

Coxey-House synthesis

Reactants: $R-X, R'-X$

Reagent: (i) ether
 CuX (ii)

~~Reagent~~: $R'-X$ (iii)

Intermediate: R_2CuLi

Product: $R-R', LiX, CuX$

Frankland's reaction

Higher symmetrical Alkane formation

Reagent: Zn dust

Reactant: $R-X$

Product: $R-R, ZnX_2$

Intermediate: ~~Zinc di-alkyl~~
di-alkyl Zincate

Physical properties

Alkane (C1-C4) \rightarrow colorless & odorless (gas)

Alkane (C5-C17) \rightarrow colorless & odorless (liquid)

(C18 \rightarrow) \rightarrow colorless solids

M.P., B.P. increase with molecular mass
decrease with branching

even-C Alkanes M.P. > odd-C Alkanes

better crystal
lattice fitting

Alkanes are lighter than water

Halogenation (except fluorination)

Reactant: Alkane

Reagent: $Cl_2/h\nu$

Intermediate: free radical

Product: Alkyl halide

Halogen Exchange Finkelstein reaction

Reactant: Alkyl halide

Reagent: Sodium halide
(in DMSO, Acetone)

Product: Alkyl Sodium
Sodium chloride

Nitration

~~Reactant~~ Alkane

Reagent: HNO_3 (150°C - 147°C)

Product: Nitroalkane
or Nitroalkyl-
intermediate

Sulphonation:

Ex - 1

Reactant: Alkane (C6 \rightarrow)

Reagent: H_2SO_4 (i)

burning H_2SO_4 (ii)

Reed's reaction

Reactant: propene

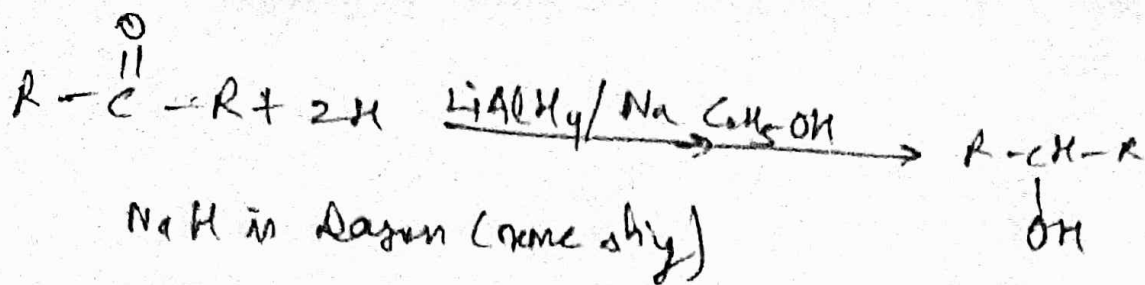
Reagent: $SO_2 \& Cl_2$ (i)

$h\nu$ (ii)

Product: propyl sulphonyl
chloride

use: Detergents (industrially)

(After Alkaline hydrolysis)



Clemmensen reduction

Aryl benzene \rightarrow Alkyl benzene

~~Ph-Ph~~ ! bond angle $101^\circ, 28'$

~~Ph-Ph~~ ! Non-(acid sensitive) Aldehydes and ketones

Reduction occurs on Zinc surface

Reagent: $Zn(Hg)$, $Na(Hg)$, HCl

Wittig-Fisher reduction

Sensitive

Reagent: KOH or KO \leftarrow

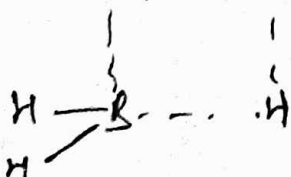
Hydroboration reduction

Reduction rxn

Reagent: B_2H_6 (i)

CH_3COOH (ii)

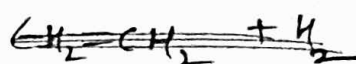
Transition state: $R-\overset{\overset{|}{\text{H}}}{\underset{\underset{|}{\text{H}}}{\text{C}}}-CH_2-\overset{\overset{|}{\text{H}}}{\underset{\underset{|}{\text{H}}}{\text{C}}}-CH_3$



Product: Alkane + water.

Reactant: Alkene

Catalytic hydration



breaks double bond

Reagent: $Ni/Pd/Pt + H_2$

cis addition

Alkyl Borane coupling

Reagent: $AgNO_3$, $NaOH$

Reactant: R_3B (Alkyl borane)

Product: $R-R$

Wittig reaction

Reactant: $R-X$

Reagent: Na , dry ether

Product: $R-R$, NaX

Intermediate: carbanion

isomerisation

Alkane (C₄→)

Reactant: Alkanes

Reagent: AlCl_3 , 400°C

or

$\text{AlX}_3 + \text{HX}$

or

$\text{Al}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$, 200°C

Product: stable Alkane isomers.

used: make good short branched fuel in petroleum industries.

combustion

Reactant: Alkanes

Reagent: excess O_2

Product: water
~~to~~ CO_2

Aromatisation

converts Aliphatic to aromatic

Reagents: $\text{Cr}_2\text{O}_3 - \text{Al}_2\text{O}_3$ (i)

Δ (ii)

Elimination reaction: removes 2 groups
proton
leaving group.

Types:

- 1) α -elimination (1,1) (same carbon elimination)
- 2) β -elimination (1,2) (adjacent carbon elimination)

Terms

Base: Negative molecule or neutral lone pair molecule.

Leaving group: Atom leaving the substrate with on extra pair of electron.

Leaving group tendency $\propto \frac{1}{\text{basic strength}}$; $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

Types of β mechanism

1) E1 -mechanism (C^\oplus formation) (Significant role of leaving group to base)
(polar solvent favours)

2) E2 -mechanism

3) ~~E3 -mechanism~~
(transition state similar to $\text{S}_{\text{N}}2$)

Reactivity: $3^\circ > 2^\circ > 1^\circ$
prefers non-polar solvent.

Completed Birch Reduction

Reactant: Alkene

Reagent: Na (i)
 $\text{NH}_3(\text{liq})$ (ii)

Product: $\text{R}-\text{CH}_2-\text{CH}_2-\text{R}'$

3) E1CB (CB means conjugate base formation)

Proton removal from α -carbon
 C^\ominus intermediate.

Drunk $\text{KOH} \neq$

Reactant: Alkyl halide $\text{R}-\text{X}$
Reagent: $\text{KOH} \neq \text{NaOH}$ (Alc.) (i)
 H-X (ii)

Product: Alkene.

Kind of reaction

Reactant: Alkyne

Reagent: H_2 ; Pd, BaSO₄ (poisoned palladium)

Product: Alkene

Possible poisons: BaSO₄, CaCO₃ (stop rxn after Alkene is reached).

Liquid Nitrogen & Glass wool rxn (Hydrolysis)

Reactant: Esters (R_1-O-R_2)

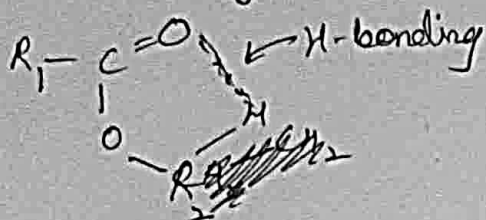
Reagent: Liquid N_2 + Glass wool (450°C)
(made from glass)

Product:

Alkyl pent \longrightarrow Alkene (cis)

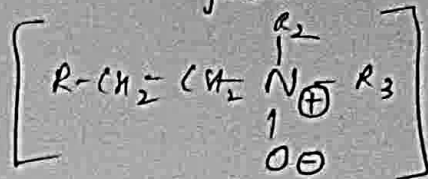
Alkanoate pent \longrightarrow Acid.

Intermediate: cyclic T.S.



Cope elimination

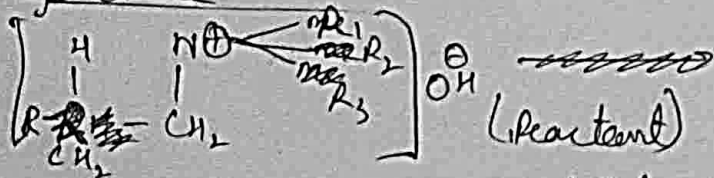
Reactant: Tertiary Ammonium hydroxide.



Reagent (Δ) heat (just heat)

Product: $R-CH=CH_2$ (ii) R_3-N-R_2 (OH (ii))

Quaternary ammonium (Hofmann's elimination)



Reagent: Heat (Δ) (just that, yeah, weird).

Products: $R-CH=CH_2 + H_2O + \overset{\overset{R_2}{|}}{\underset{\underset{R_3}{|}}{N}}-R_1$

Physical properties

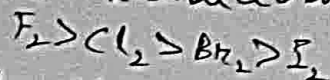
- (i) C_2-C_4 (colorless odorless gas)
- C_5-C_{17} (colorless liquids)
- C_{18} (solids)

Halogenation (vicinal)

Reactant: Alkene

Reagent: CCl_4 (polar solvent)

Product: vicinal dihalide.



(ii) insoluble in water (can't form H-bond)

(iii) B.P. & M.P. decreases with branching.

(iv) $M.P_{cis} < M.P_{trans}$ (trans packs more tightly in crystal)

monohalogenation

Reactant: Alkene

Reagent: HX (or HI)

Product: monohaloalkane

intermediate: \oplus

Mechanism Preference

Reactivity increases with C^+ stability
Capt. carb with $E2$)

geminal (same carbon)

vicinal (Alternate carbon)

Dihalide Reduction (coupling)

Reactant: $R-CHX_2$ (geminal)

Reagent: Zn (metal)

Product: $R-CH=CH-R'$ (i)

ZnX_2 (ii)

Yield: Self \uparrow Mechanism \uparrow

vicinal Halo removal

Reactant: $R-CH_2-CH_2-X$ (vicinal)

Reagent: Zn (metal)

Product: $R-CH_2-CH_3$ (No coupling)
 $+ ZnX_2$

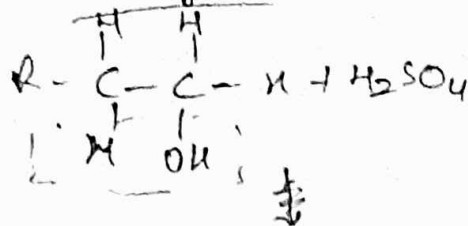
Halide cyclisation

Reactant: Non-geminal - Non-vicinal Alkyl halide

Reagent: Zn

Product: cyclising
 $+ ZnX_2$

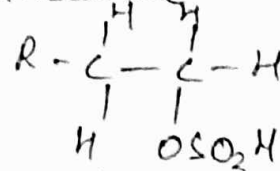
Dehydration (Acidic)



Reactant: $R-CH_2-CH_2-OH$
Alcohol

Reagent: H_2SO_4 ($160^\circ C$)

Intermediate:



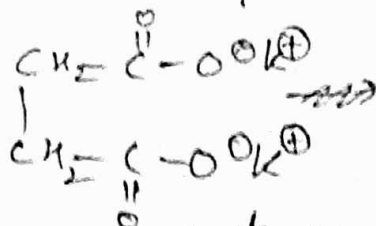
Product: Alkene

Alternate agents: Al_2O_3
 ThO_2

(give OH^- or H^+ somehow)
So it can leave.

Kolbe synthesis

Reactant: Na/K succinate



Anode product: Alkene
(degrade $-COO^-$)

Cathode product: KOH (i)
 H_2 (ii) \uparrow (gas)

~~Reaction~~

Bayer's reaction

Reactant: Alkene

Reagent: $[O]$ (oxidation) Alkaline $KMnO_4$ (i)
(Bayer's reagent)

Product: (bcr(ii))
vicinal diol

Hydroxylation

$R-C=C-R$ Reactant: Alkene

Reagent: OsO_4 (Osmium tetroxide) (i)
(ii) hot



intermediate: 5 membered ring (221)
($2C-2O\frac{1}{2}-1Os$)

between Alkene & reagent.

Product: (+/-) Racemic vicinal diol.

Ozonolysis (Reductive part)

~~Reactant~~ Reactant: Alkene

Reagent: O_3 (Ozone) - Zn, H_2O or CCl_4

Product: Ozonoid ring (5-membered)
(~~2C-3O~~ $2C-3O$) between in plane
of double ring.

Epoxidation

~~Reactant~~ $R_2C=CR_2 + \frac{1}{2} O_2$

Reactant: Alkene
Reagent: O_2 (g) (i)
(oxygen)

Harsh Silver
(Ag) (ii)

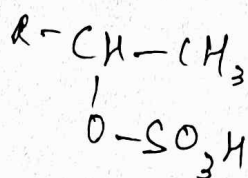
Product: cycloperoxy
ring
(epoxide)

Alkene reaction with H_2SO_4 (C^+)

(a) reactant: Alkene

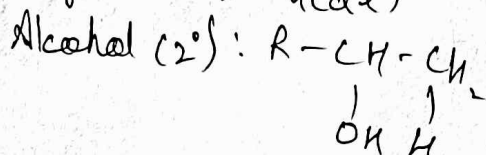
reagent: H_2SO_4 (conc.)

Alkyl hydrogen sulphate (product)



(b) reactant: Alkene (C^+)

reagent: H_2SO_4 (dil)



no mark rearrangement

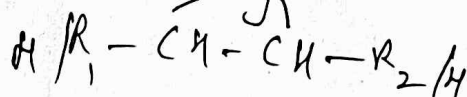
(Alkene \rightarrow Alcohol)

oxidation demercuration H^+

Reactant: Alkene

Reagent: $Hg(OAc)_2$ (i), H_2O (ii) $NaBH_4$ (iii)

intermediate: Hg^+-OAc



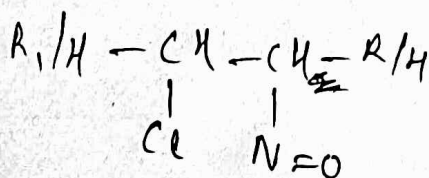
Product: Alcohol.

Addition of Nitrosyl halide (C^+) (Tilden's reaction)

Reaction: Alkene

Reagent: $O=N-Cl$ (Nitrosyl chloride) [Tilden's reagent]

Product: Alkyl nitrosyl chloride



Acidic $KMnO_4$ oxidation

Reactant: Alkene

Reagent: $KMnO_4/H^+$

Product: Acid (i)

(if not alkene)

CO_2 (ii)

(g) \uparrow

(iii) H_2O

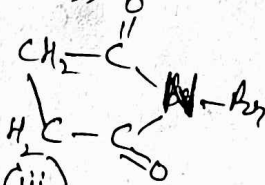
(makes acid)

unlike vicinal diol for
Bayer's)

Allylic/Benzylic Bromination

Reactant: Allyl, Benzy (C^+)

Reagent: NBS



Product: Bromoallyl
/ Bromobenzyl