Electrochemistry

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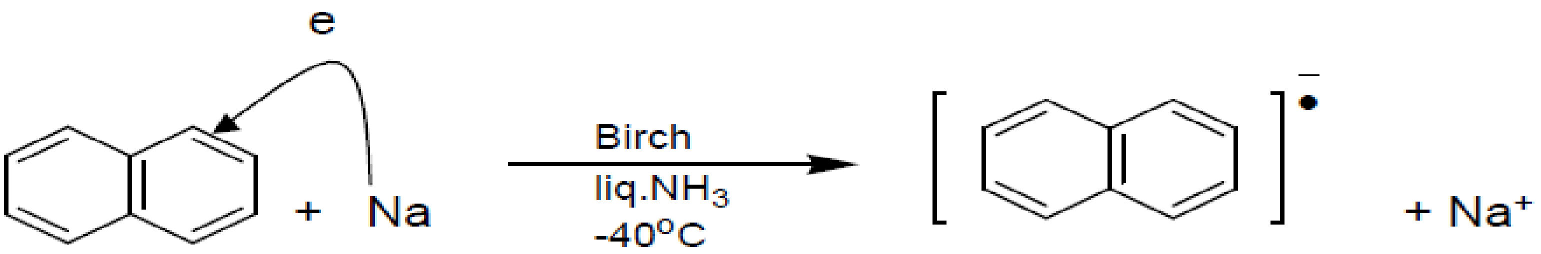
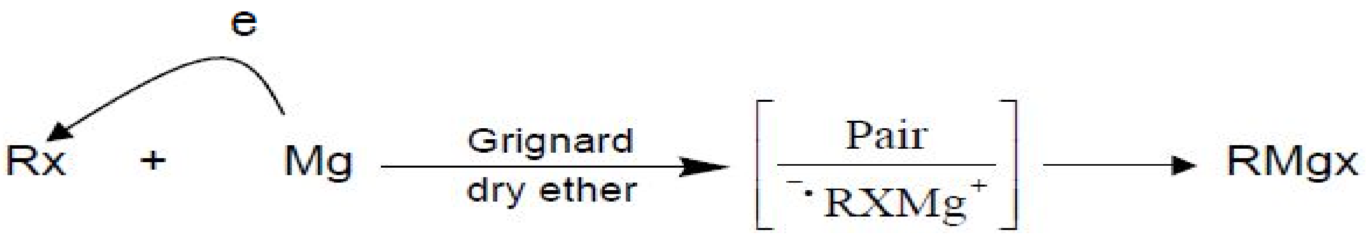
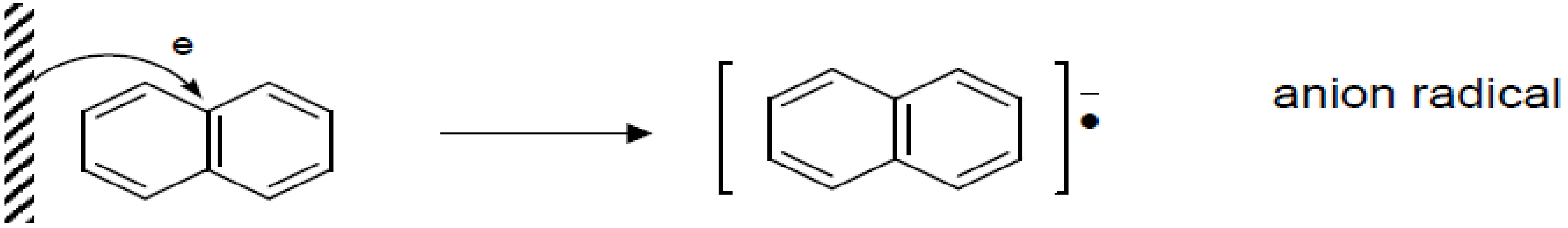
Two typical examples of one electron transfer reactions in conventional chemical organic synthesis are the Brich reduction and the Grignard reaction





In electrolytic cells the ET reactions would be effected by direct ET from the cathode to the organic molecule,



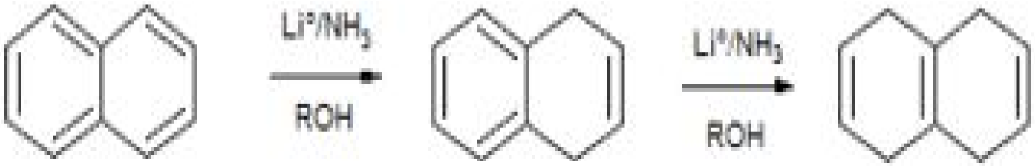
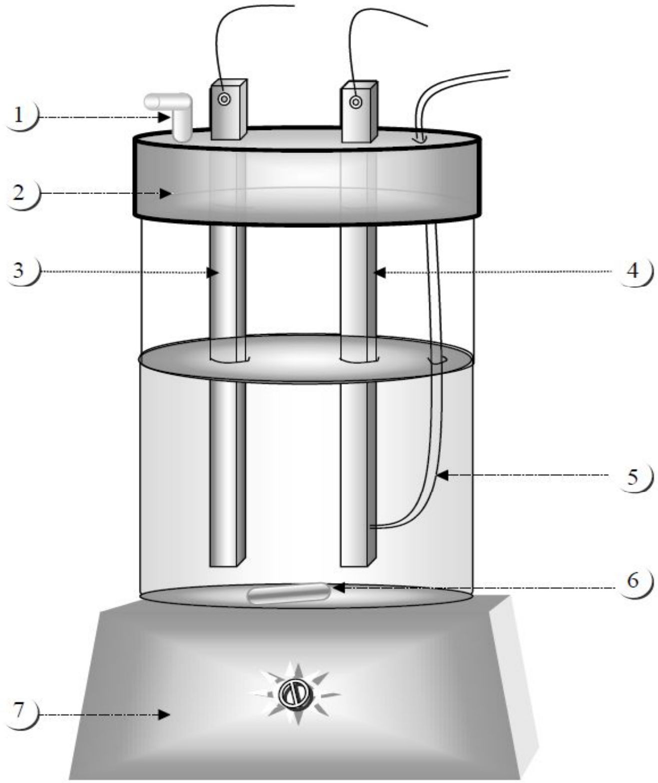


Fig: 3.1: BEAKER TYPE UNDIVIDED CELL



1) Gas Vent

2) Bakelite Cap

3) Counter Electrode

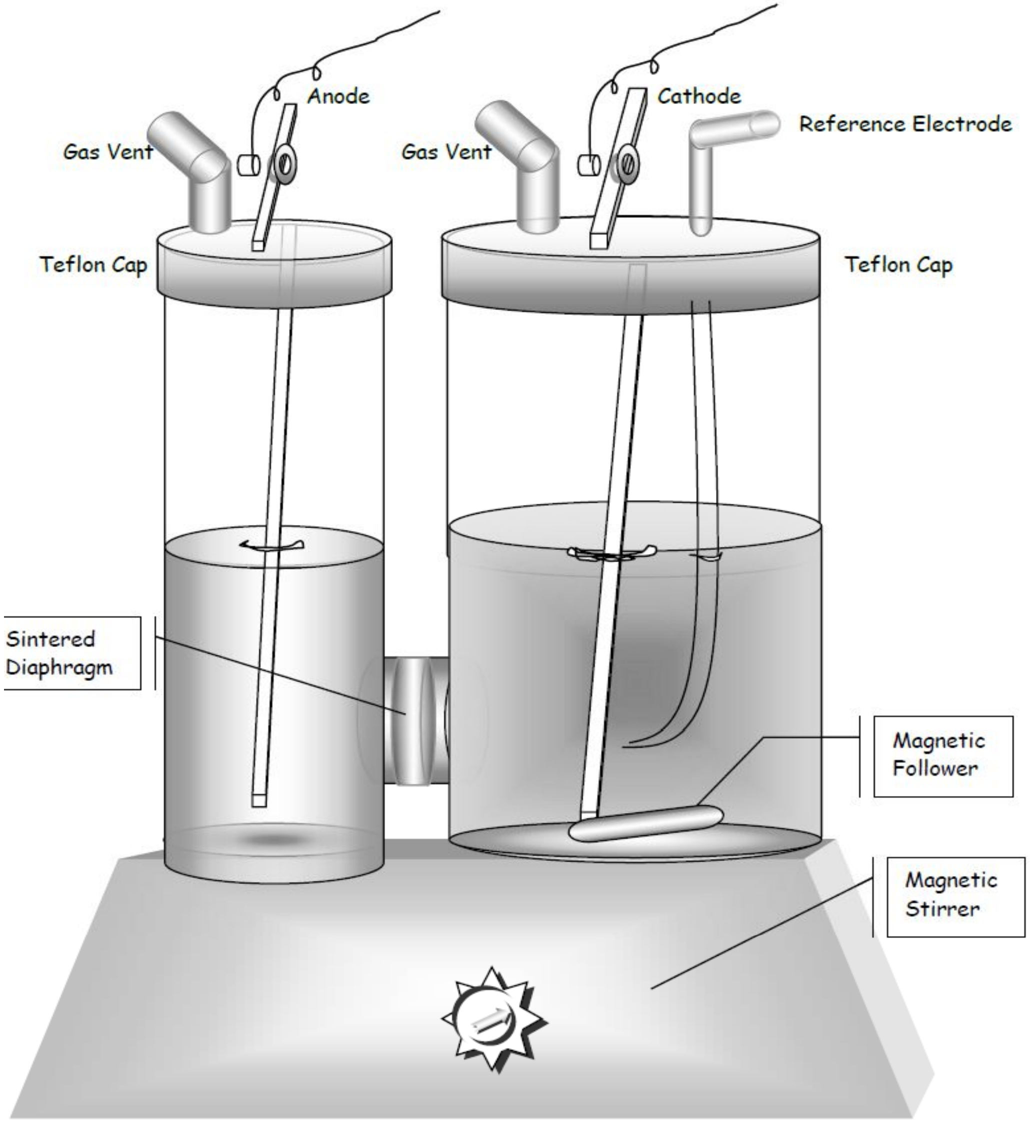
4) Working Electrode

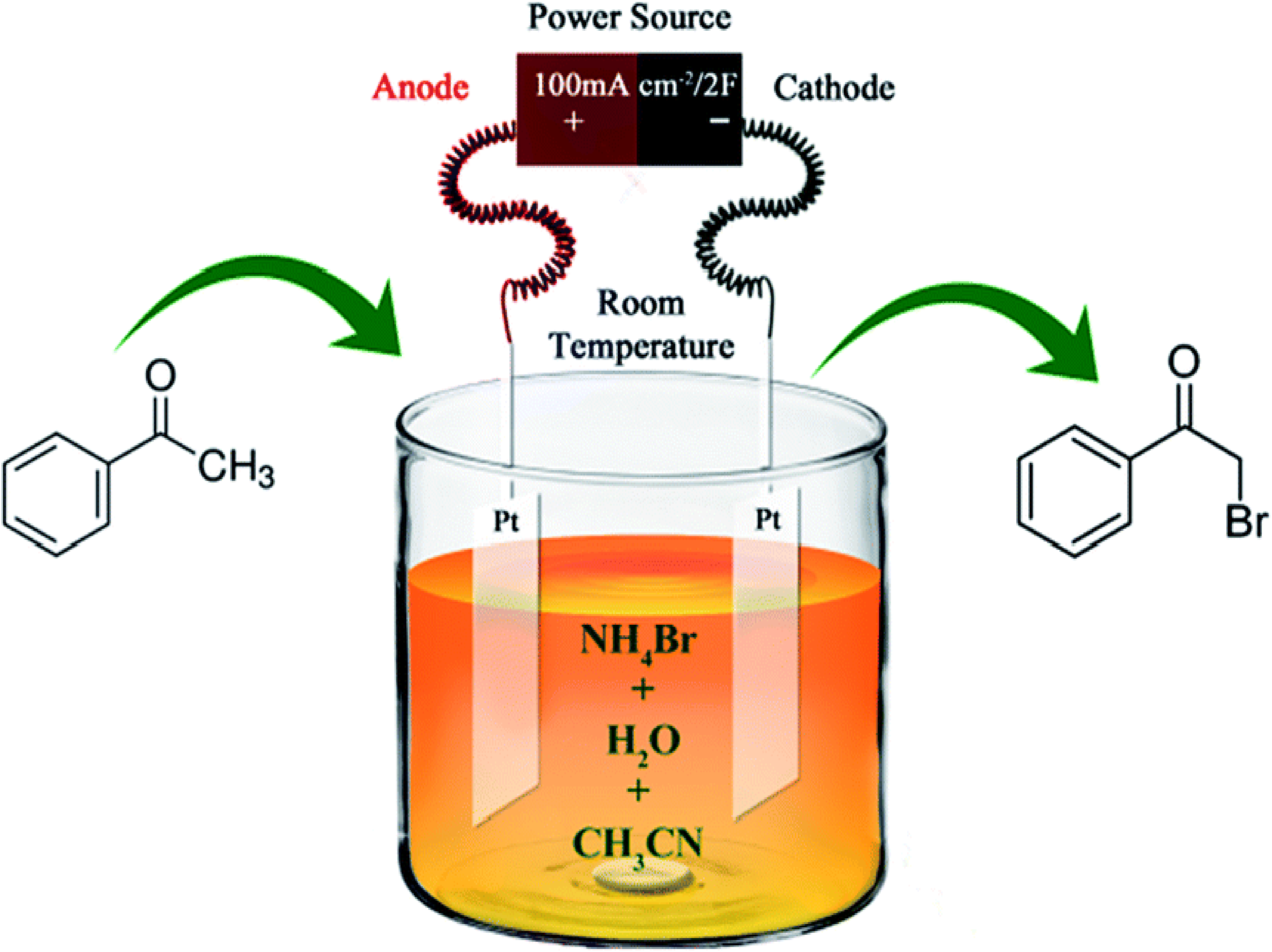
5) Luggin Capillary

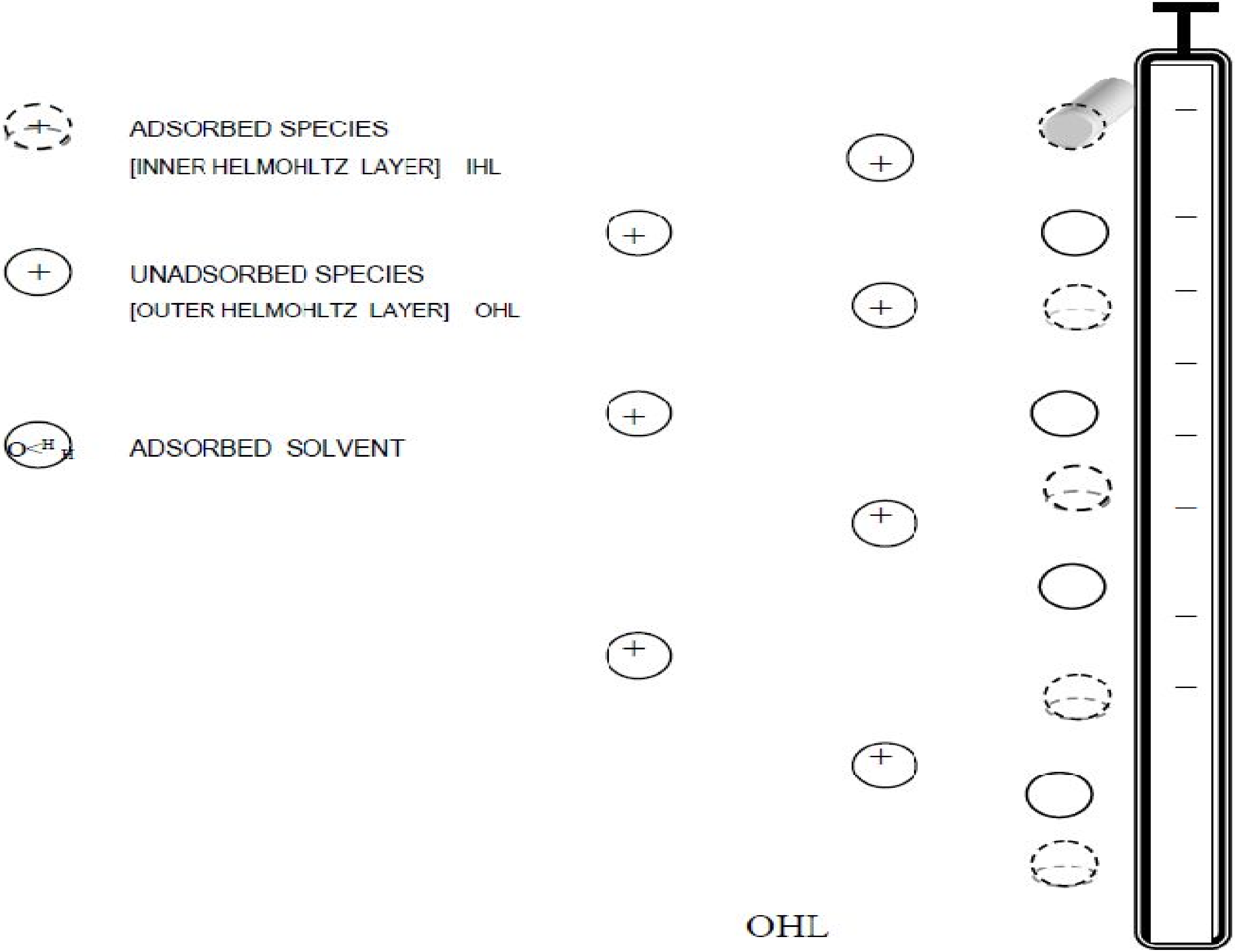
6) Magnetic Follower

7) Magnetic Stirrer

FIG: 3.2: DIVIDED H - CELL

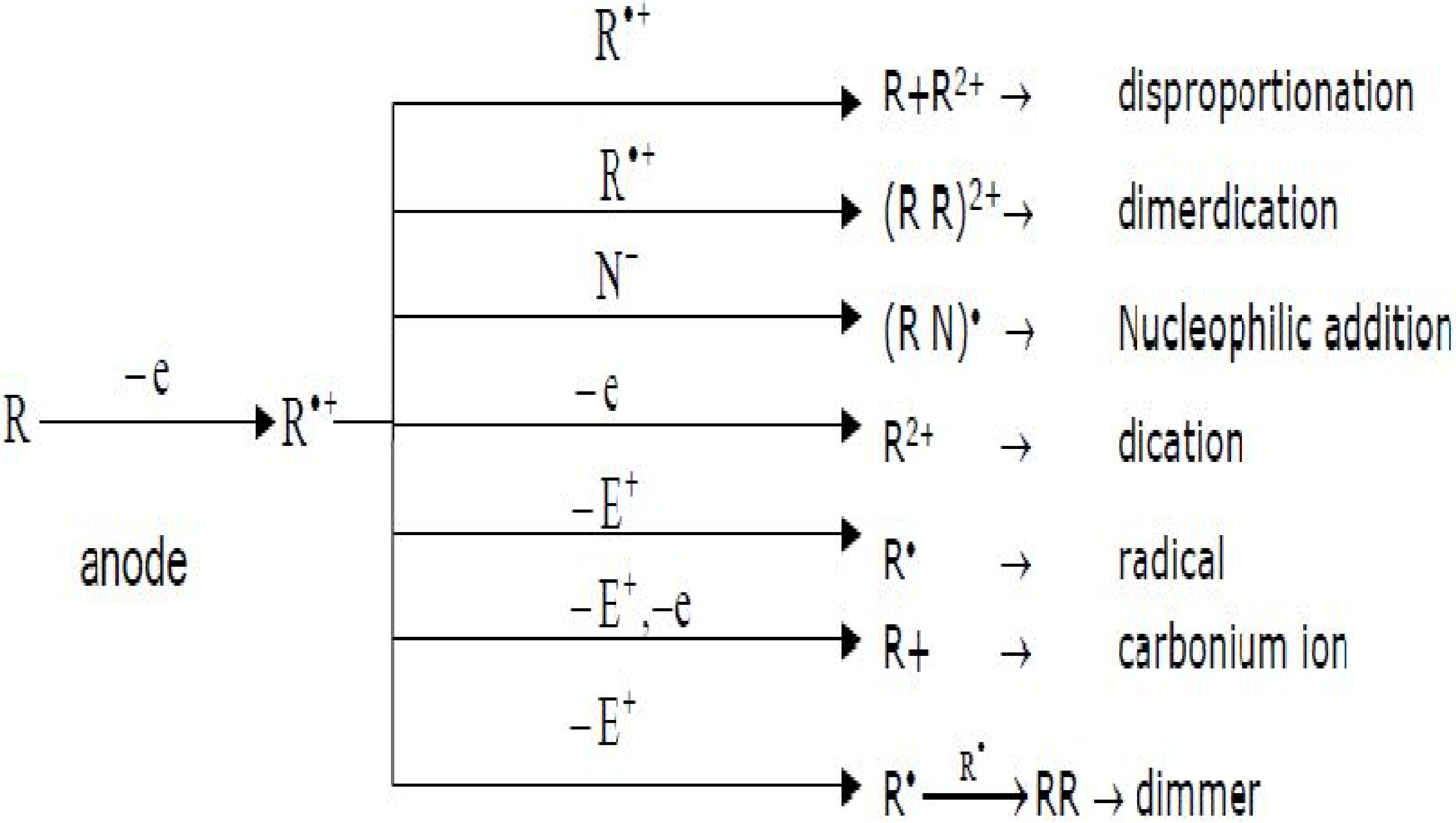



Power Source
Anode
100mA cm-2/2F
+
−
Cathode
Room Temperature
O
CH3
Pt
Pt
NH4Br
+
H2O
+
CH3CN
O
Br


ADSORBED SPECIES
[INNER HELMOHLTZ LAYER] IHL
UNADSORBED SPECIES
[OUTER HELMOHLTZ LAYER] OHL
O<H H
ADSORBED SOLVENT
OHL

I. Direct Reactions

a. *Anodic Reactions*



$R \xrightarrow{-e} R^{\bullet +}$

anode

$R^{\bullet +} \xrightarrow{R^{\bullet +}} R + R^{2+} \rightarrow$ disproportionation

$R^{\bullet +} \xrightarrow{R^{\bullet +}} (R\,R)^{2+} \rightarrow$ dimerdication

$R^{\bullet +} \xrightarrow{N^{-}} (R\,N)^{\bullet} \rightarrow$ Nucleophilic addition

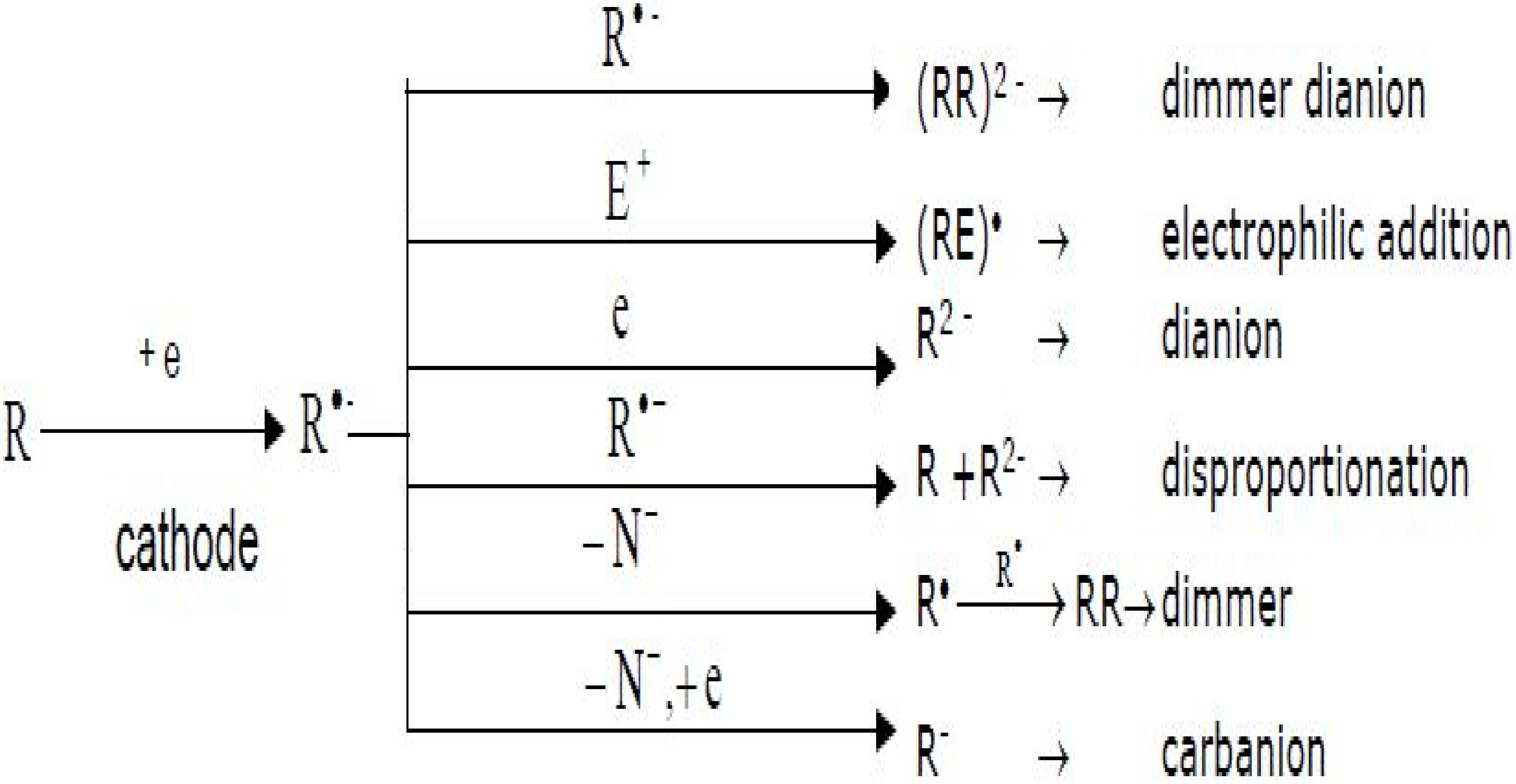
$R^{\bullet +} \xrightarrow{-e} R^{2+} \rightarrow$ dication

$R^{\bullet +} \xrightarrow{-E^{+}} R^{\bullet} \rightarrow$ radical

$R^{\bullet +} \xrightarrow{-E^{+}, -e} R+ \rightarrow$ carbonium ion

$R^{\bullet +} \xrightarrow{-E^{+}} R^{\bullet} \xrightarrow{R^{\bullet}} RR \rightarrow$ dimmer

b. *Cathodic Reactions*



$R \xrightarrow[\text{cathode}]{+e} R^{\bullet -}$

$\xrightarrow{R^{\bullet -}} (RR)^{2-} \rightarrow$ dimmer dianion

$\xrightarrow{E^{+}} (RE)^{\bullet} \rightarrow$ electrophilic addition

$\xrightarrow{e} R^{2-} \rightarrow$ dianion

$\xrightarrow{R^{\bullet -}} R + R^{2-} \rightarrow$ disproportionation

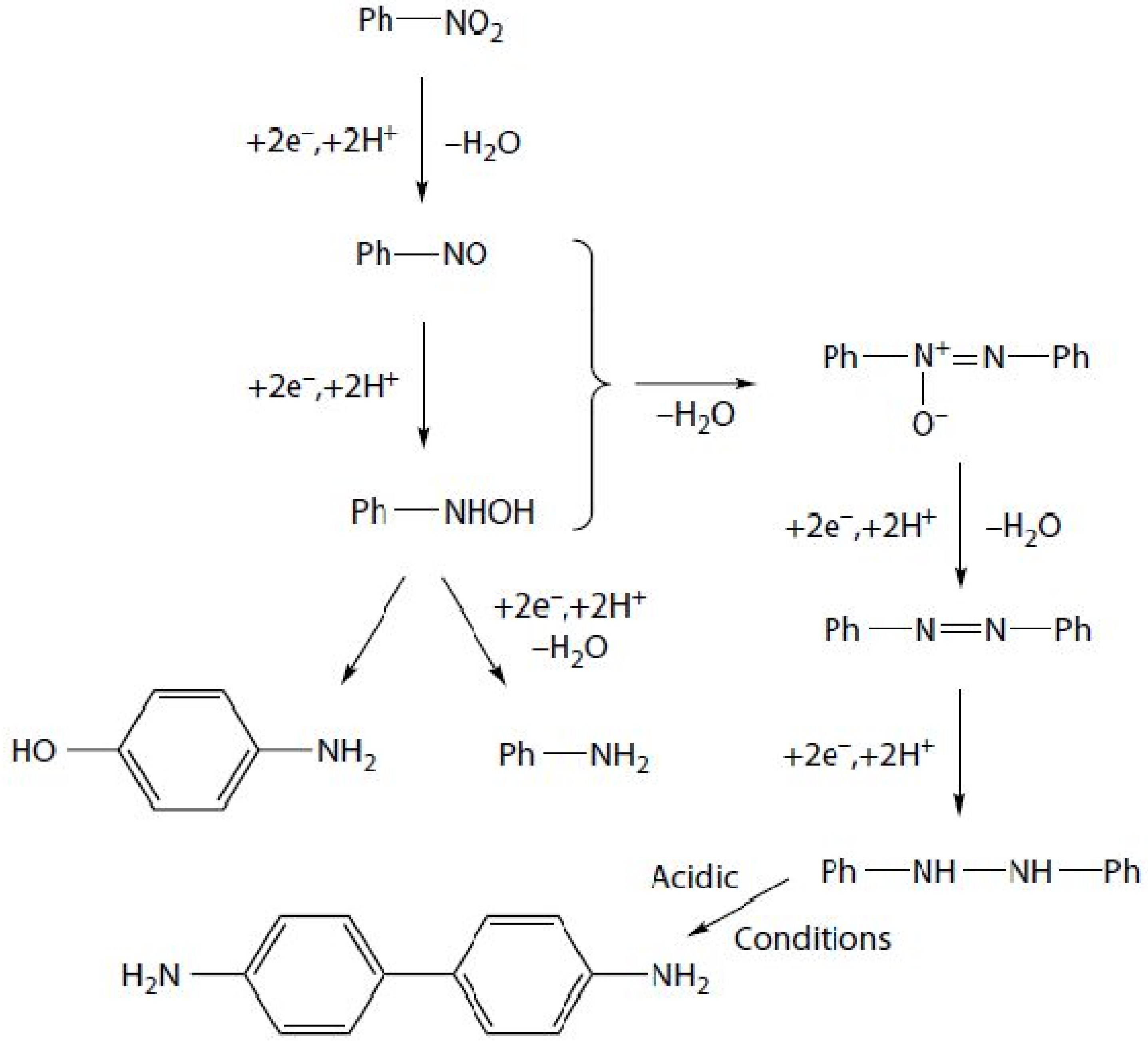
$\xrightarrow{-N^{-}} R^{\bullet} \xrightarrow{R^{\bullet}} RR \rightarrow$ dimmer

$\xrightarrow{-N^{-}, +e} R^{-} \rightarrow$ carbanion

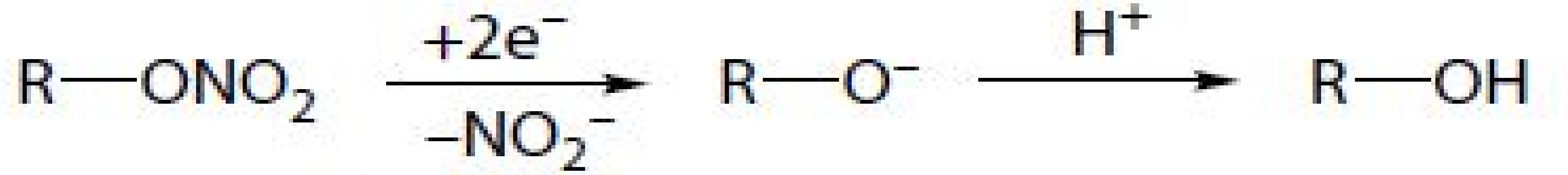
II. Indirect or Mediated Reactions

$$M \xrightarrow[\text{Cathode}]{+e} M^{\bullet -} \xrightarrow{R} R^{\bullet -} + M$$

$$M \xrightarrow[\text{anode}]{-\, e} M^{\bullet +} \xrightarrow{R} R^{\bullet +} + M$$



SCHEME 30.1 Overview of the products that may result from the reduction of nitrobenzene.



$$R\text{—}ONO_2 \xrightarrow[-NO_2^-]{+2e^-} R\text{—}O^- \xrightarrow{H^+} R\text{—}OH$$

The anodic oxidation of hydrocarbons is a convenient method for the preparation of a number of useful products that in many cases can be prepared only with difficulty by other methods. Examples

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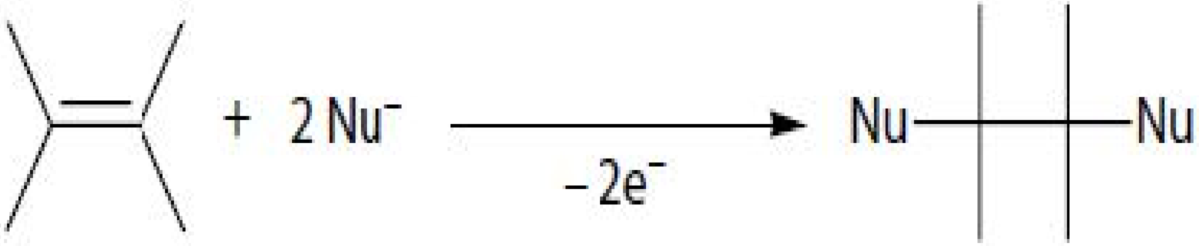
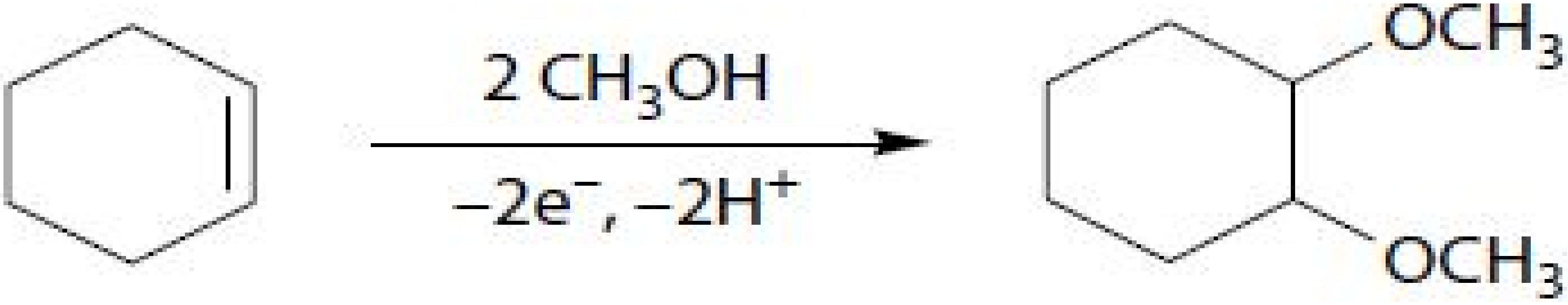
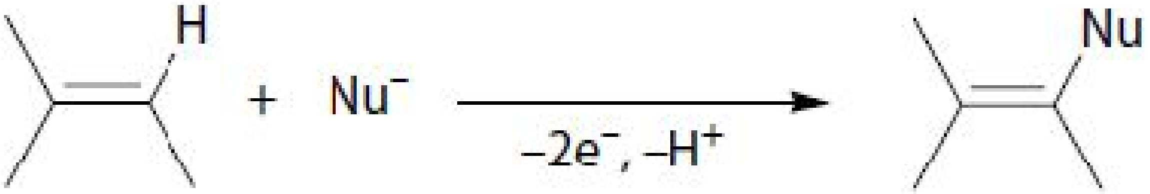
A. ADDITION REACTIONS

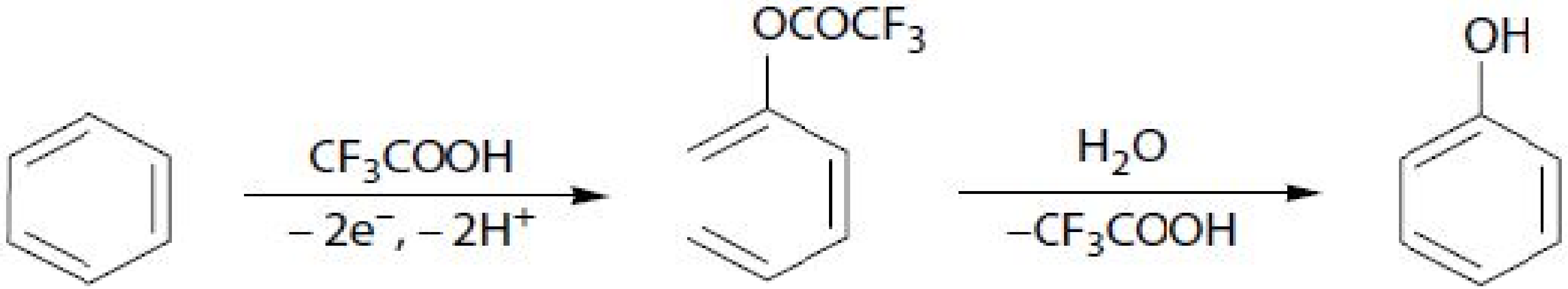




B. SUBSTITUTION REACTIONS

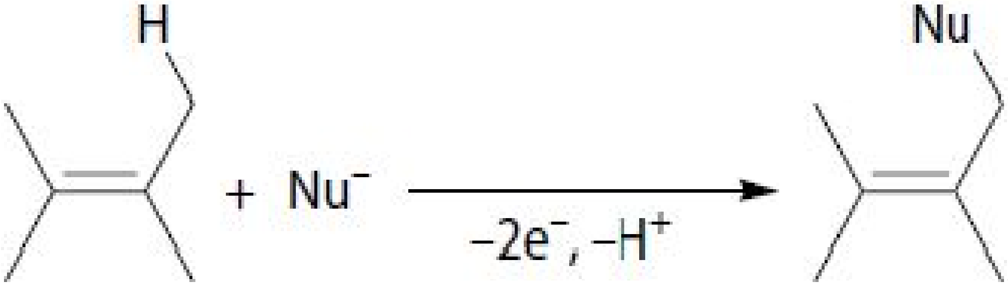
1. Nuclear Aromatic Substitution

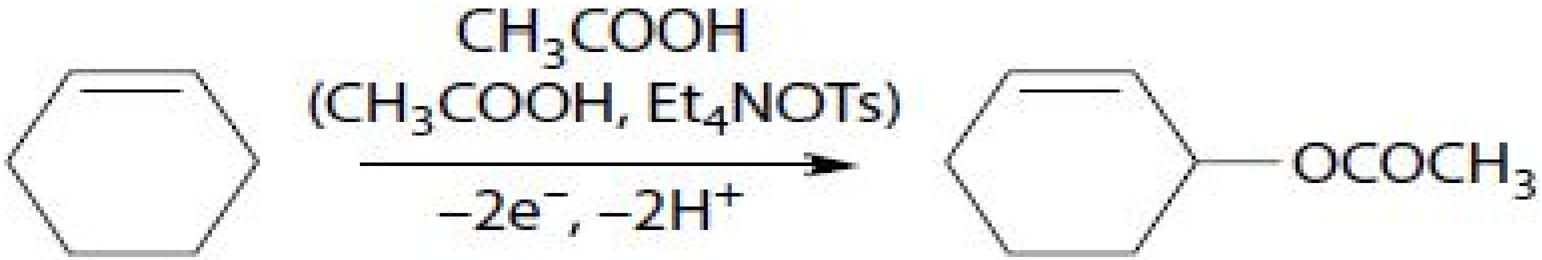




2. Alkyne Substitution

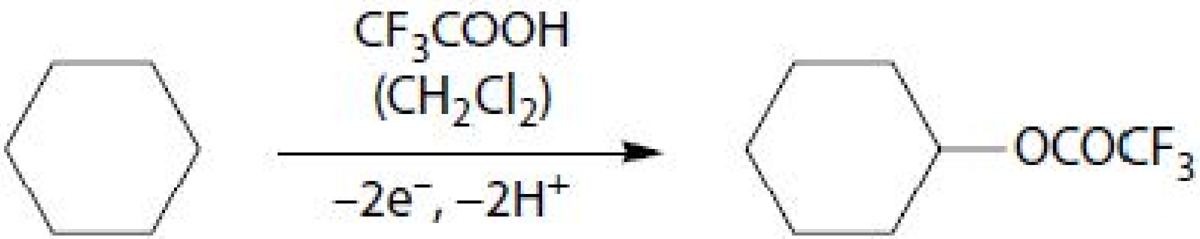
3. Substitution at α-Carbon Atoms



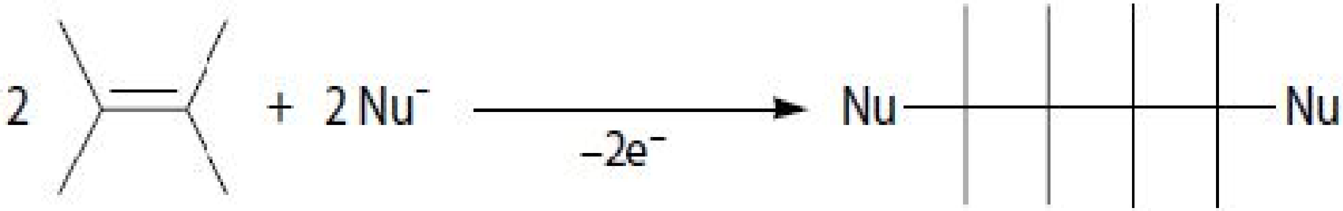


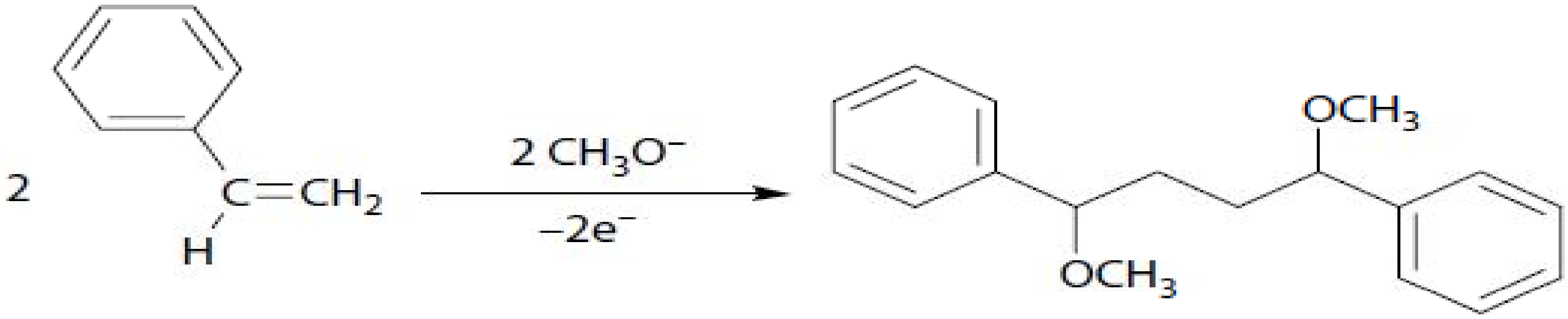
4. Substitution in Saturated Aliphatic Hydrocarbons

$$R{-}H + Nu^- \xrightarrow[-2e^-,\ -H^+]{} R{-}Nu$$



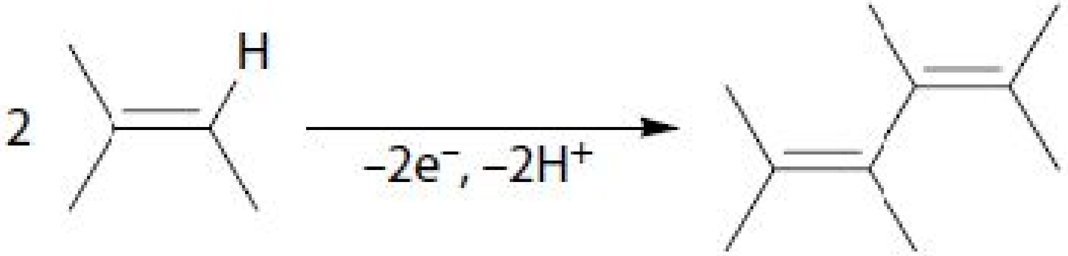
C. DIMERIZATION–ADDITION REACTIONS

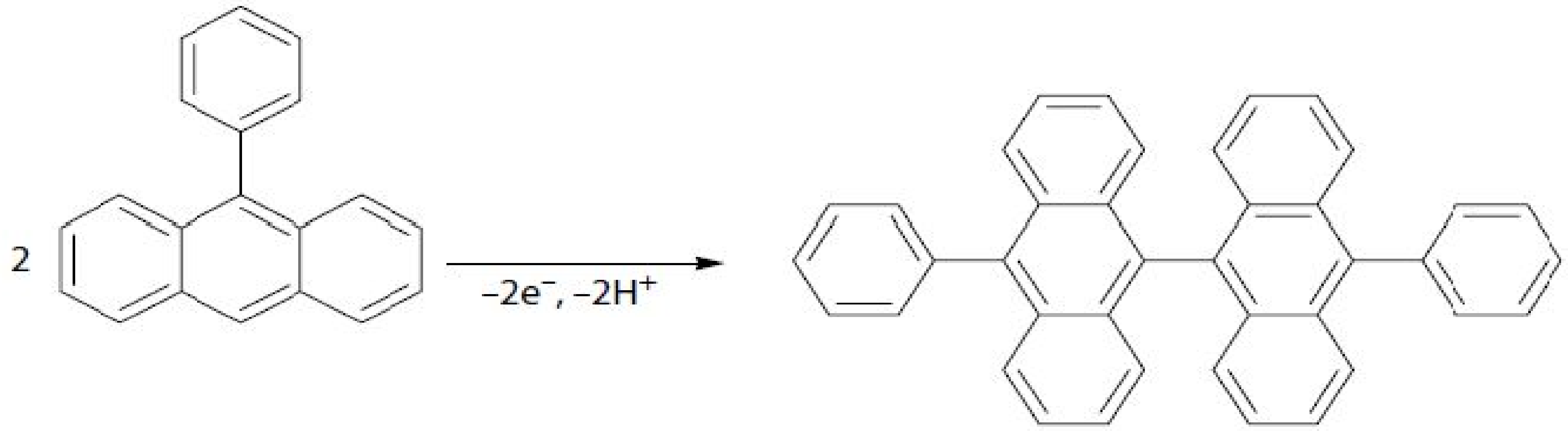




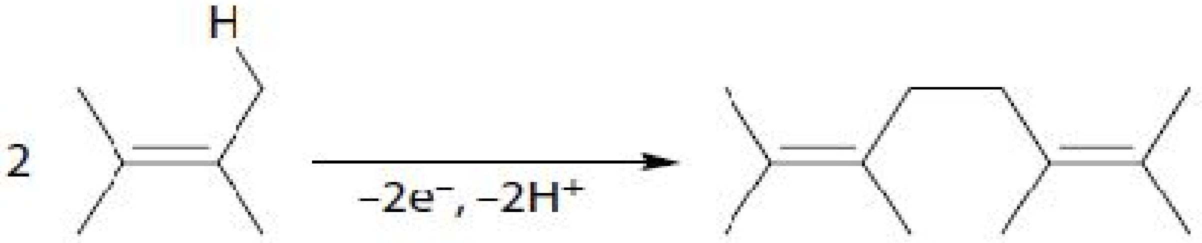
D. DIMERIZATION–ELIMINATION REACTIONS

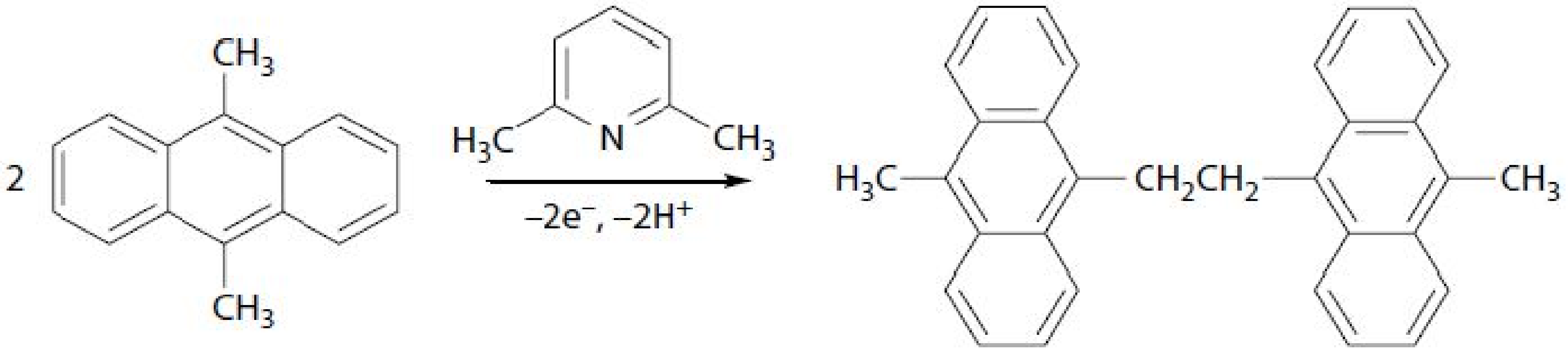
1. Nuclear Dimerization and Dimerization of Alkenes





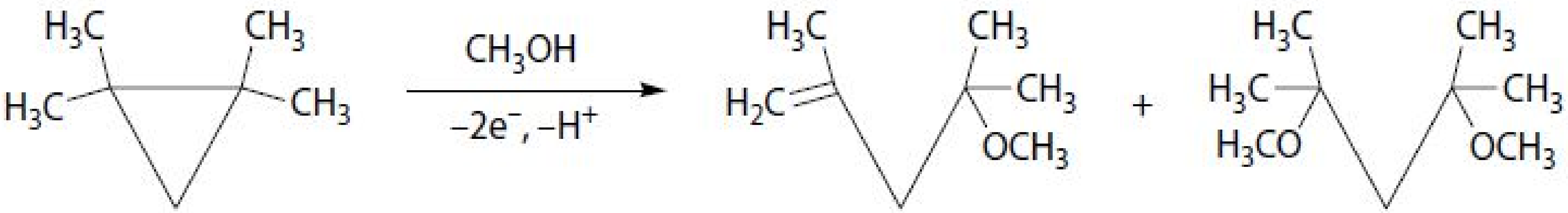
2. Dimerization at α-Carbon Atoms





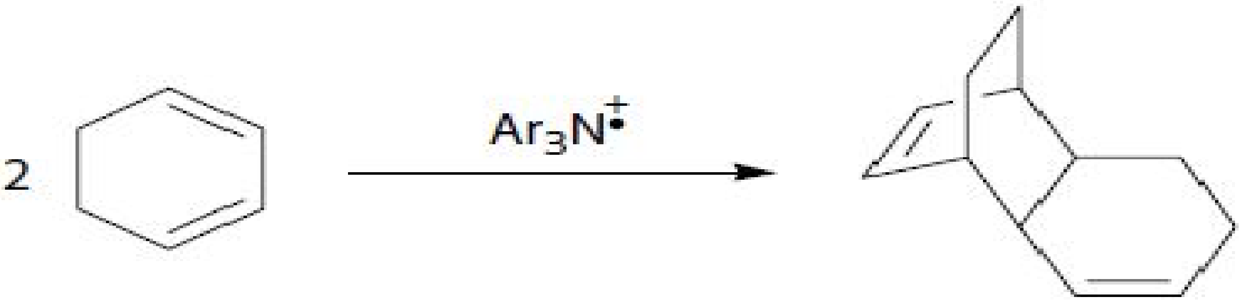
E. CLEAVAGES

The release of steric strain plays a central role in the anodic oxidative ring opening of cyclopropanes.

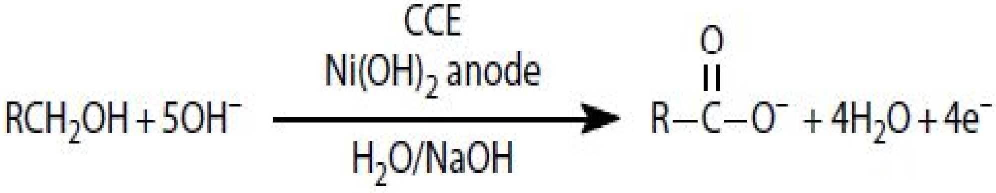


F. CHAIN REACTIONS

The radical cation catalyzed cycloadditions of the Diels–Alder type are well known and have been

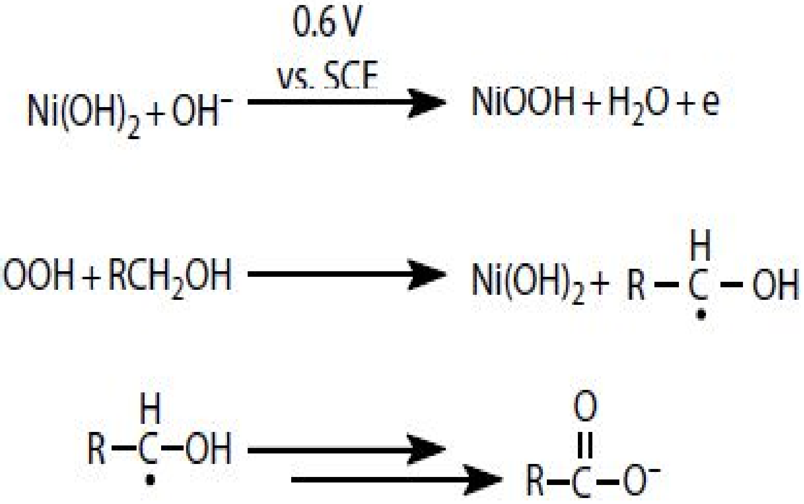


The nickel electrode has to be activated prior to electrolysis by the deposition of a thin $Ni(OH)_2$ film from an aqueous basic Ni(II) salt solution. From this film, a black surface layer of Ni(III) oxide hydroxide is continuously electrogenerated during electrolysis (see Scheme 26.10) [31,32]. After the rate-determining radical hydrogen abstraction, an α-hydroxyl radical is formed that is readily oxidized to the ketone in the case of secondary alcohols and to carboxylic acid in the case of aldehydes



$$RCH_2OH + 5OH^- \xrightarrow[H_2O/NaOH]{\text{CCE, } Ni(OH)_2 \text{ anode}} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^- + 4H_2O + 4e^-$$

SCHEME 26.9 Alcohol oxidation on the $Ni(OH)_2$ electrode.



$$Ni(OH)_2 + OH^- \xrightarrow{0.6\text{ V vs. SCE}} NiOOH + H_2O + e$$

$$NiOOH + RCH_2OH \longrightarrow Ni(OH)_2 + R-\overset{H}{\underset{\bullet}{C}}-OH$$

$$R-\overset{H}{\underset{\bullet}{C}}-OH \longrightarrow\longrightarrow R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^-$$

SCHEME 26.10 Mechanism for electro-oxidations on the $Ni(OH)_2$ electrode.

ii) Kolbe's electrolytic method:

An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms at the anode.

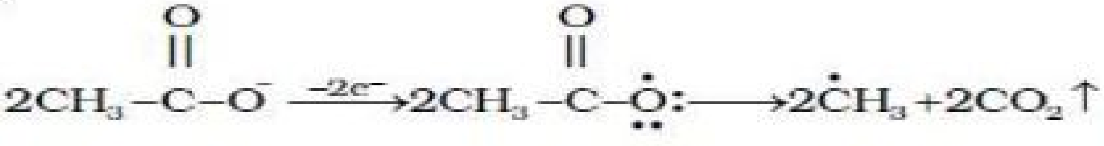
$$\underset{\text{Sodium acetate}}{2CH_3COO^-Na^+} + 2H_2O \xrightarrow{\text{Electrolysis}} CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$

The reaction is supposed to follow the following path:

i)

$$2CH_3COO^-Na^+ \rightleftharpoons 2CH_3-\overset{\overset{O}{\|}}{C}-O^- + 2Na^+$$

ii)At anode:



$$2CH_3-\overset{\overset{O}{\|}}{C}-O^- \xrightarrow{-2e^-} 2CH_3-\overset{\overset{O}{\|}}{C}-\underset{\cdot\cdot}{\dot{O}}: \longrightarrow 2\dot{C}H_3 + 2CO_2\uparrow$$

Acetate ion

Acetate free radical

Methyl free radical

iii) $H_3\dot{C} + \dot{C}H_3 \longrightarrow H_3C-CH_3\uparrow$

iv)At cathode:

$H_2O + e^- \rightarrow {}^-OH + \dot{H}$

$2\dot{H} \rightarrow H_2\uparrow$