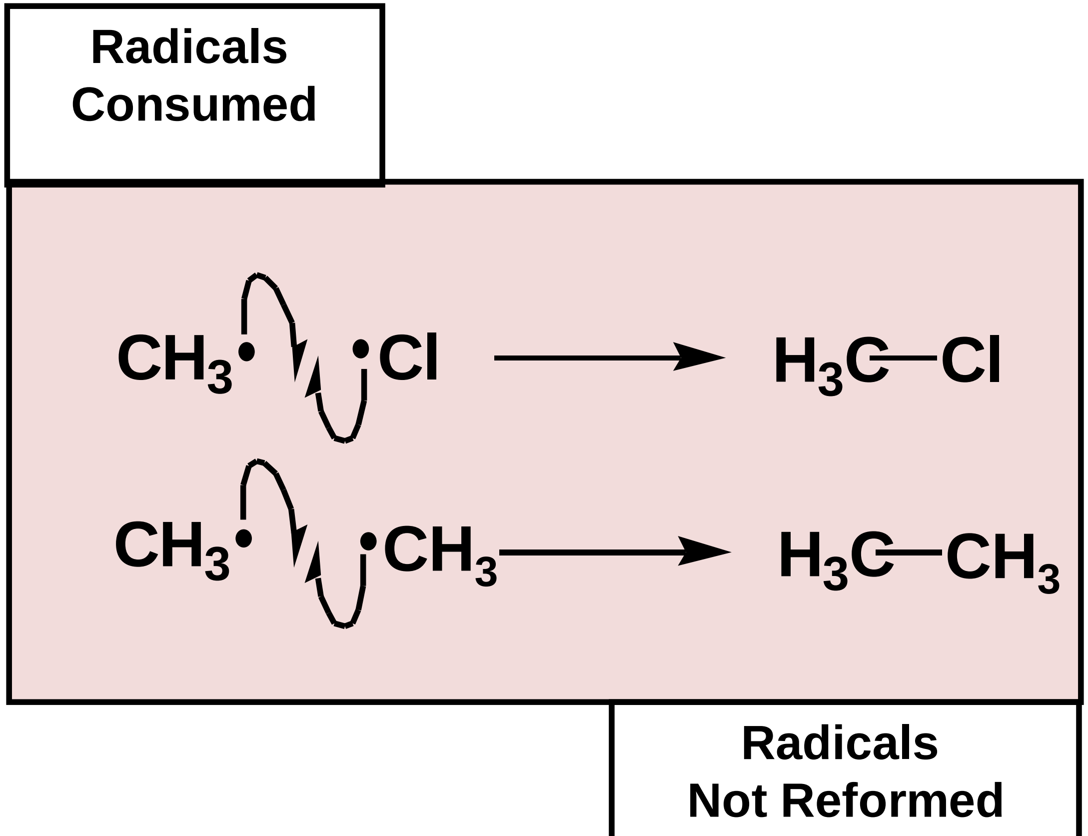
Propagation

reaction of the chlorine radicals with methane, which generates methyl radicals and HCl. Followed by the methyl radicals reacting with diatomic chlorine, to afford chloromethane and a chlorine radical.



Termination

reaction of two radical species leading to nonradical products.



Further Free Radical Chlorination Reactions

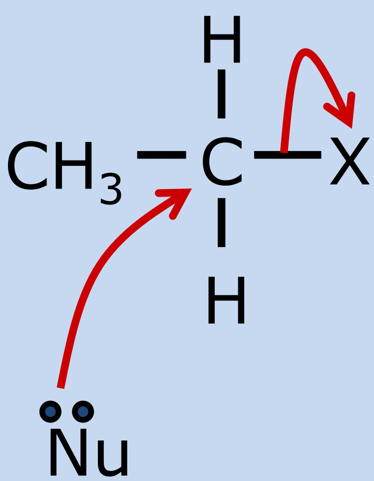
$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

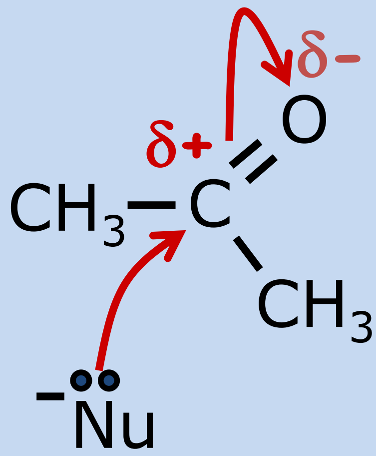
$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

Summary of the Chemistry Looked at

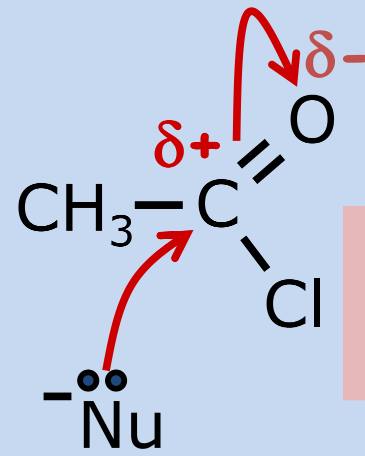
Nucleophilic Substitution



Nucleophilic Addition

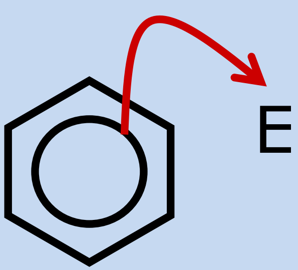


Nucleophilic Addition-Elimination

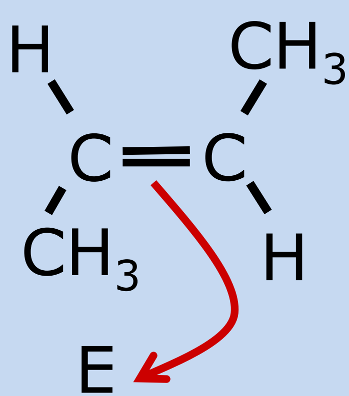


Then elimination of Cl^-

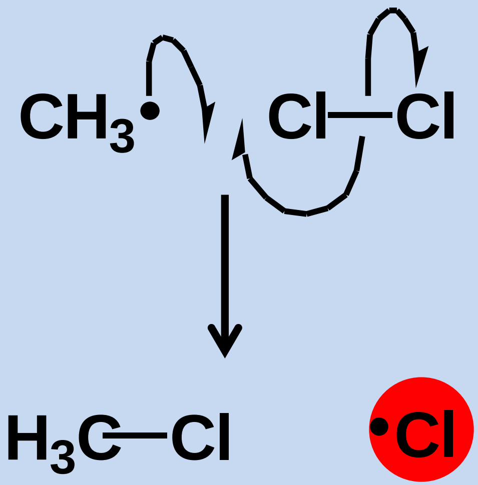
Electrophilic Substitution



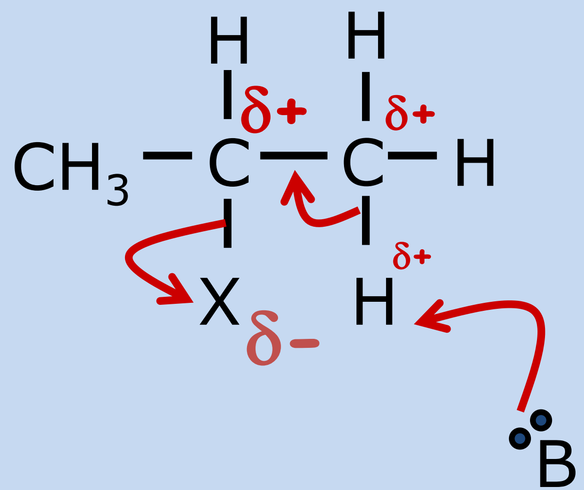
Electrophilic Addition



Free Radical Substitution



Elimination of HX



Concluding Comments

Is the reaction light induced?

Yes

Look for a bond with little or no electronegativity difference in a bonded pair of atoms

Initiate: Cleave bond homolytically

Propagate: generate new radicals

terminate: react radicals together

No

Identify bonds with large differences in **electronegativity** in a bonded pair of atoms.

Identify **polarity** to identify **electrophilc** centre

Identify **nucleophilic** centre in other reagent (lone pair of electrons) or **bonded pair of electrons** to donate to electrophilic centre

THANK YOU