GREEN CHEMISTRY

Laurea Magistrale in Scienze Chimiche

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6 CFU – AA 2017-2018

Green Chemistry 12

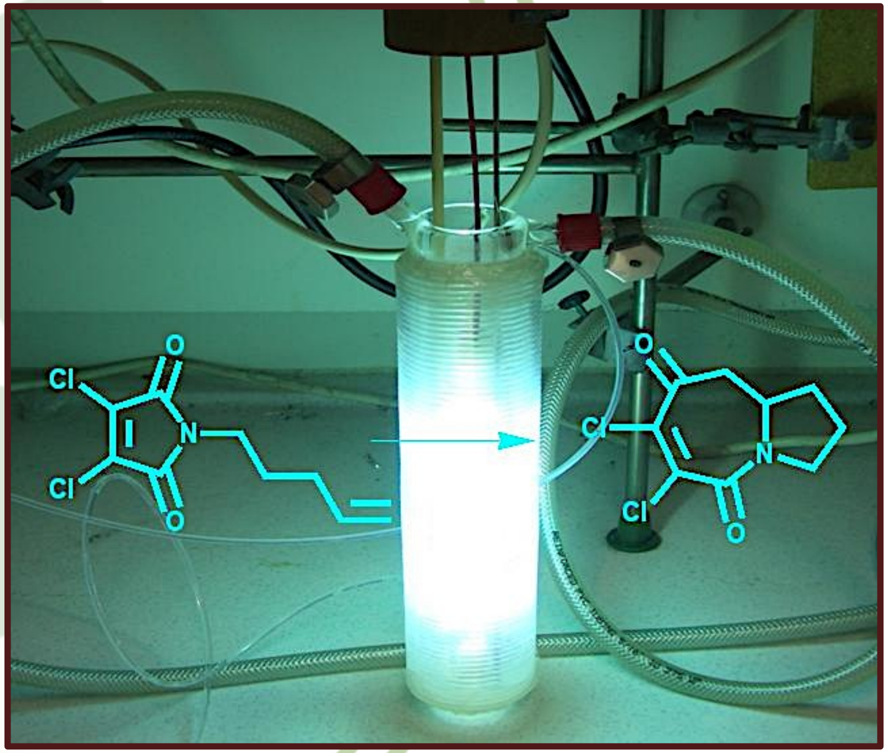
GREEN TECHNIQUES FOR ORGANIC SYNTHESIS IV

PHOTOCHEMICAL SYNTHESIS IN GREEN CHEMISTRY

INTRODUCTION

Introduction

Photochemistry is the study of the chemical reactions and physical changes that result from interactions between matter and visible or ultraviolet light.



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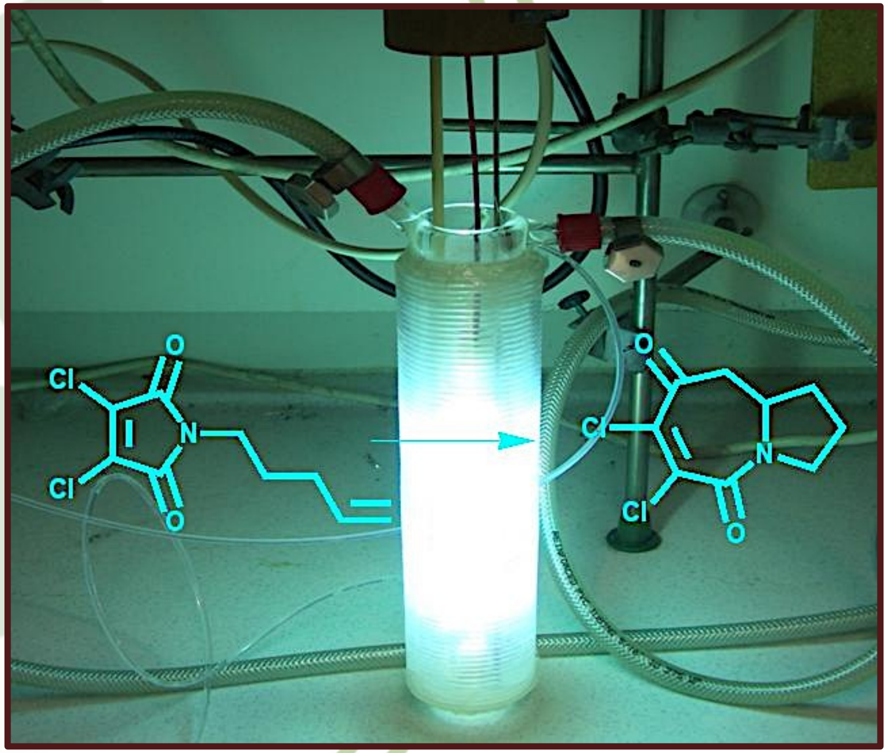


Introduction

The production of the electronically-excited state by photon absorption is the feature that characterizes photochemistry and separates it from other branches of chemistry.

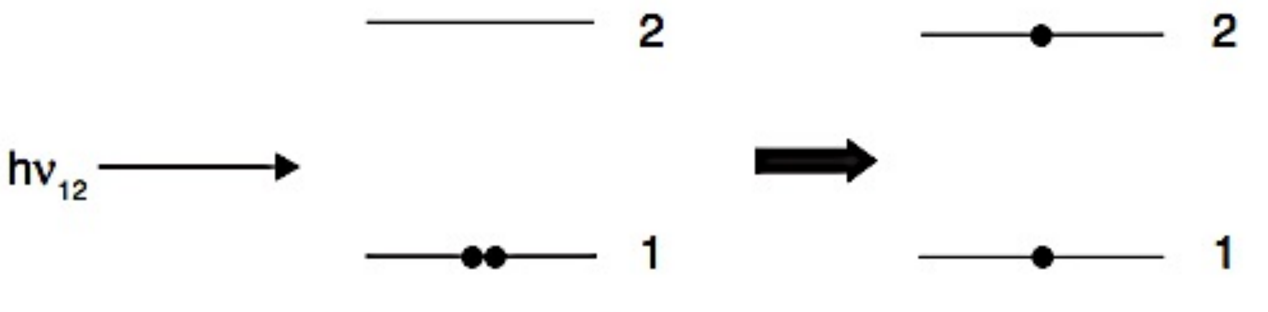


Figure 1.2 The process of light absorption

Introduction

There are three basic processes of light-matter interaction that can induce transfer of an electron between two quantized energy states:

1. In absorption of light, a photon having energy equal to the energy difference between two electronic states can use its energy to move an electron from the lower energy level to the upper one, producing an electronically-excited state. The photon is completely destroyed in the process, its energy becoming part of the total energy of the absorbing species.

$$R + h\nu_{12} \rightarrow R^*$$

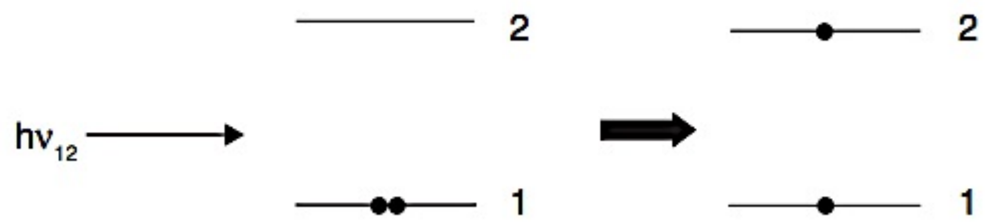


Figure 1.2 The process of light absorption

Introduction

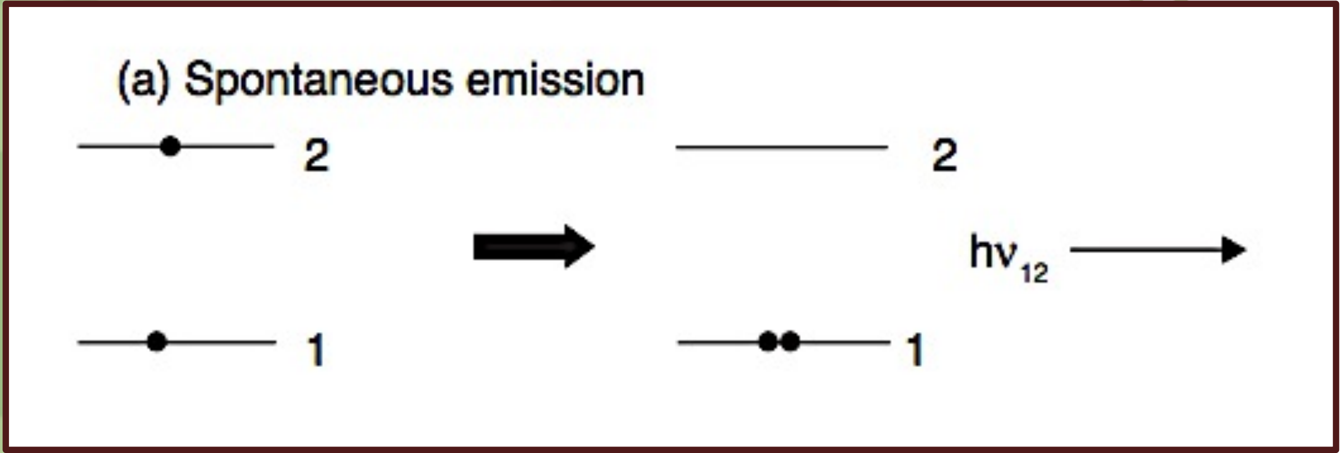
Two fundamental principles relating to light absorption are the basis for understanding photochemical transformations:

- The Grotthuss–Draper law states that only light which is absorbed by a chemical entity can bring about photochemical change.
- The Stark–Einstein law states that the primary act of light absorption by a molecule is a one-quantum process. That is, for each photon absorbed only one molecule is excited.

Introduction

There are three basic processes of light-matter interaction that can induce transfer of an electron between two quantized energy states:

2. Spontaneous emission occurs when an excited atom or molecule emits a photon of energy equal to the energy difference between the two states without the influence of other atoms or molecules

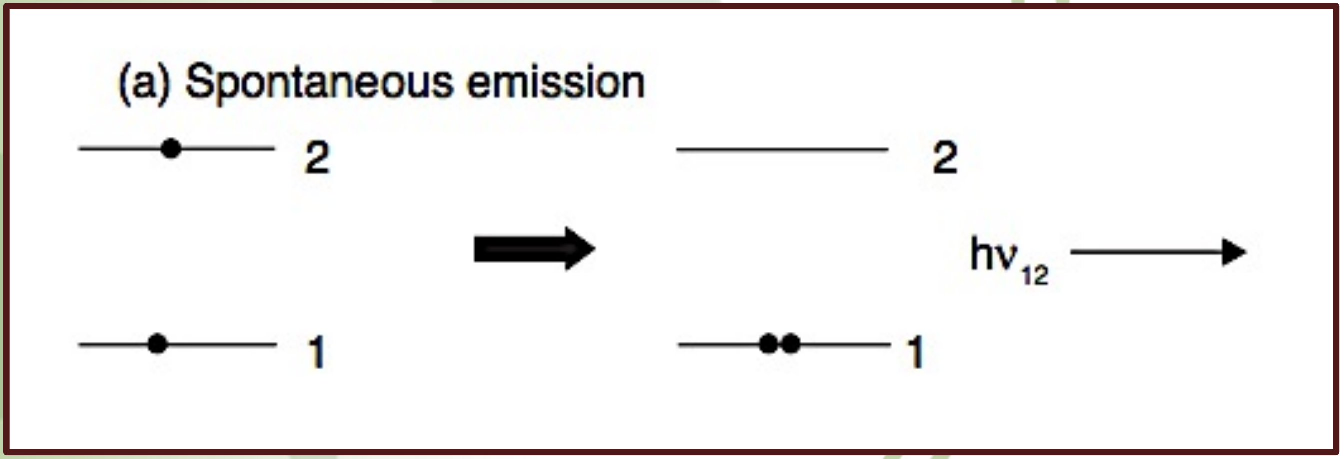


Introduction

2. Spontaneous emission occurs when an excited atom or molecule emits a photon of energy equal to the energy difference between the two states without the influence of other atoms or molecules

Light is emitted from the bulk material at random times and in all directions, such that the photons emitted are out of phase with each other in both time and space. Light produced by spontaneous emission is therefore called incoherent light.

$$R^* \rightarrow R + h\nu_{12}$$

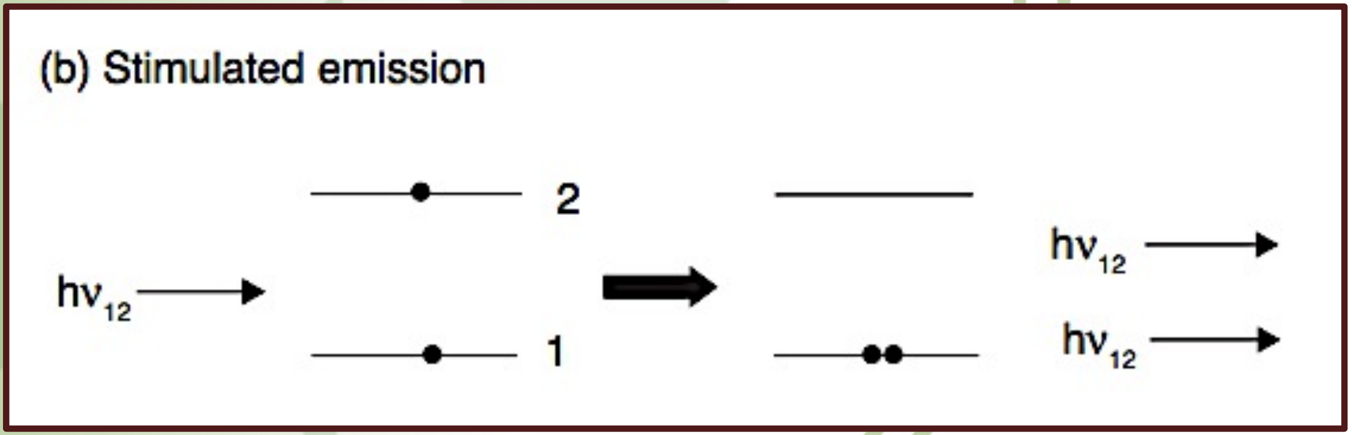


Introduction

3. Stimulated emission occurs when a photon of energy equal to the energy difference between the two states interacts with an excited atom or molecule

The photons produced by stimulated emission are in phase with the stimulating photons and travel in the same direction; that is, the light produced by stimulated emission is coherent light.

$$R^* + h\nu_{12} \rightarrow R + 2h\nu_{12}$$



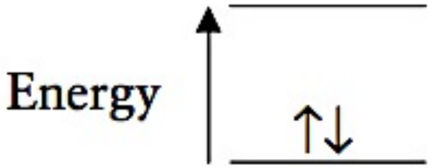
Introduction

The total spin, S, of a number of electrons can be determined simply as the sum of the spin quantum numbers of the electrons involved and a state can be specified by its spin multiplicity:

$$S = \sum m_s$$

$$\text{Spin multiplicity} = 2S + 1$$

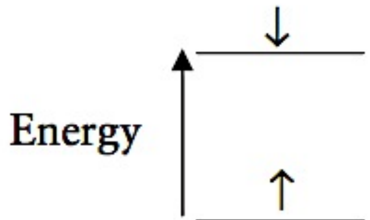
Introduction



$$\text{Total spin } S = \frac{1}{2} - \frac{1}{2} = 0$$

$$\text{Spin multiplicity} = (2S+1) = 1$$

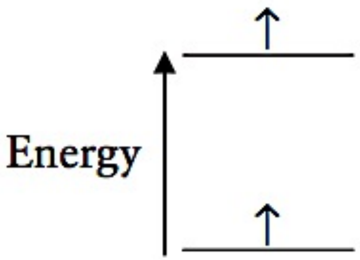
ground-state singlet



$$\text{Total spin } S = \frac{1}{2} - \frac{1}{2} = 0$$

$$\text{Spin multiplicity} = (2S+1) = 1$$

excited singlet state



$$\text{Total spin } S = \frac{1}{2} + \frac{1}{2} = 1$$

$$\text{Spin multiplicity} = (2S+1) = 3$$

excited triplet state

Introduction

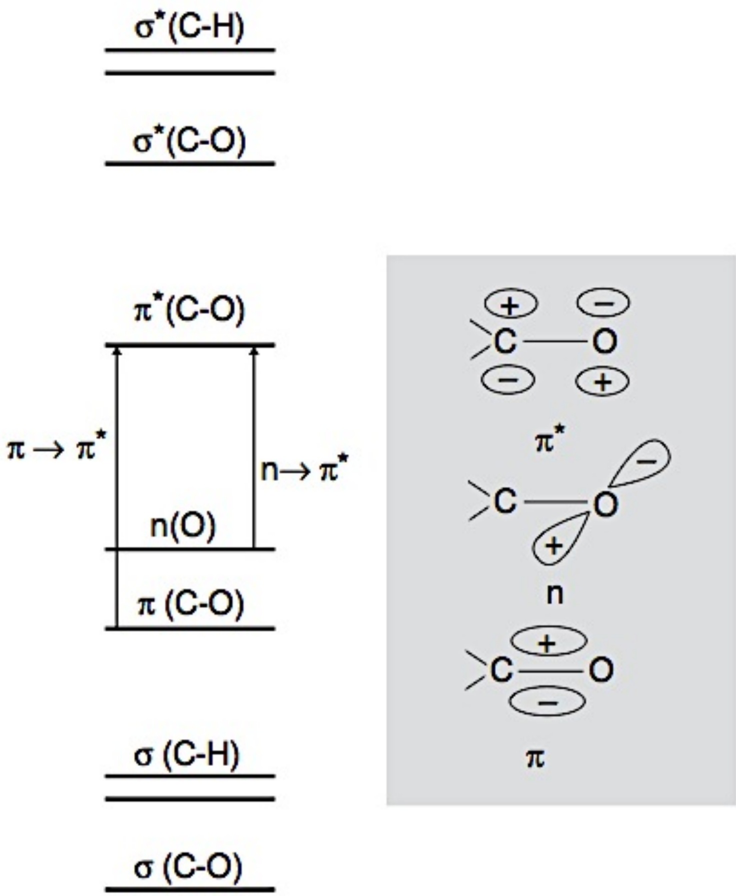


Figure 1.9 Molecular orbital diagram for methanal, showing the n → π* and π → π* transitions. The boundary surfaces of the π, n and π* molecular orbitals are also shown

Introduction

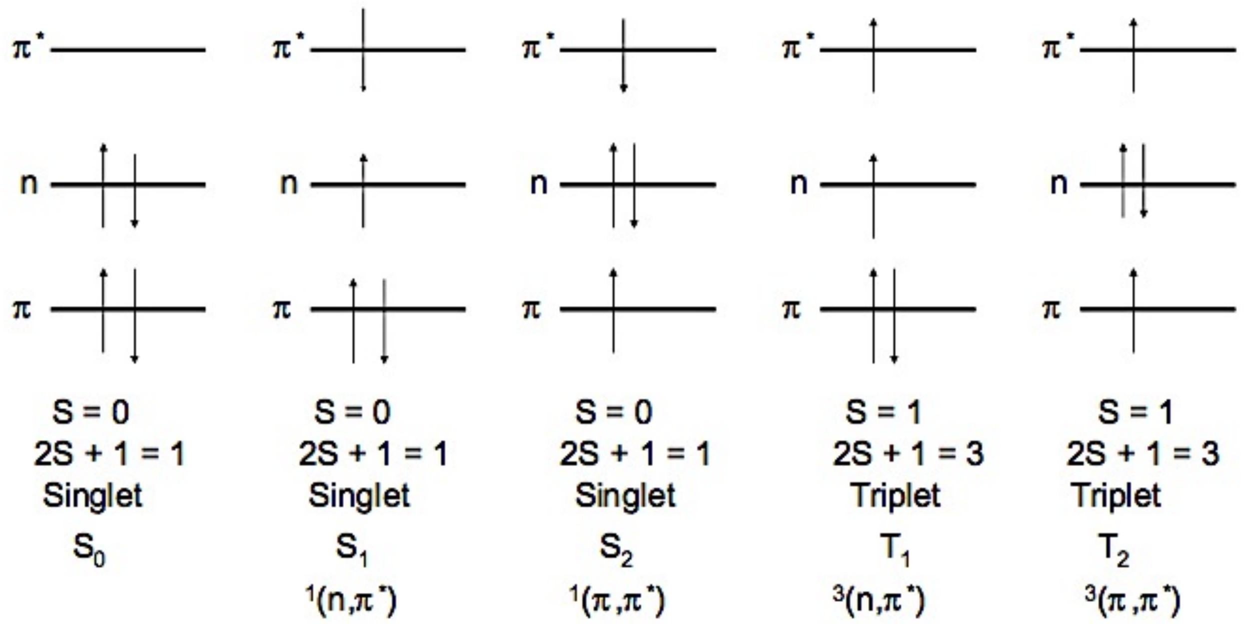


Figure 1.10 Configurations of the ground state and excited electronic states of methanal

Introduction

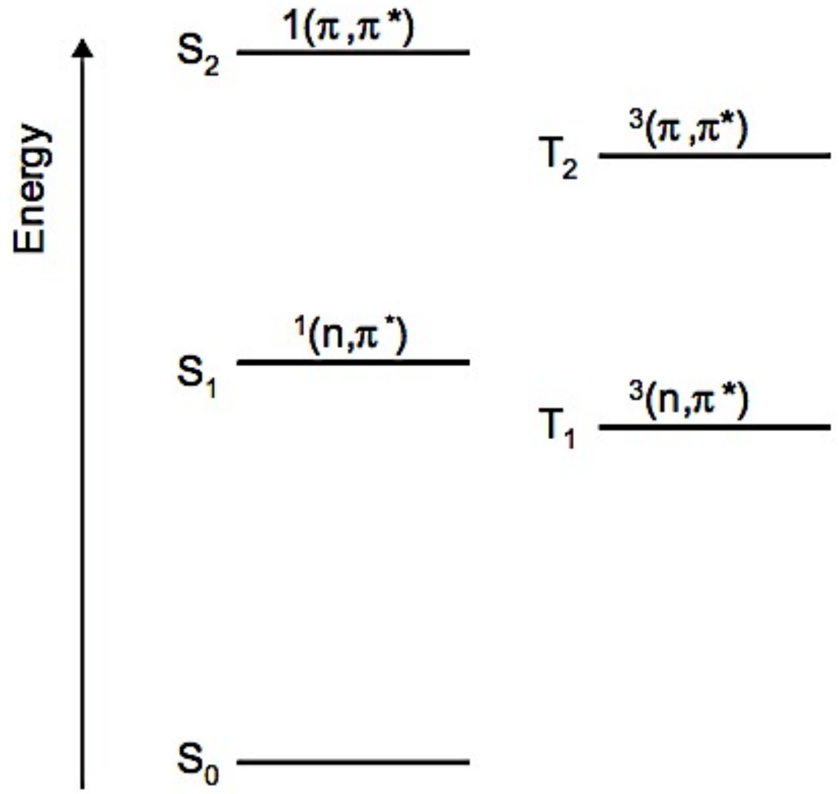


Figure 1.11 State diagram for methanal

Introduction

Photochemistry has been considered one of the key approaches to green chemistry

- **extremely mild conditions under which such reactions are carried out;**
- **the photon can be considered the green reagent par excellence;**
- **photochemistry is currently rarely considered in organic preparations even at laboratory scale, let alone in industrial practice.**

Introduction

Photochemistry has been considered one of the key approaches to green chemistry:

- **photochemical reactions are not sufficiently clean for use in synthesis and mixtures are generally formed;**
- **complex and expensive experimental apparatus is required;**
- **the course of such reactions is not easily predicted, or at any rate not rationalized through the well**
- **established paradigms used in thermal chemistry;**
- **photochemical syntheses are rarely used in the industry and thus it does not make sense to introduce**
- **a methodology that is unlikely to be scaled up.**

Introduction

The lamps most used are:

1. **low pressure mercury arcs**, emitting at 254 nm, typically 8–15 W; these are long (10–20 cm) tubes, well suited for the external illumination of the reaction vessels, cooling is not required or is obtained by means of a fan when lamps are in a confined space;
2. the same lamps, fitted with an **outside phosphor** that converts light to longer wavelength, the most common ones having an emission band centered at 310 or 365 nm;
3. **medium pressure mercury arcs**, emitting most intensively in the near UV, typically 100 W and more; these are compact sources (2–5 cm), suited for internal illumination through an immersion well; are shorter-lived and more expensive and require water cooling (often under pressure for the high wattage, 500 W).

Introduction

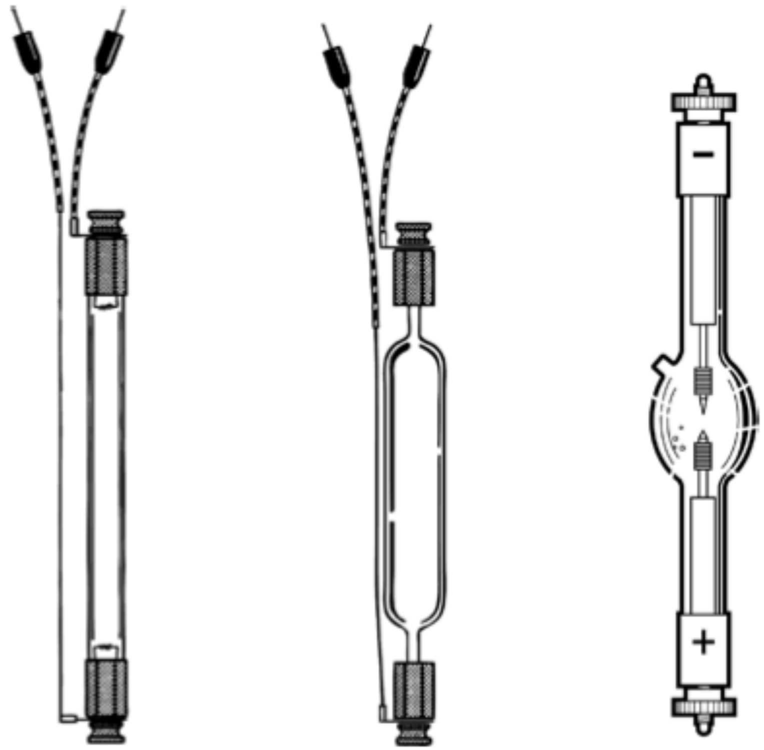


Figure 3.1 Examples of low (left), medium (middle) and high pressure (right) mercury arc lamps. Reproduced by permission of Ace Glass Inc. and Newport Corp, Oriel Product Line

Introduction

Table 3.1 *Cut off wavelengths of common solvents*[a]

Solvent	Cut off wavelength/nm
Water	185
Acetonitrile	190
n Hexane	195
Methanol	205
Diethyl ether	215
Ethyl acetate	255
Carbon tetrachloride	265
Benzene	280
Pyridine	305
Acetone	330

[a]Adapted from ref. 1.

Introduction

Table 1.1 Choosing a solvent with reference to the reagent irradiated.

Solvent	λ_{lim} [a]	Reagent	λ [b]
Acetone	329	Aniline	308
Acetonitrile	190	2 Cyclohexenone	310
Benzene	280	Stilbene	333
Cyclohexane	205	Benzophenone	360
Dichloromethane	232	1,4 Naphthoquinone	385
Diethyl ether	215	Uracil	285
N,N Dimethylformamide	270	Phenanthrene	345
Dimethylsulfoxide	262	Anthracene	378
Ethanol	205	Pyrrole	238
Pyridine	305		
Pyrex, Vicor	λ_{lim} [c] ca. 300		

[a] Limiting wavelength; the wavelength at which a 1 cm layer of the solvent absorbs 90% of the light impinging; use only when the reagent absorbs above this value.

[b] The longest wavelength at which the reagent has absorbance $A = 1$ at a 0.01 M concentration.

[c] Wavelength at which a 1 mm layer of the glass absorbs 90% of the light.

Introduction

Figure 3.9 Left: a photochemical reactor with immersed configuration with the lamp and a power source. Right: detail of the immersion well. Reproduced by permission of Ace Glass Inc

Introduction

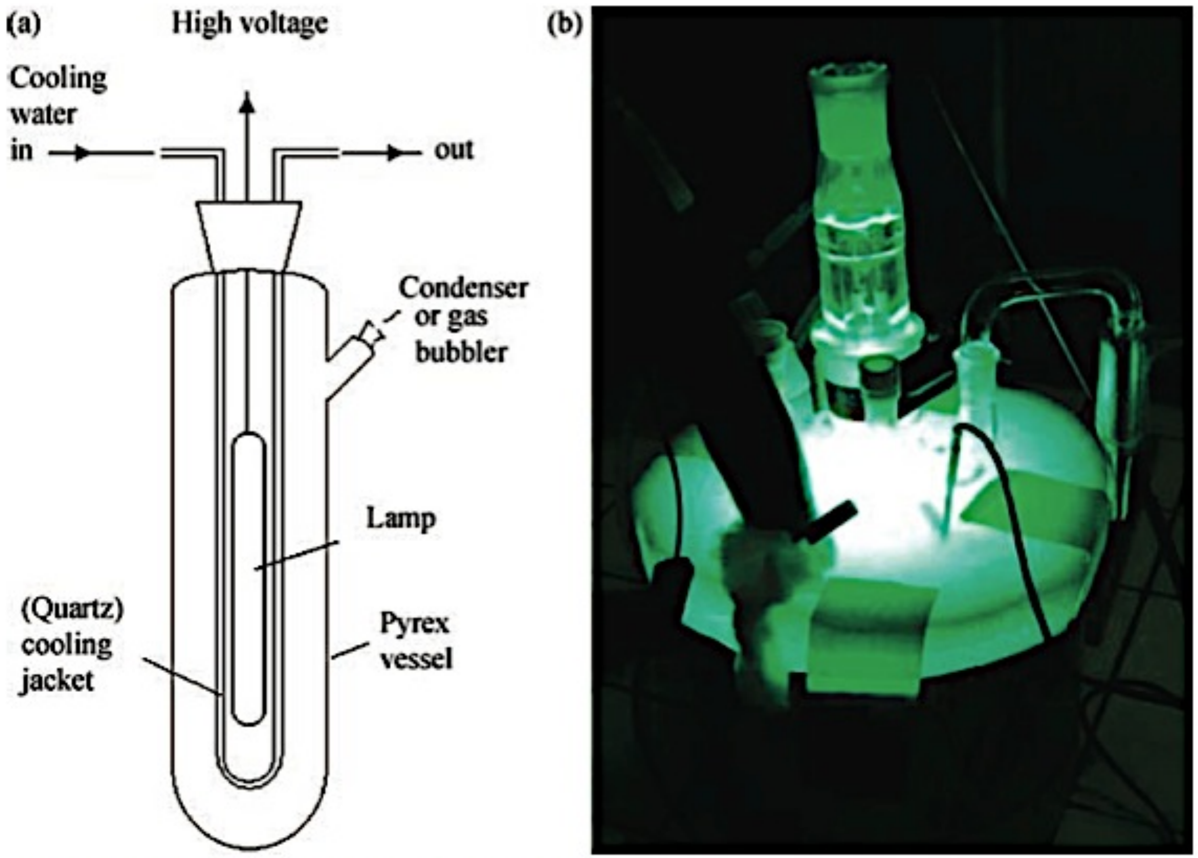


Figure 1.4 (a) Immersion well irradiation apparatus; (b) a refrigerated apparatus for conducting reactions at low temperature.

Introduction

Figure 3.10 Rayonet photochemical reactor (*external configuration*). Reproduced by permission of Southern New England Ultra Violet Company

Introduction

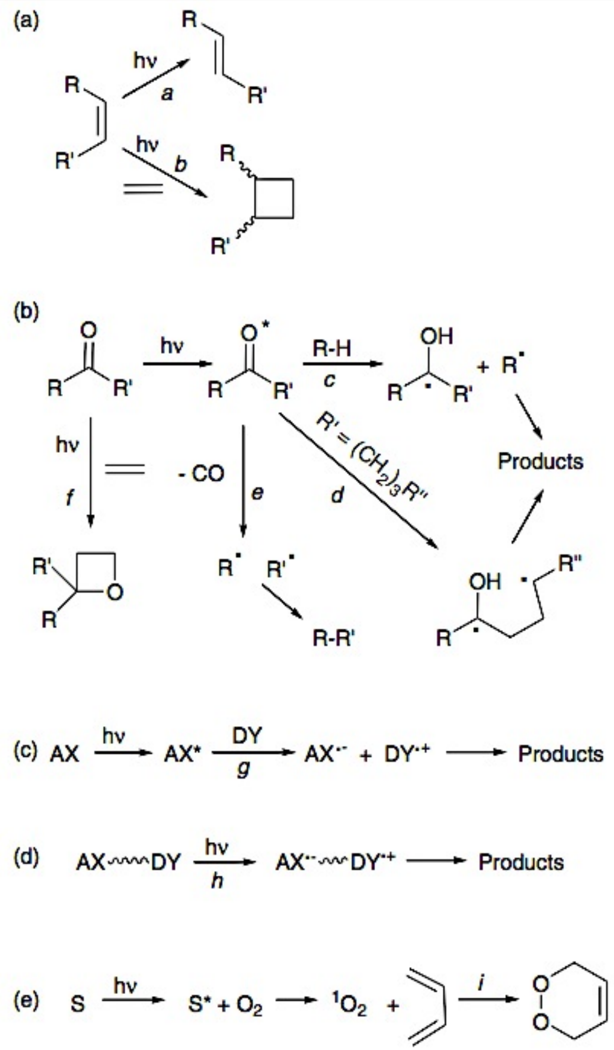
Figure 1.3 Two pairs of lamps used for external irradiation. In the arrangement shown, only a small fraction of the light flux is used.

Introduction

Figure 3.11 Solar simulator. Reproduced by permission of Newport Corp, Oriel Product Line

Reactions

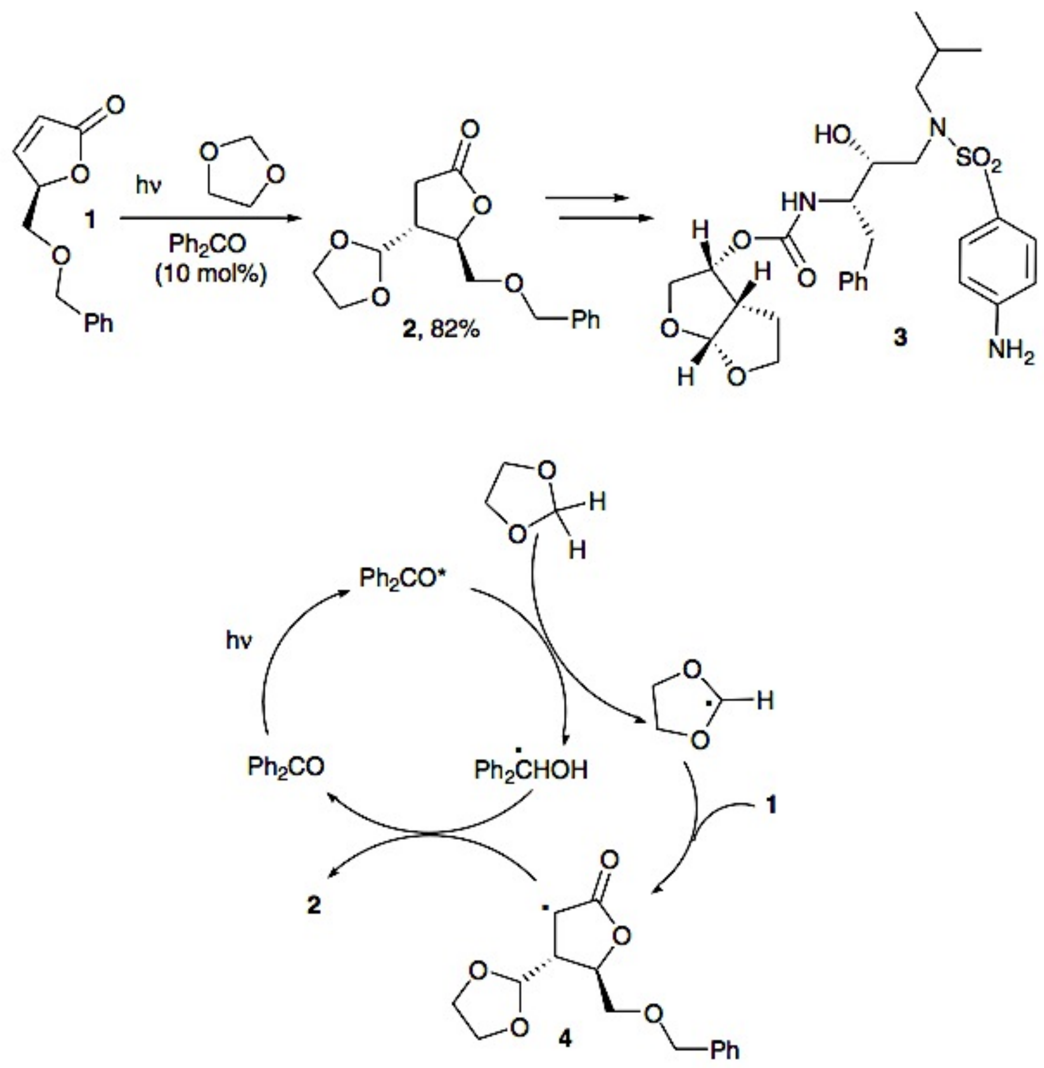
Synthesis and Rearrangement of Open-Chain Compounds



Scheme 14.1 *An overview of the most important photoreaction classes involving organic compounds.*

Reactions

Synthesis and Rearrangement of Open-Chain Compounds



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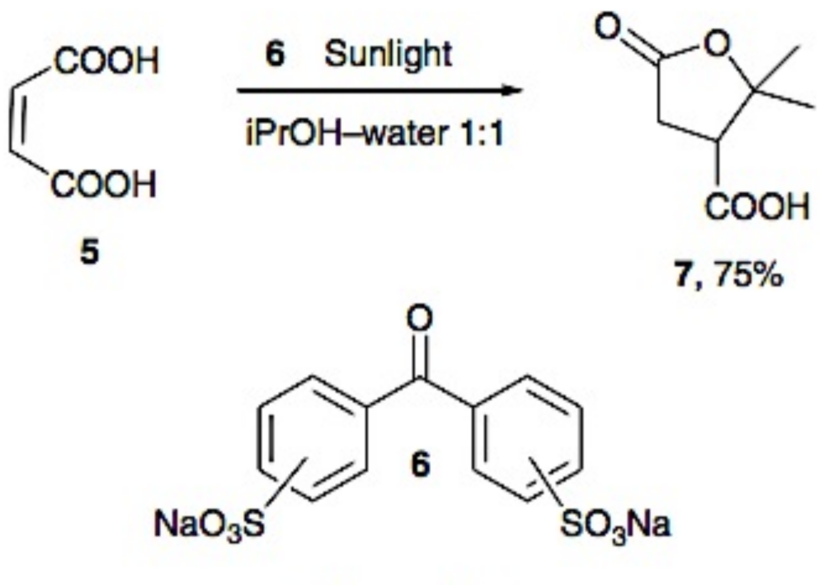
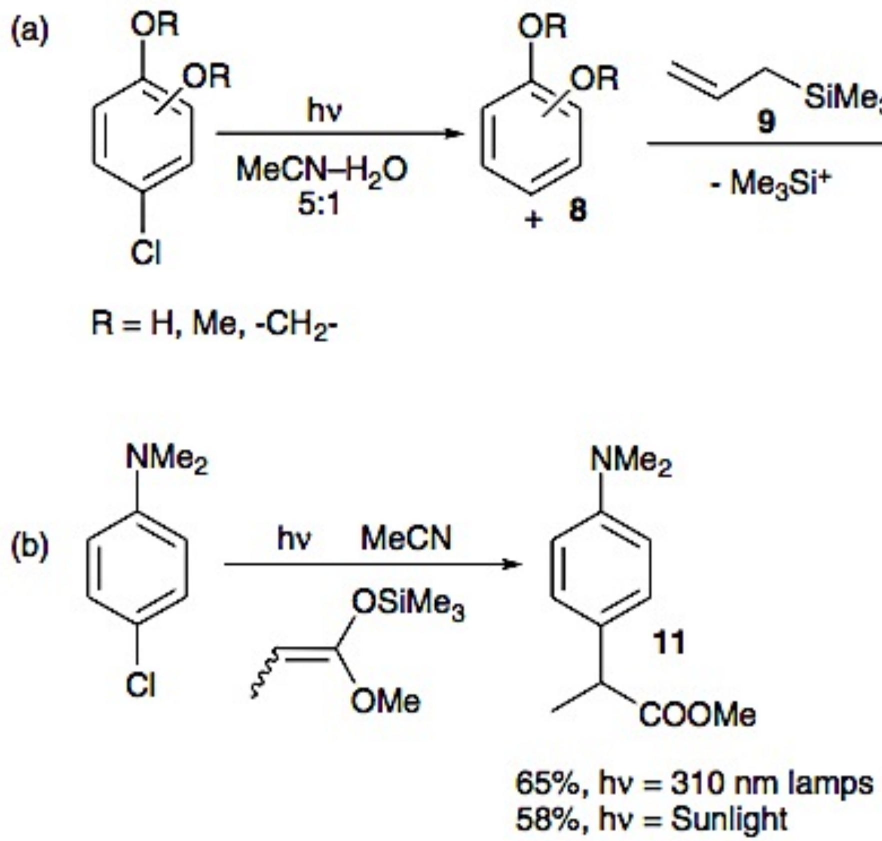


Scheme 14.3

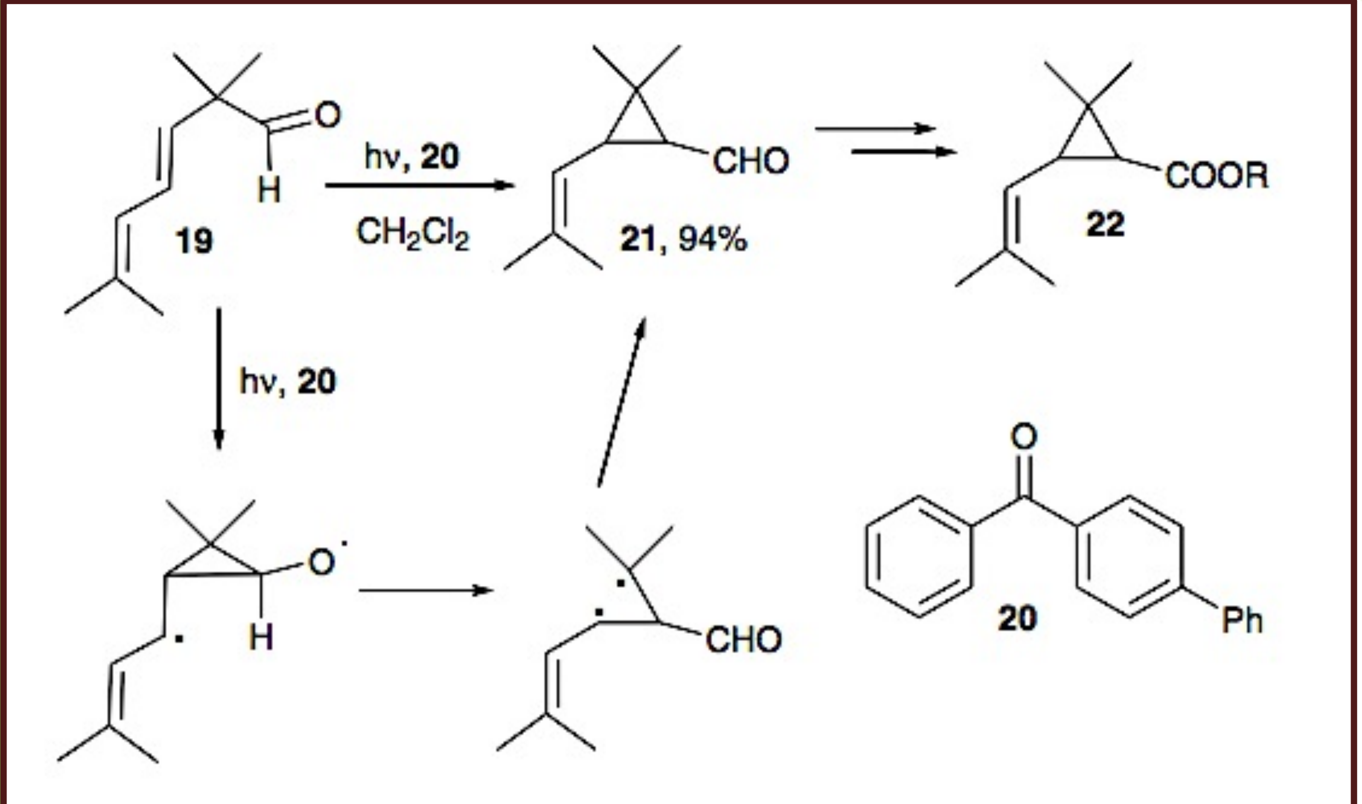
Reactions

Synthesis and Rearrangement of Open-Chain Compounds



Reactions

Synthesis of Three- and Four-Membered Rings



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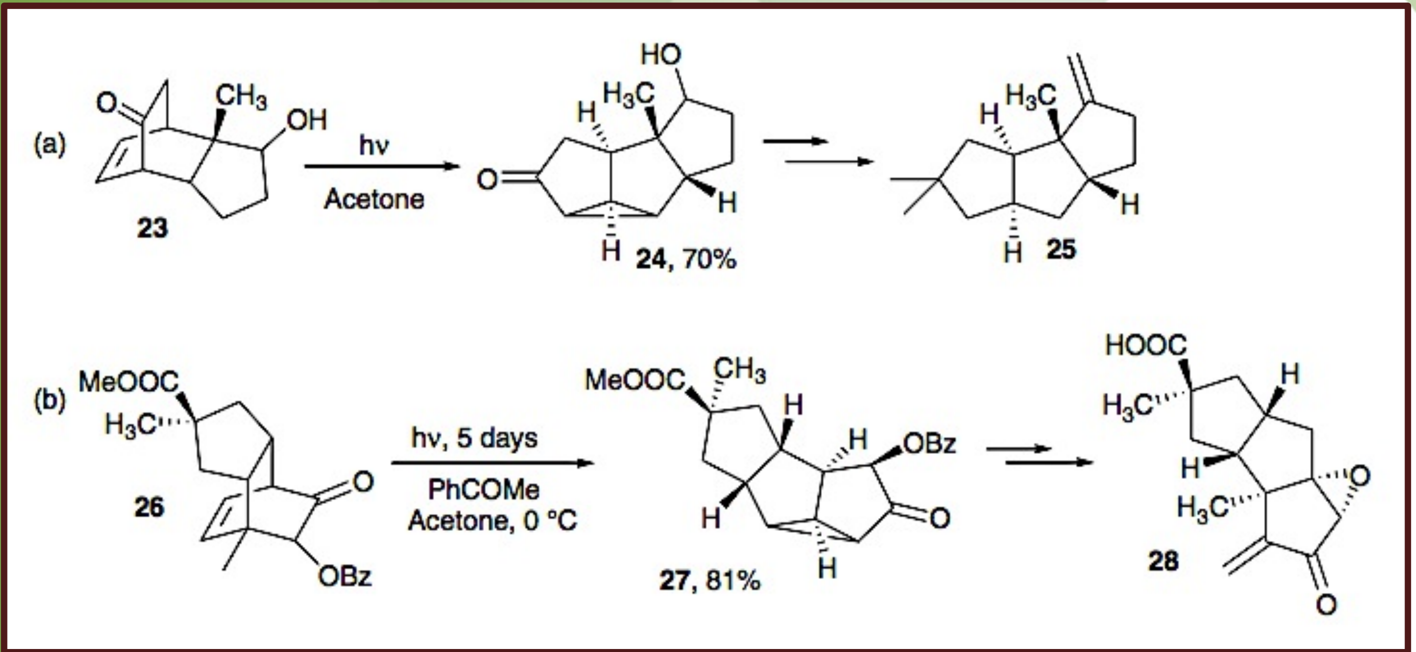

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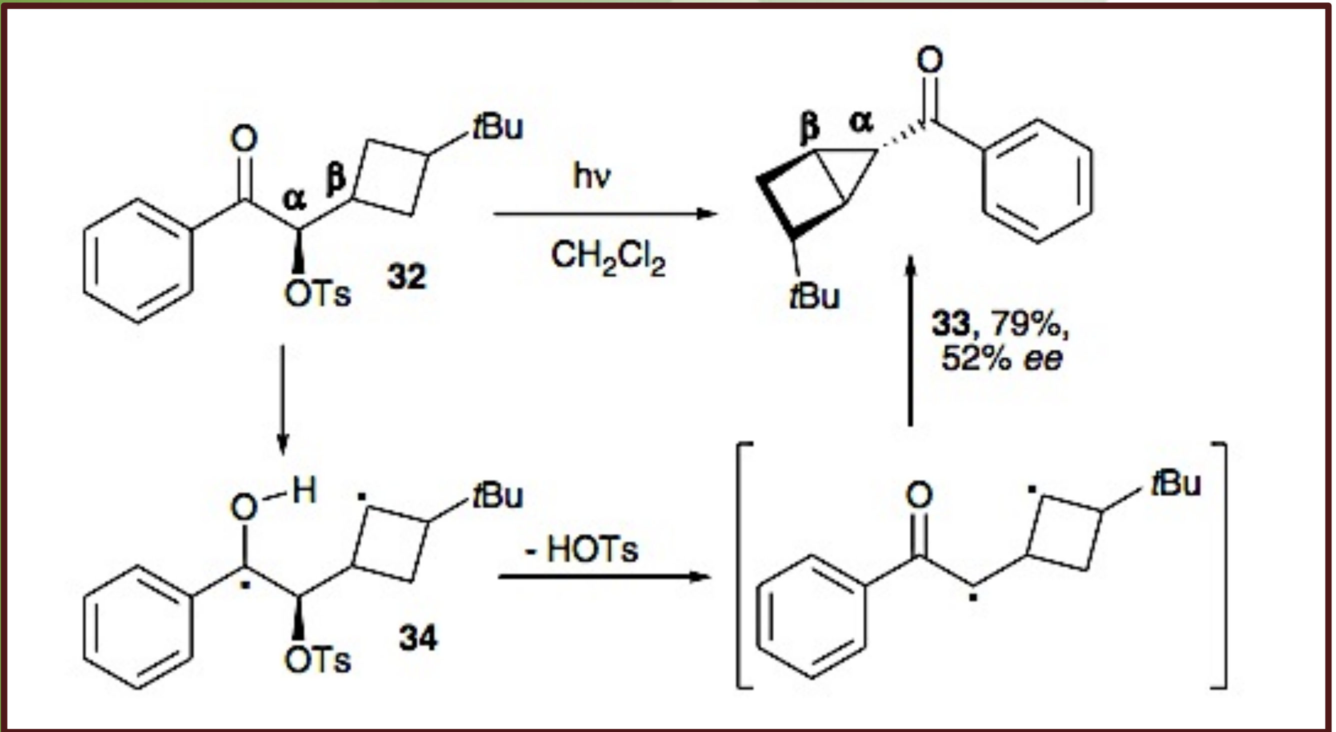

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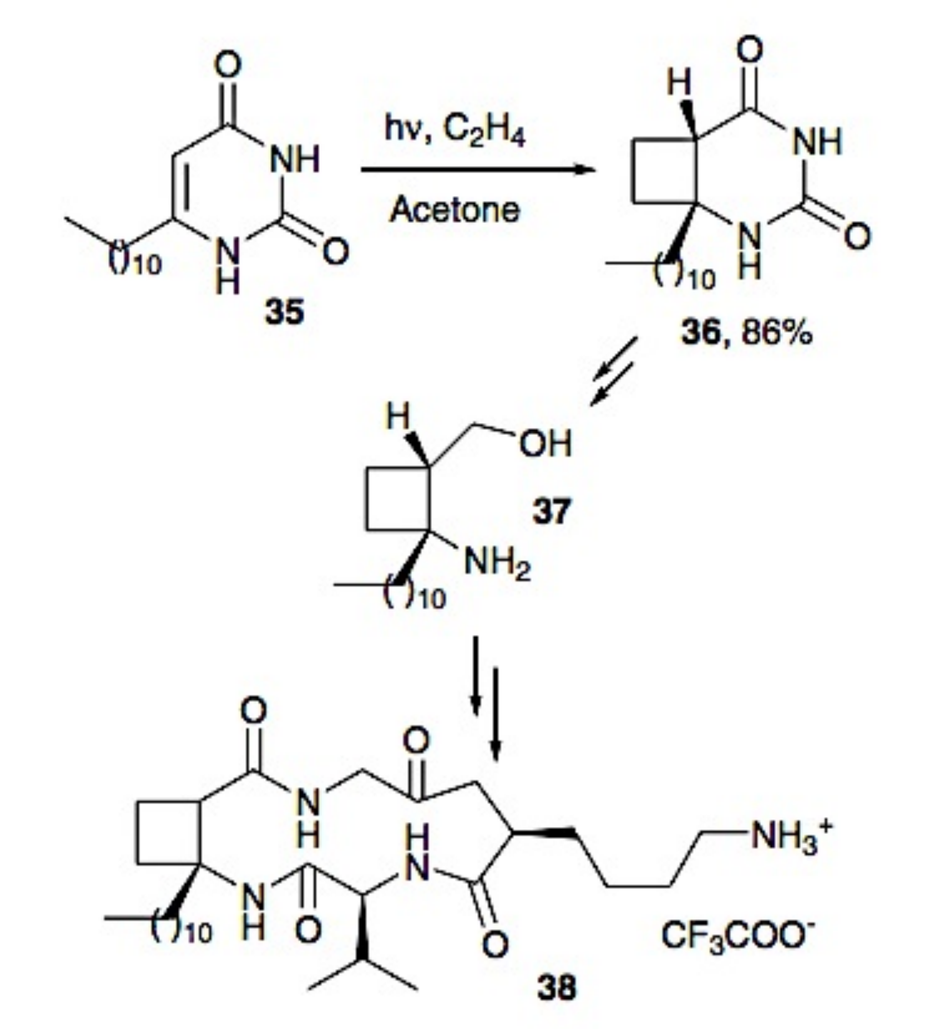

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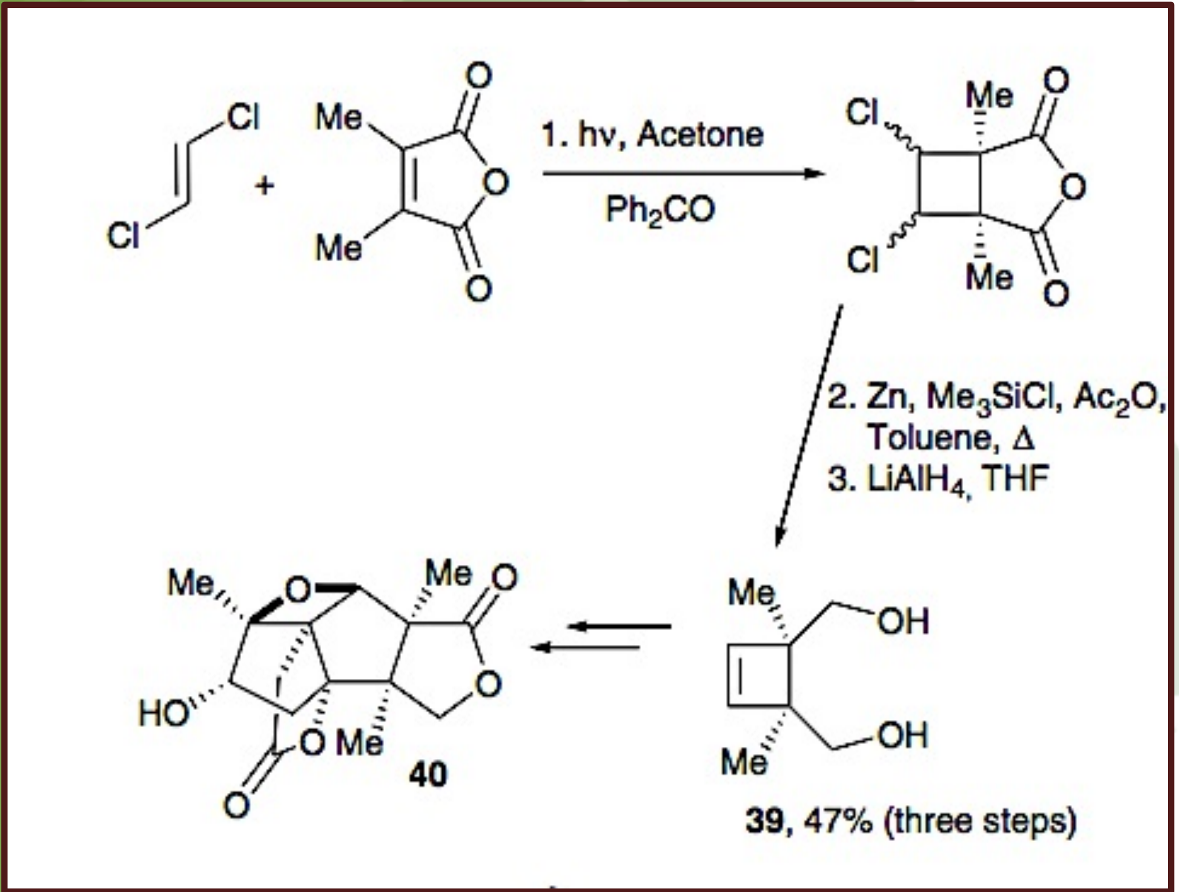

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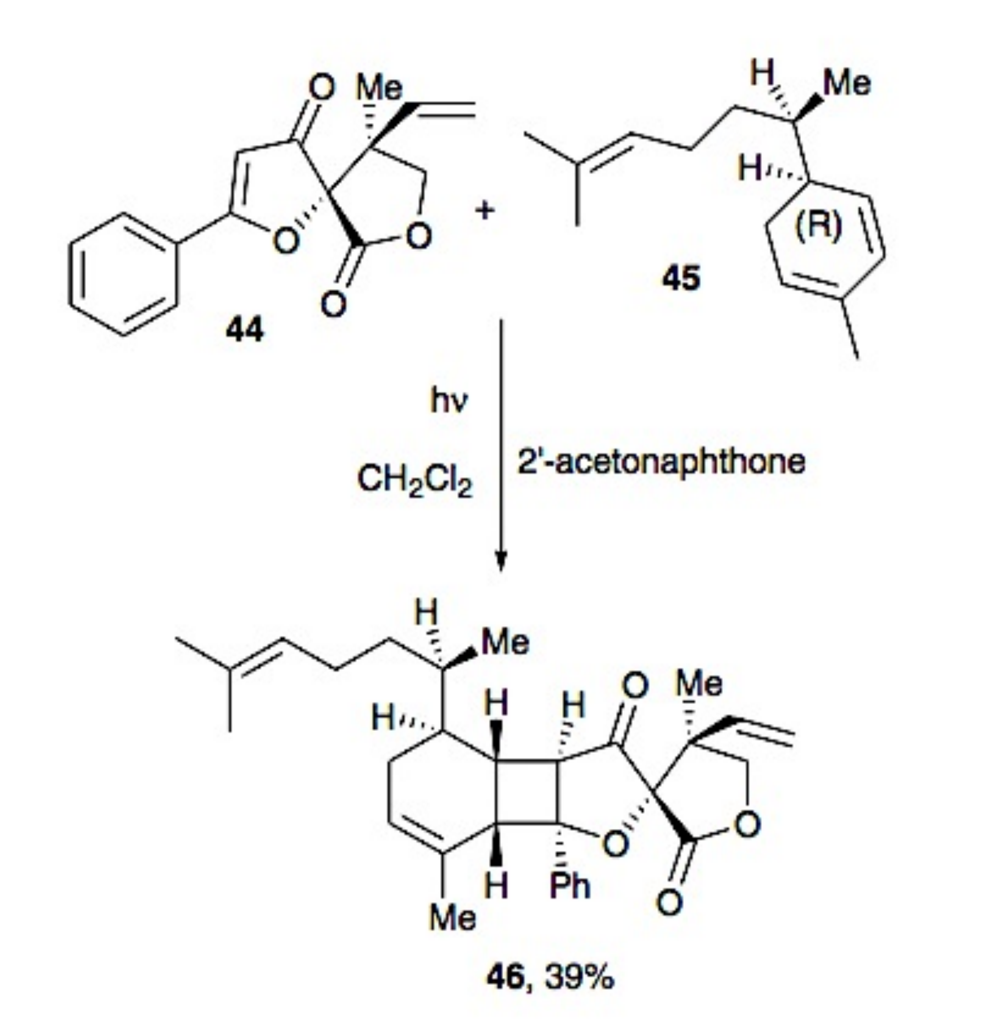

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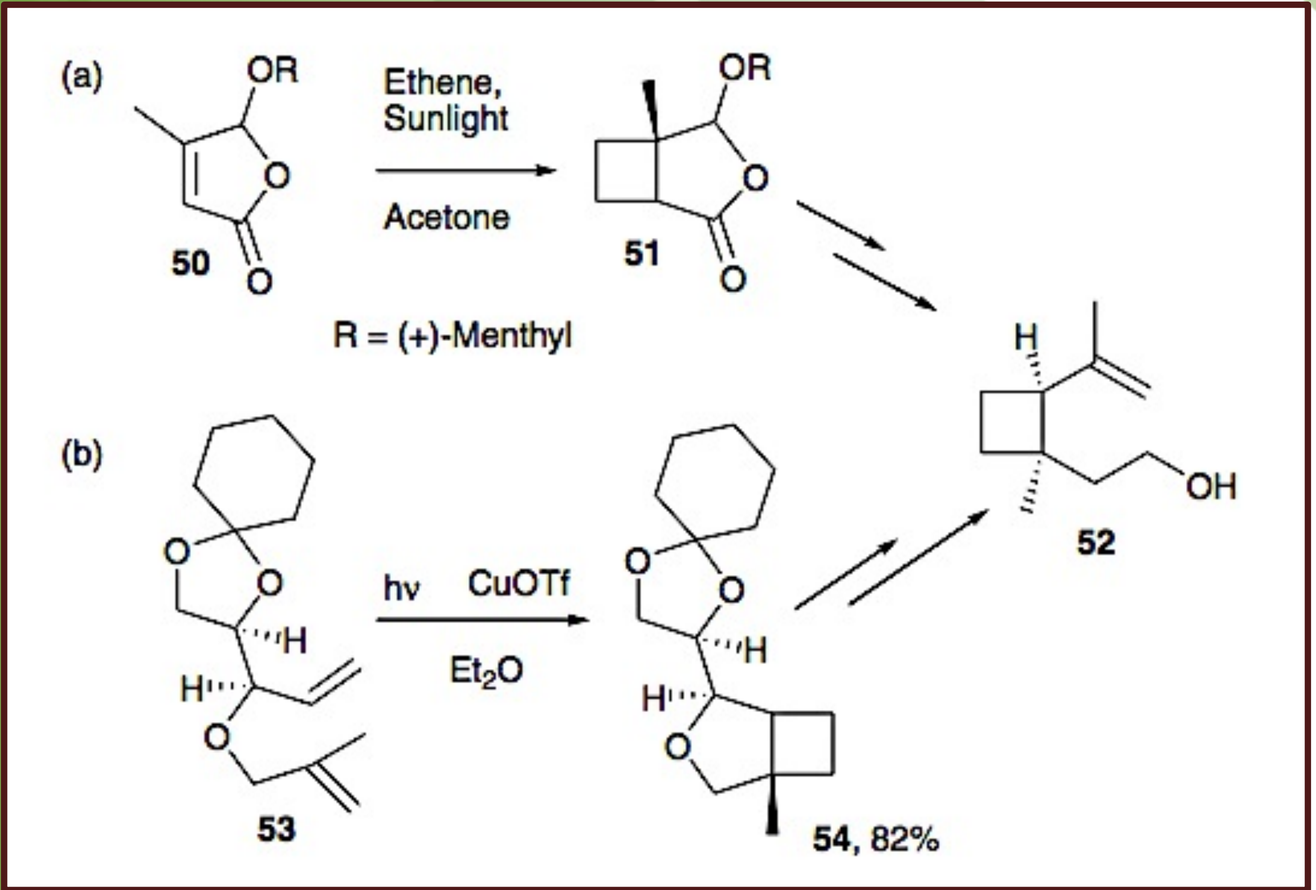

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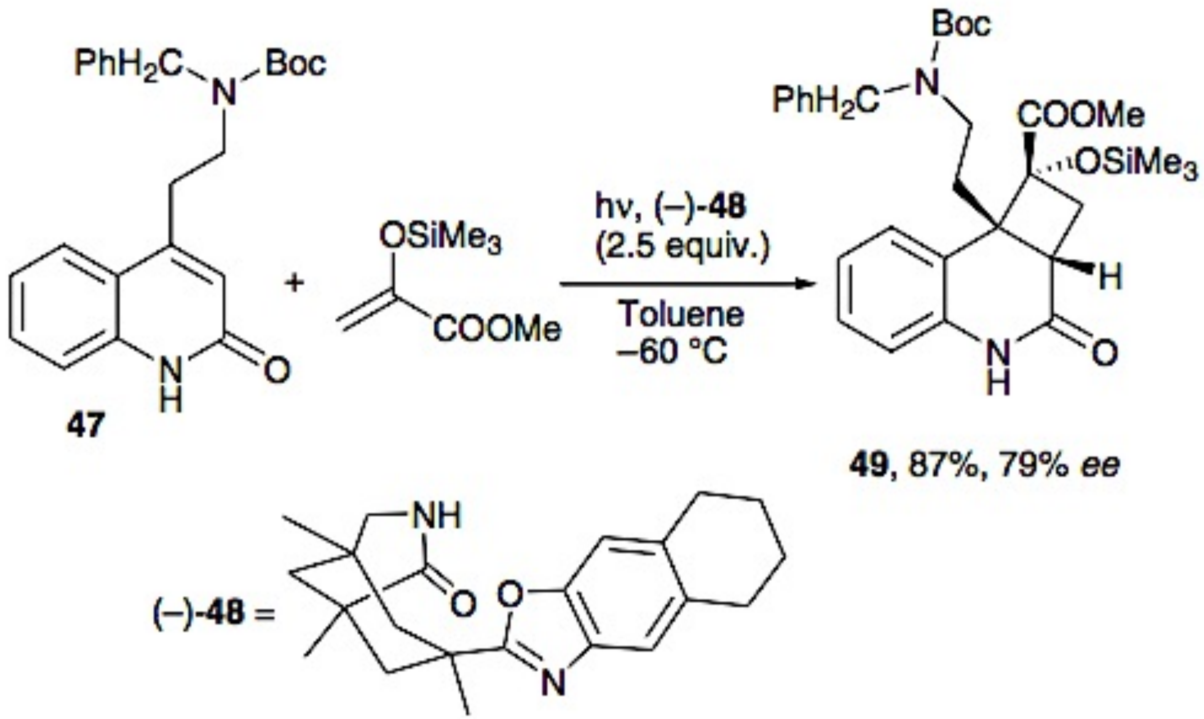

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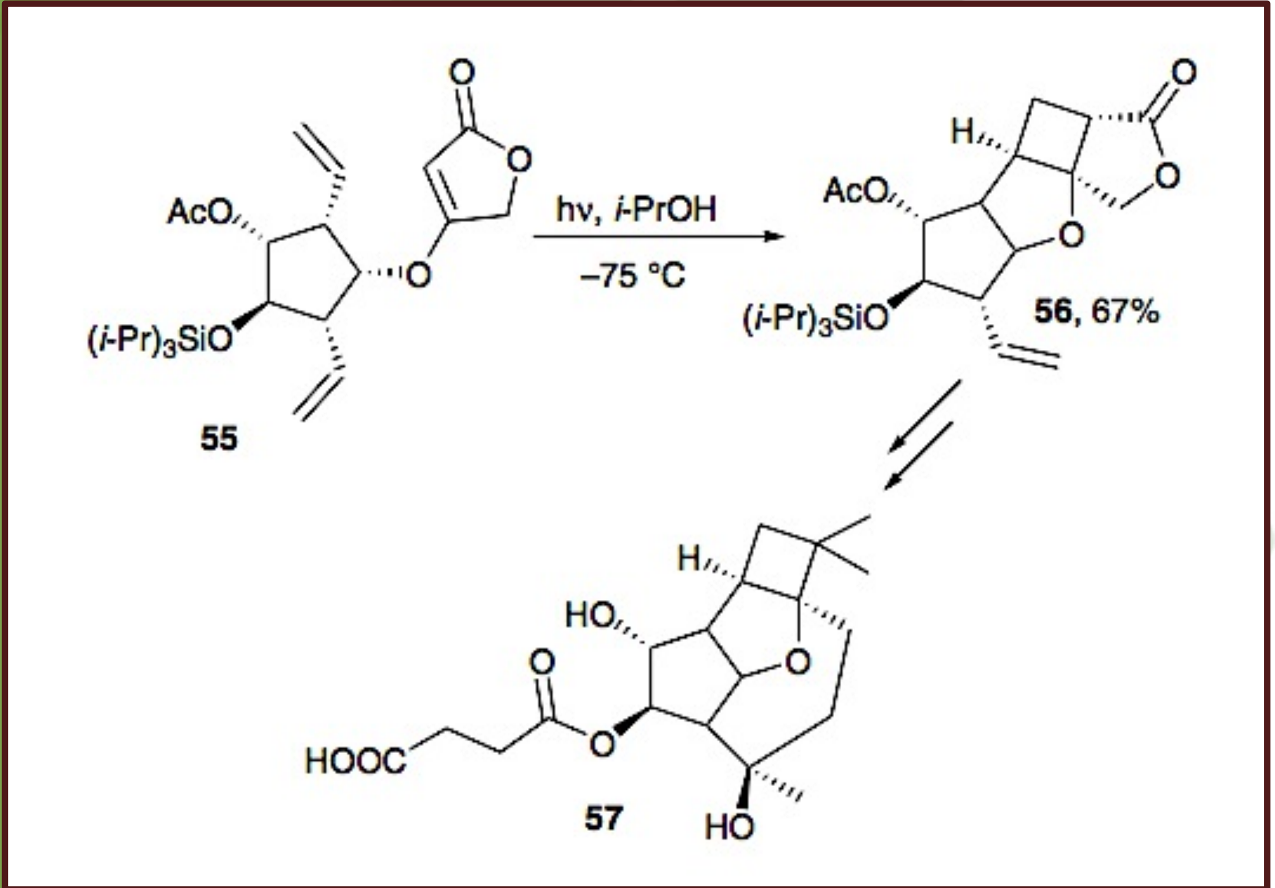

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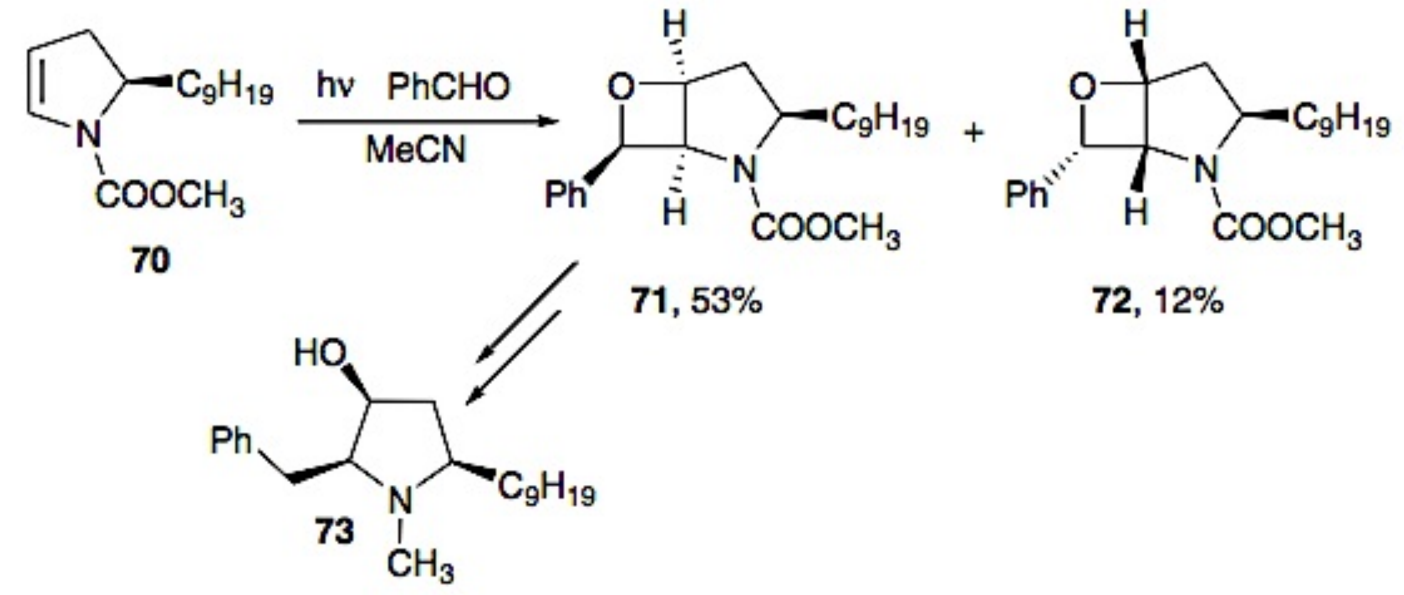
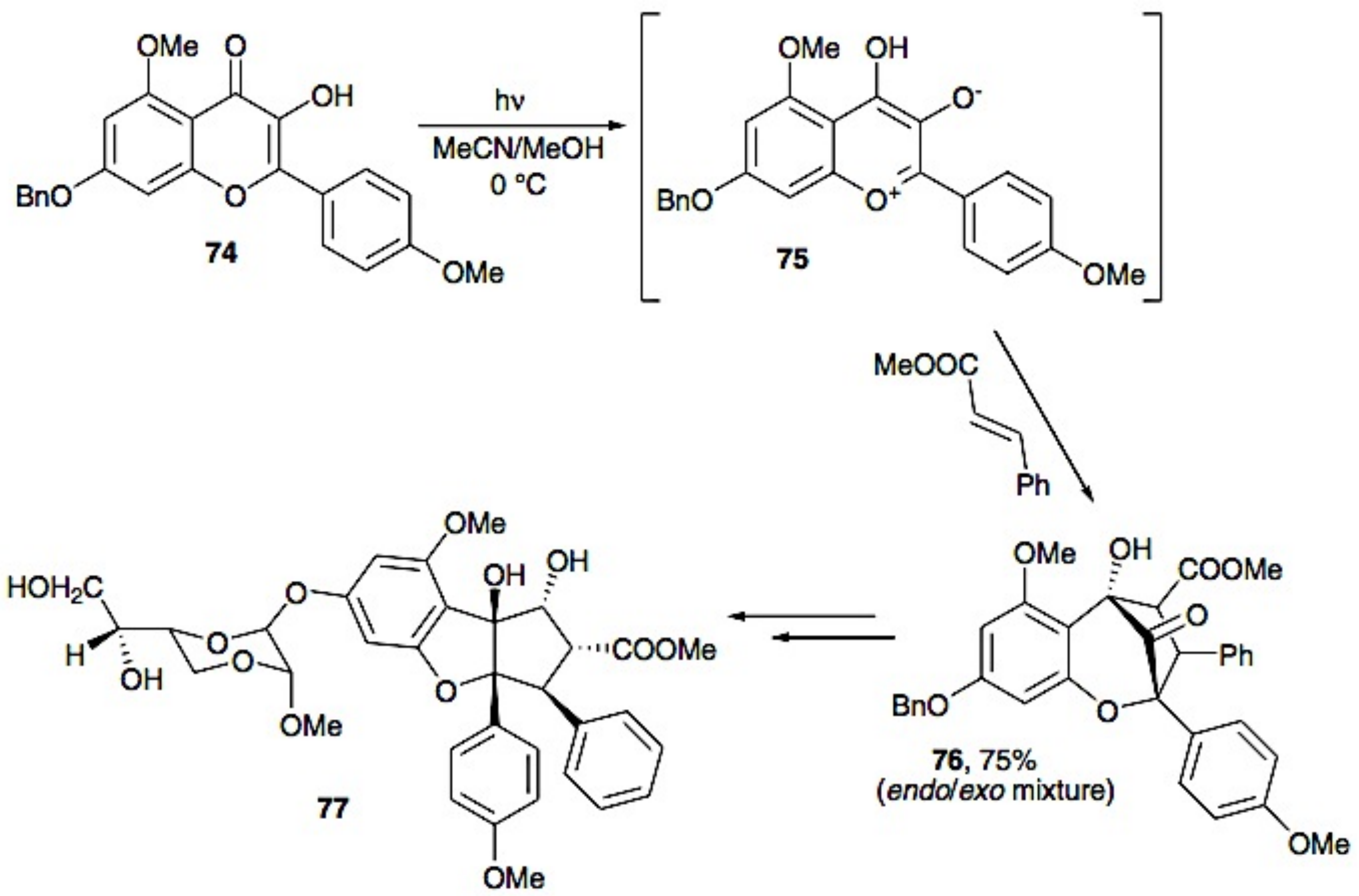


Reactions

Synthesis of Five-, Six (and Larger)-Membered Rings



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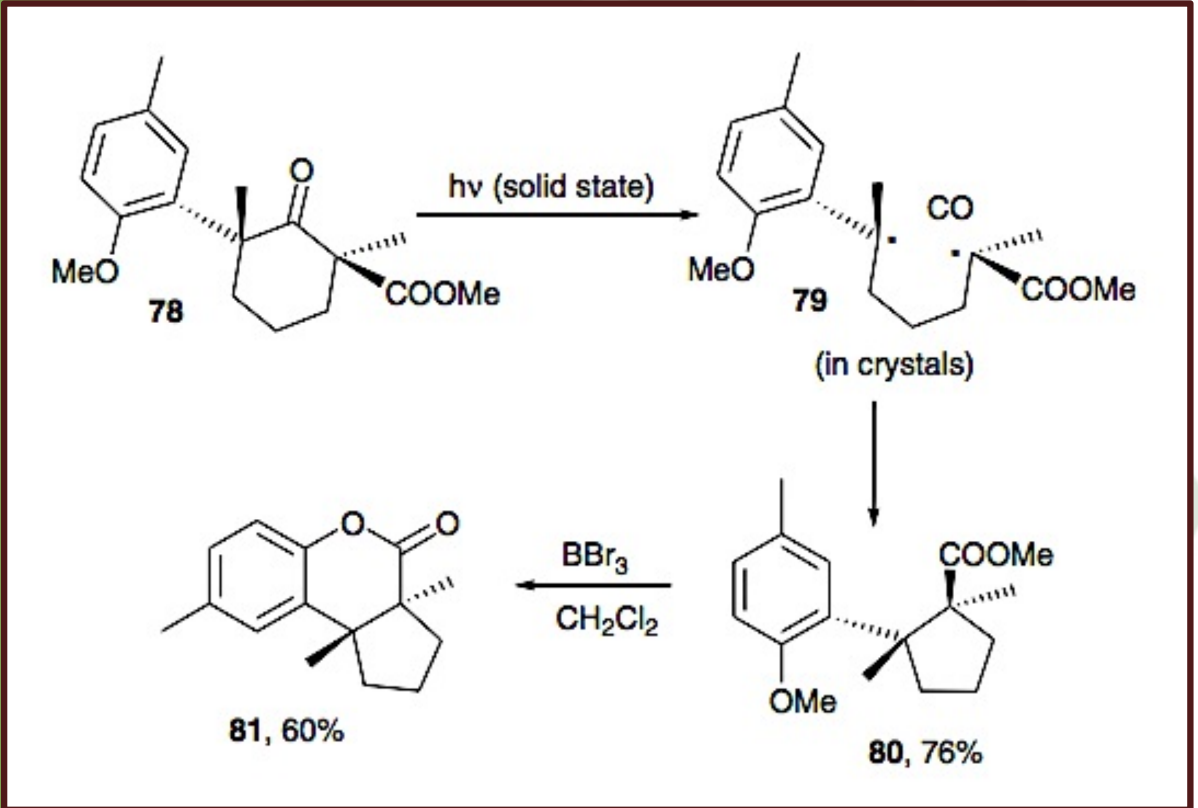

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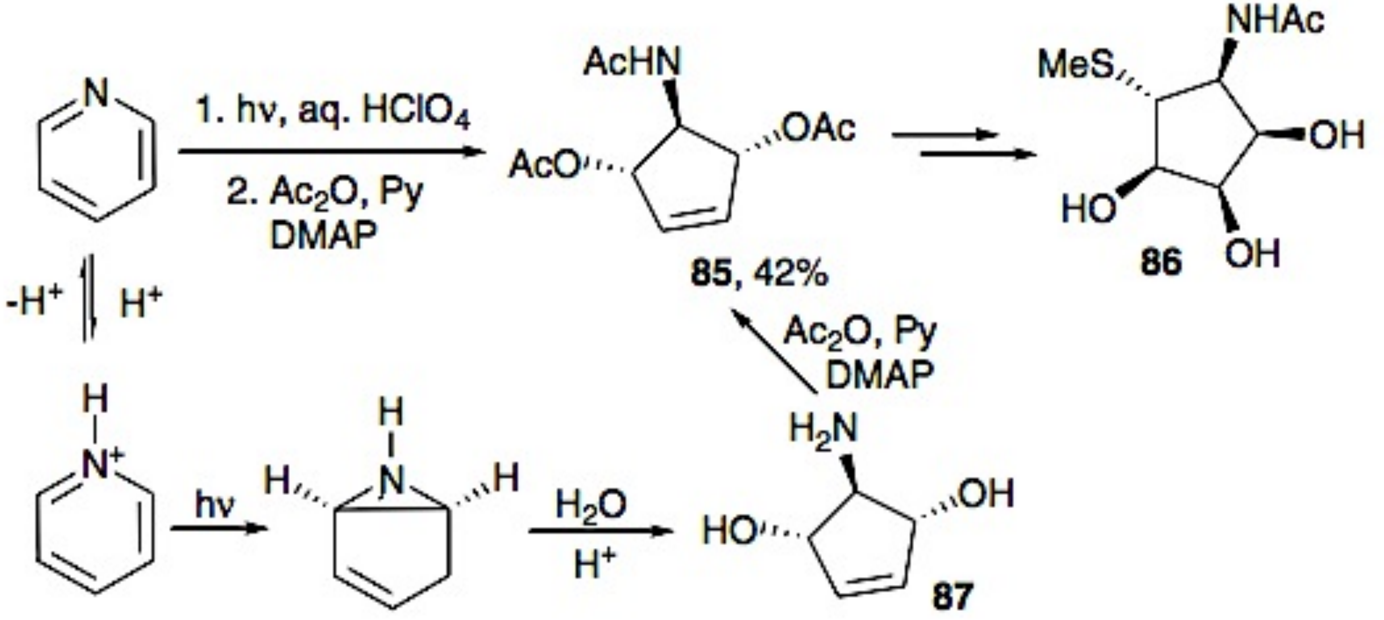

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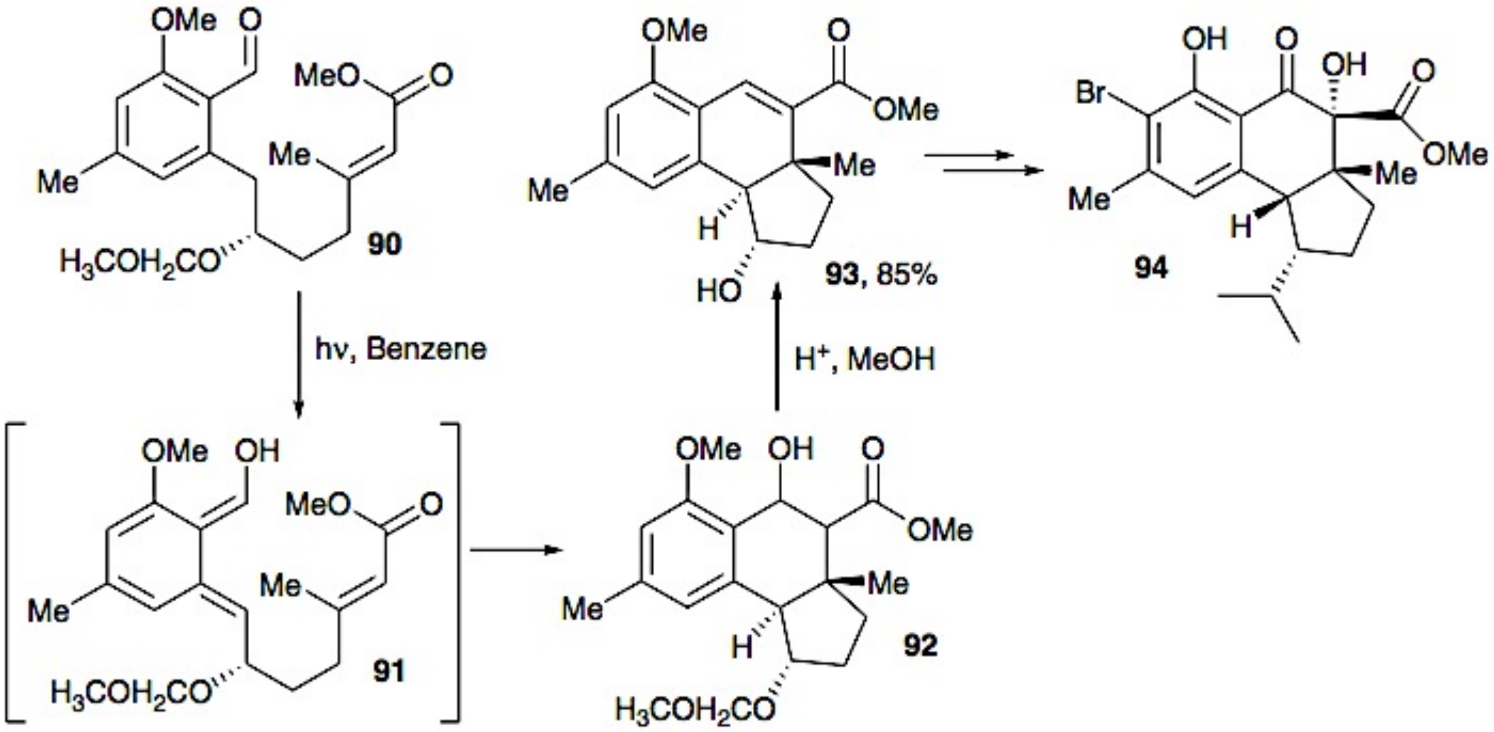
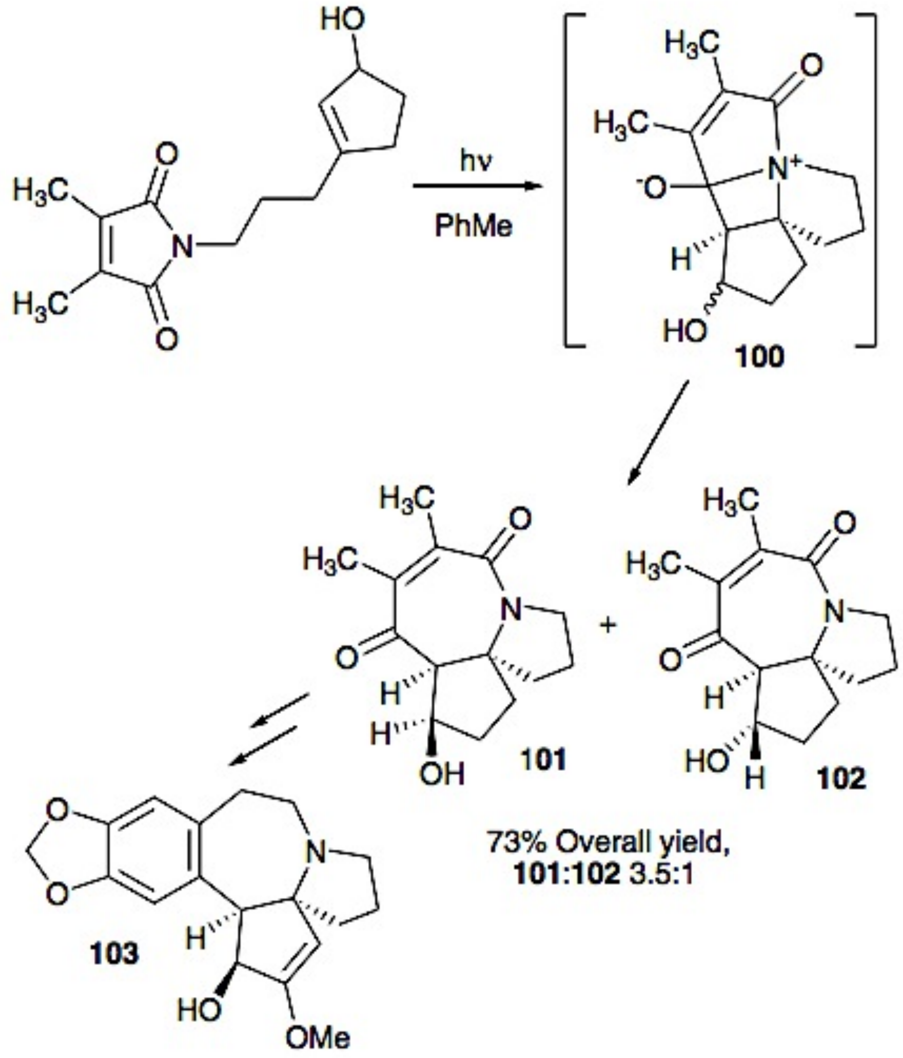


Reactions

Synthesis of Five-, Six (and Larger)-Membered Rings



Reactions

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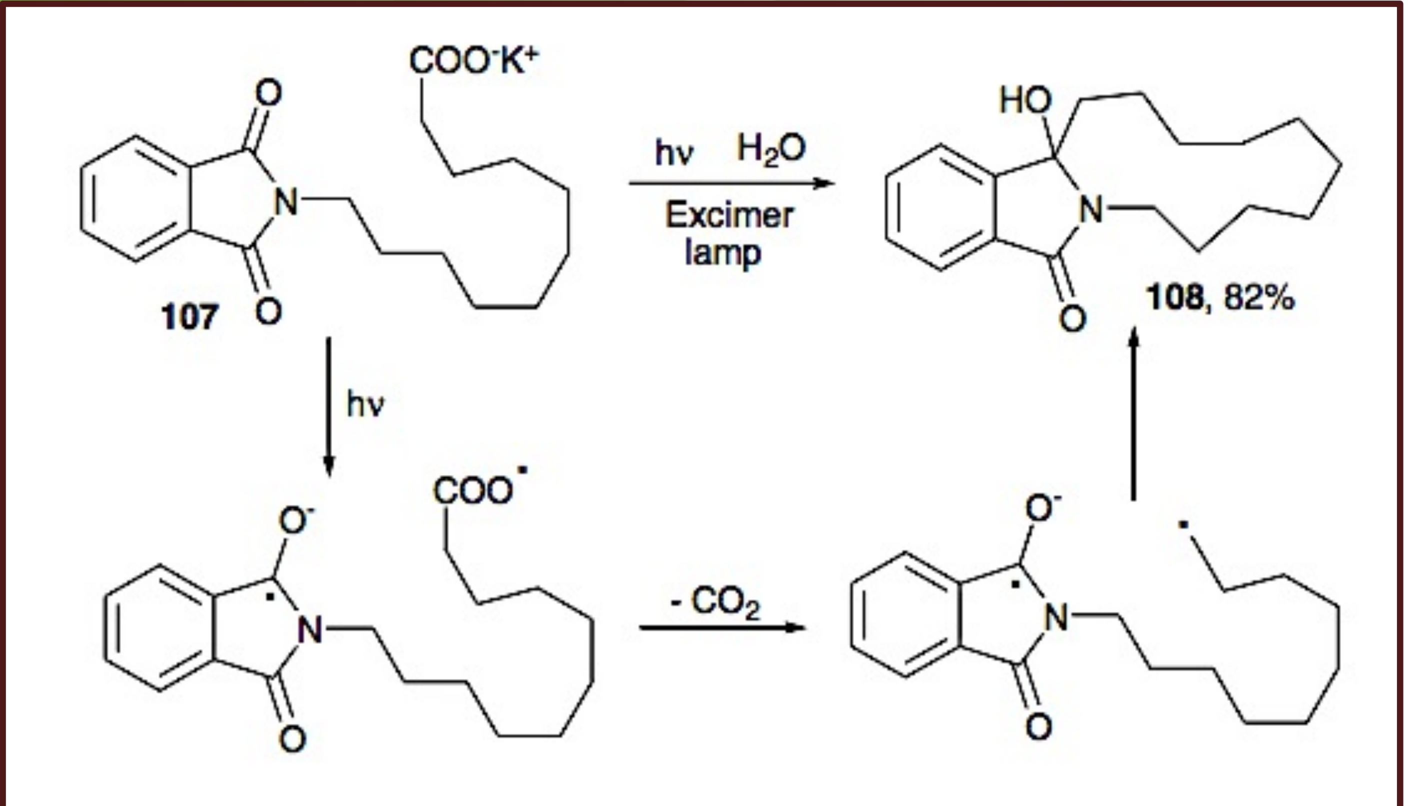
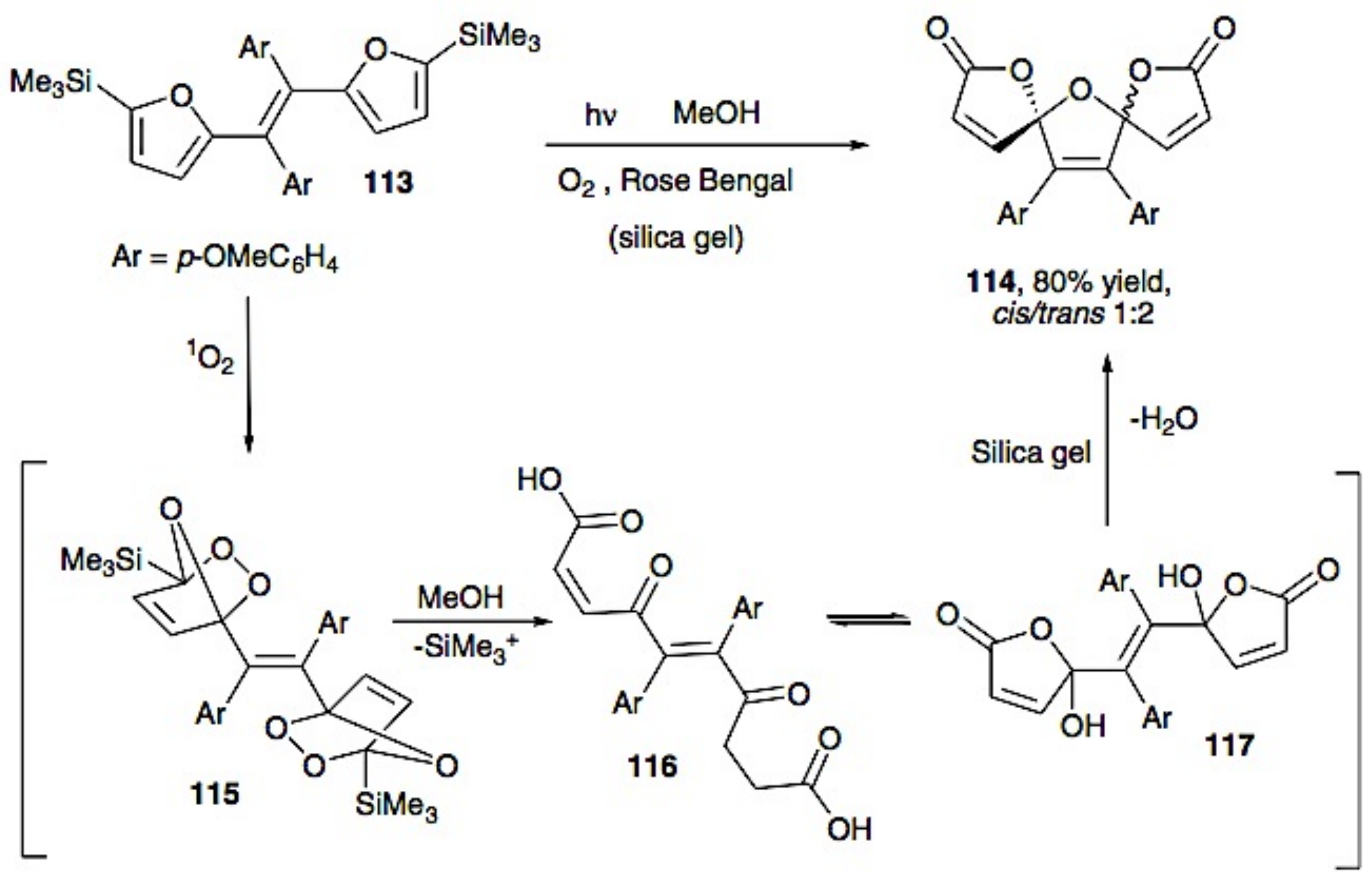


Reactions

Oxygenation and Oxidation



ORGANIC ELECTROSYNTHESIS IN GREEN CHEMISTRY

INTRODUCTION

Introduction

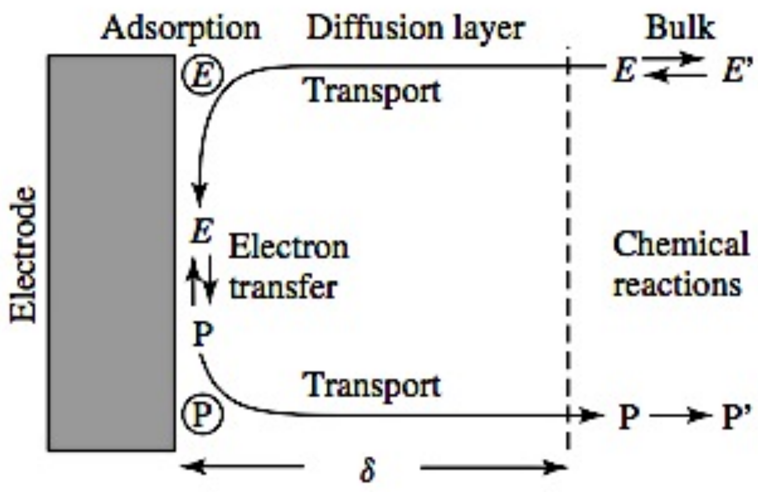


Fig. 1 Steps constituting a typical organic electrode reaction; E, E′: educt, P, P′: product; circles indicate adsorbed molecules.

Introduction

$$A^{2+} \underset{+e}{\overset{-e}{\rightleftharpoons}} A^{+} \underset{+e}{\overset{-e}{\rightleftharpoons}} A \underset{-e}{\overset{+e}{\rightleftharpoons}} A^{-} \underset{-e}{\overset{+e}{\rightleftharpoons}} A^{2-}$$

$$A^{-} \underset{-e}{\overset{+e}{\rightleftharpoons}} A^{\bullet} \underset{+e}{\overset{-e}{\rightleftharpoons}} A^{+} \qquad (2\text{-}1)$$

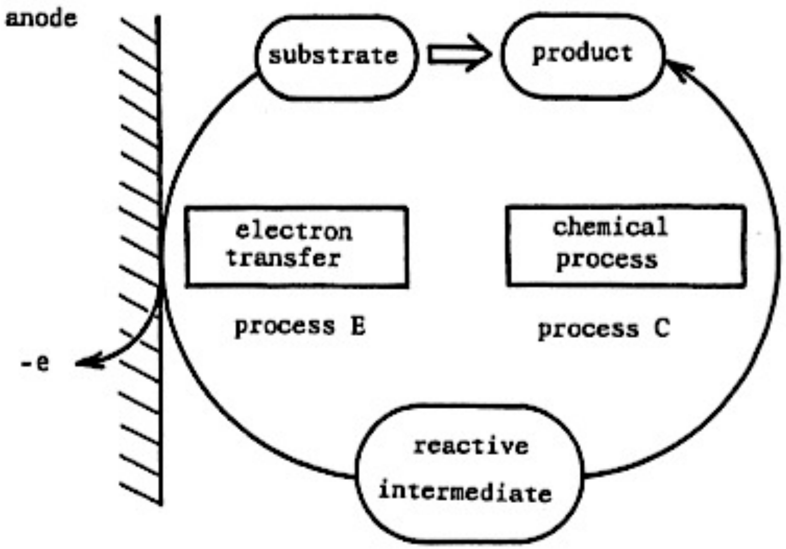


Fig. 2.1. Schematic depiction of an electroorganic oxidation as combination of processes E and C

Introduction

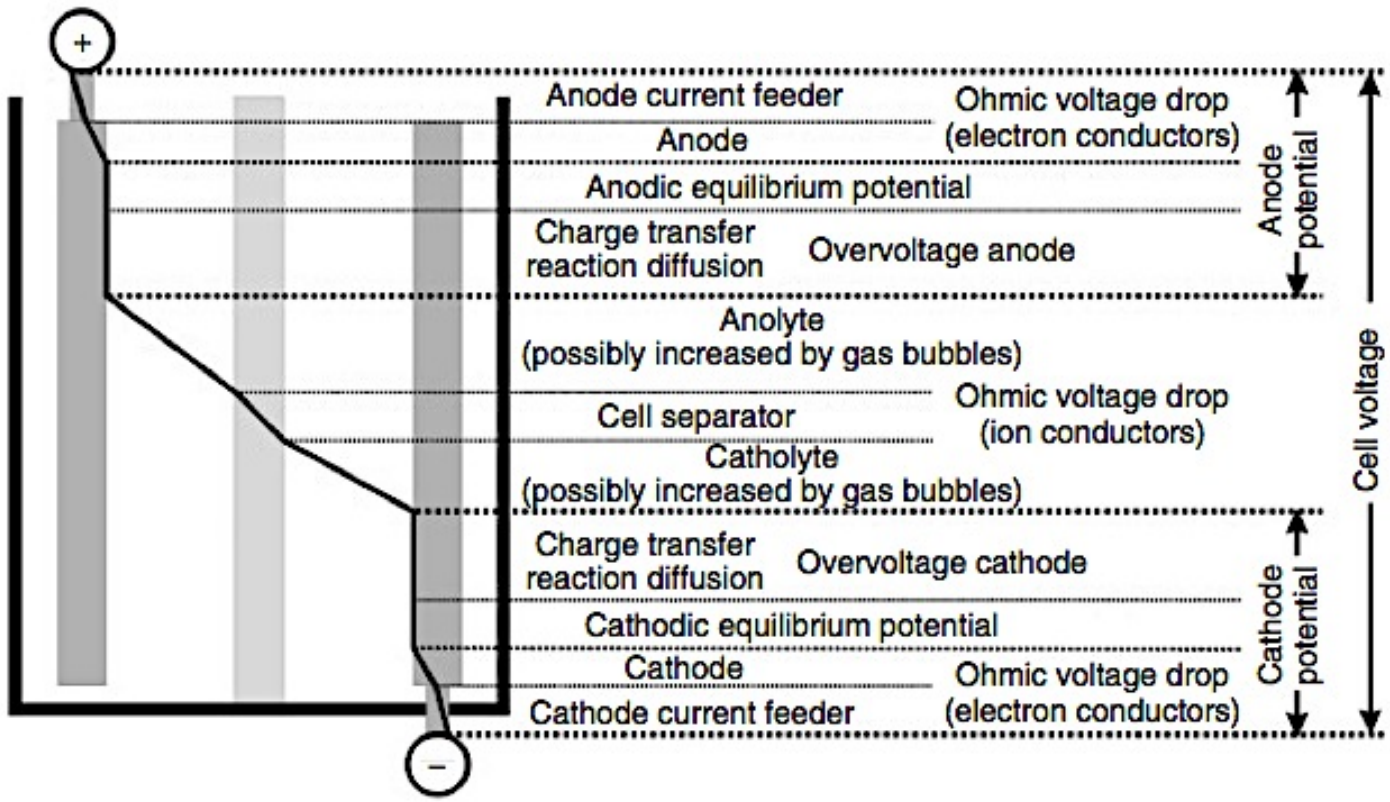


Fig. 2 Composition of the cell voltage (not in real scale).

Introduction

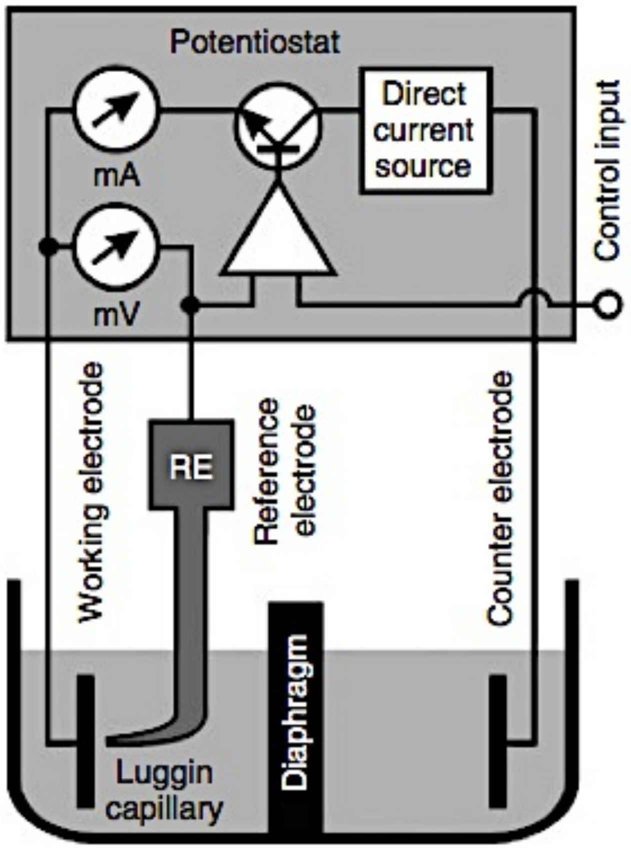
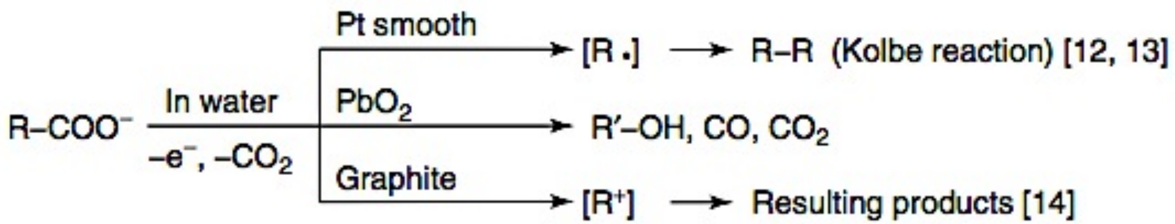


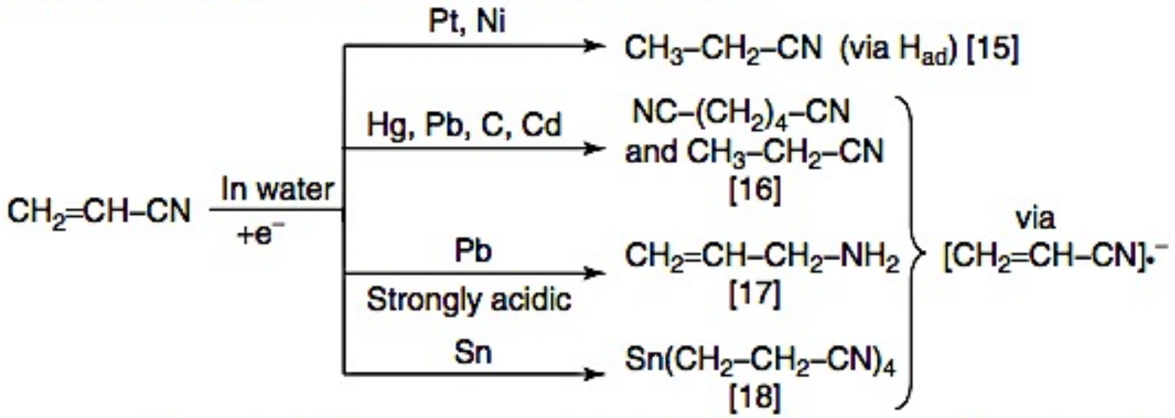
Fig. 3 Scheme of potentiostatic operation for a preparative electrolysis, using in principle a simplified cyclovoltammetry equipment. The potential of the working electrode is measured by a Luggin capillary, coupled with a reference electrode (RE, see Sect. 2.5.1.6). The control circuit in the potentiostat adjusts the cell current until the potential of the working electrode is equal to the voltage at the control input.

Introduction

- Anodic oxidation of carboxylates in aqueous solution via decarboxylation



- Cathodic reduction of acrylonitrile in aqueous solution



Scheme 1 Influence of the electrode material on the product spectrum of an electrochemical reaction.

Introduction

Tab. 1 Potential limits of some solvents at 0.1 mA cm^{-2} and 25 °C [4] sorted according to increasing dielectric constant ε (with 0.1 m $[NBu_4]ClO_4$ and platinum electrodes if not otherwise stated)

Solvent	*Abbreviation*	ε	*Potential limit [V]*	
			Cathodic	*Anodic*
1,2-Dimethoxyethane	–	3.5	−3.0[a]	+0.7[a]
Acetic acid (water free)	HAc	6.2	−1.7[a]	+2.0[b]
Tetrahydrofuran	THF	7.6	−3.3[c]	+2.1[c]
Dichloromethane (methylene chloride)	MC	9.1	−1.7	+1.8
Pyridine	Py	12.0	−2.2	+3.3
Acetone	–	21.0	−1.6	+1.6
Hexamethylphosphoric acid triamide	HMPA	30	−3.3[c]	+1.1[c]
Methanol	MeOH	31.5	−2.2[a]	+1.3
N-methylpyrrolidone	NMP	32	−3.3[a]	+1.4[c]
Nitromethane	–	35.7	−2.4[c]	+3.0[c]
Acetonitrile	ACN	36.2	−2.6	+2.7
N,N-dimethylformamide	DMF	36.7	−2.7	+1.5
N,N-dimethylacetamide	DMA	38	−2.6	+1.3
Sulfolane (tetramethylenesulfone)	–	44	−2.3[a]	+3.3
Dimethylsulfoxide	DMSO	46.6	−2.7	+1.3
Propylenecarbonate	PC	65.2	−1.9	+1.7
Water	–	80	−2.9[a]	+1.4
85–96 wt-% sulfuric acid	–	100	−1.0[a]	+2.1
Tetrahexylammoniumbenzoate (molten at 25 °C)	–	–	−1.2	+0.3
$AlCl_3/NaCl/KCl$ (molten at 150 °C)	–	–	−1.9	+1.0

[a] Mercury electrode.
[b] Sodium acetate.
[c] Lithium perchlorate.
ε = dielectric constant.

Introduction

Tab. 2 Potential limits of some anions and cations of supporting electrolytes [4] (concentration 0.1 m in water and acetonitrile at 0.1 mA cm^{-2} and 25 °C)

Ion	*Electrode*	*Potential limit [V]*	
		In water	*In acetonitrile*
J^-	Pt anode	0.30[a]	0.20
Br^-	"	0.85[a]	0.70
Cl^-	"	1.10[a]	1.15
F^-	"	(2.6)[a,b]	–
ClO_4^-	"	(1.5)	2.6
$[BF_4]^-$	"	–	3.1
$[PF_6]^-$	"	–	3.2
Li^+	Hg cathode	−2.16	−1.8
Na^+	"	−1.95	−1.7
K^+	"	−2.03	−1.8
Rb^+	"	−1.98	−1.8
NH_4^+	"	−2.00	−1.7
$N(CH_3)_4^+$	"	−2.65	−2.4
$N(C_2H_5)_4^+$	"	−2.78	−2.5
$N(C_4H_9)_4^+$	"	−2.87	−2.6
$N(C_2H_5)_3H^+$	"	−1.83	–

[a] Resulting from standard potentials.
[b] Oxygen evolution already at a lower potential.

Introduction

Table 2.1. Standard potentials of reference electrodes $E^{0'} + E_j$ (V at °C)

Reference electrodes	Molarity	$E^{0'} + E_j$ (V at °C) 20	25
AgCl/Ag	3.5 M KCl	0.208	0.205
	saturated	0.204	0.199
Hg_2Cl_2/Hg	0.1 M KCl	0.336	0.336
	1.0 M	0.284	0.283
	3.5 M	0.252	0.250
	saturated	0.248	0.244
Hg_2SO_4/Hg	saturated K_2SO_4	0.658 (22 °C)	
Hg/HgO	0.3 M NaOH	0.926	

Introduction

Table 2.2. Potential range in acetonitrile under different conditions

Supporting electrolyte	Electrodes working	reference	Potential range (V)
$(C_2H_5)_4NClO_4$	Hg	SCE	0.6 to − 2.8
$LiClO_4$	Pt	Ag/0.01 M $AgClO_4$/ 0.1 M $LiClO_4$	2.4 to − 3.5
$NaBF_4$	Pt	Ag/0.1 M $AgNO_3$	anodic to 4.0

Table 2.3. Potential ranges in dimethylformamide under different conditions

Supporting electrolyte	Electrodes working	reference	Potential range (V)
$(C_2H_5)_4NClO_4$	Hg	SCE	+ 0.5 to − 3.0
$(C_2H_5)_4NClO_4$	Pt	SCE	+ 1.6 − 2.1
$(C_4H_9)_4NClO_4$	Hg	SCE	− 0.4 − 3.0
$(C_4H_9)_4NClO_4$	Pt	SCE	+ 1.2 − 2.5

Introduction

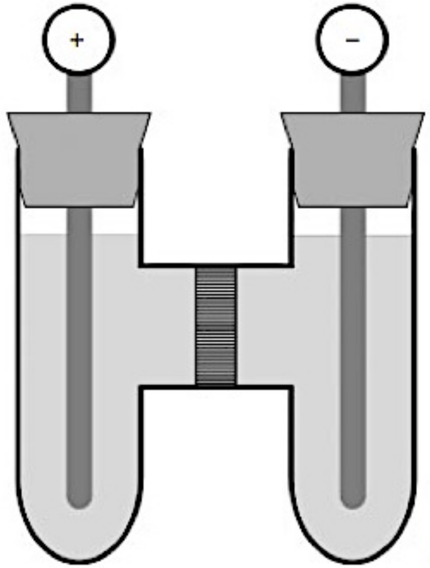


Fig. 7 H-cell.

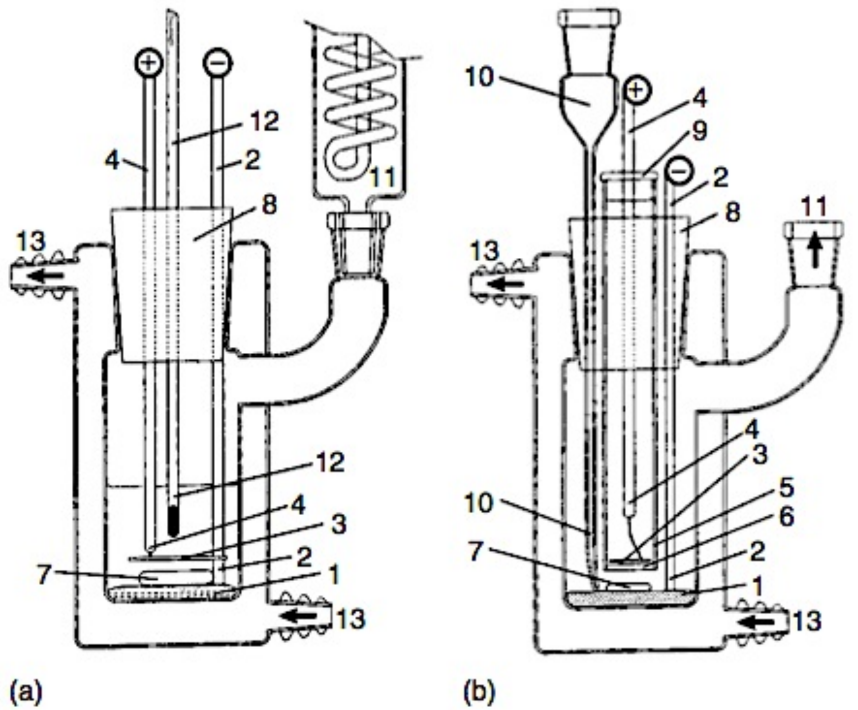


Fig. 8 Beaker glass cells (a) undivided, (b) divided. 1 mercury cathode, 2 cathode current feeder, 3 platinum mesh anode, 4 anode current feeder, 5 anolyte tube with, 6 diaphragm, 7 magnetic stirrer, 8,9 PTFE stopper, 10 reference electrode with Luggin capillary, 11 reflux condenser, 12 thermometer, 13 connection to thermostat.

Introduction

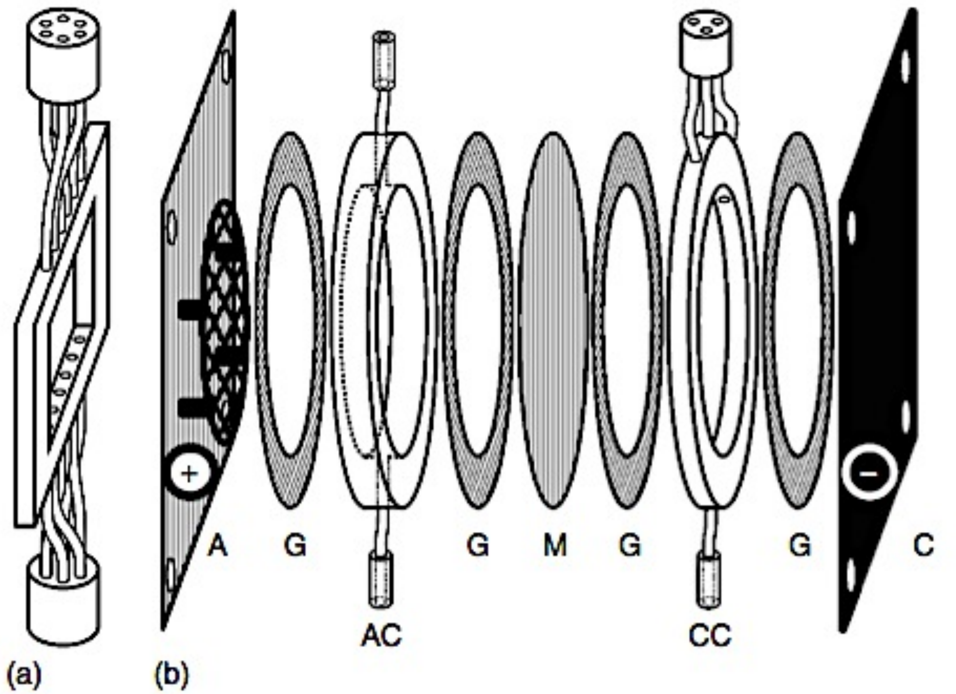
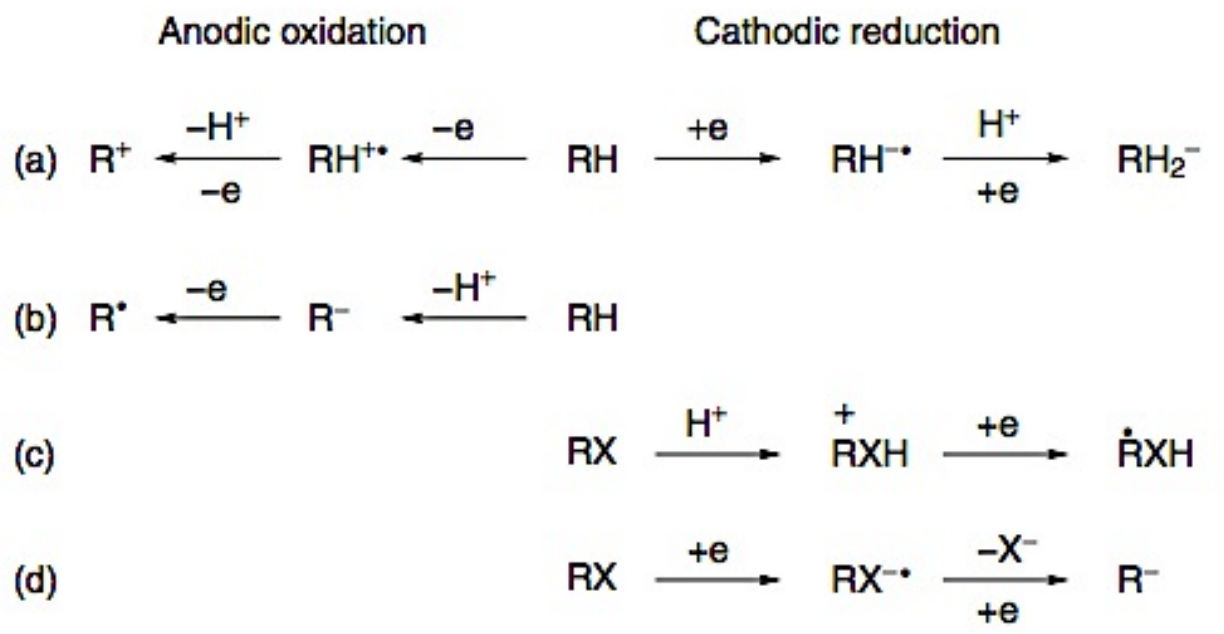


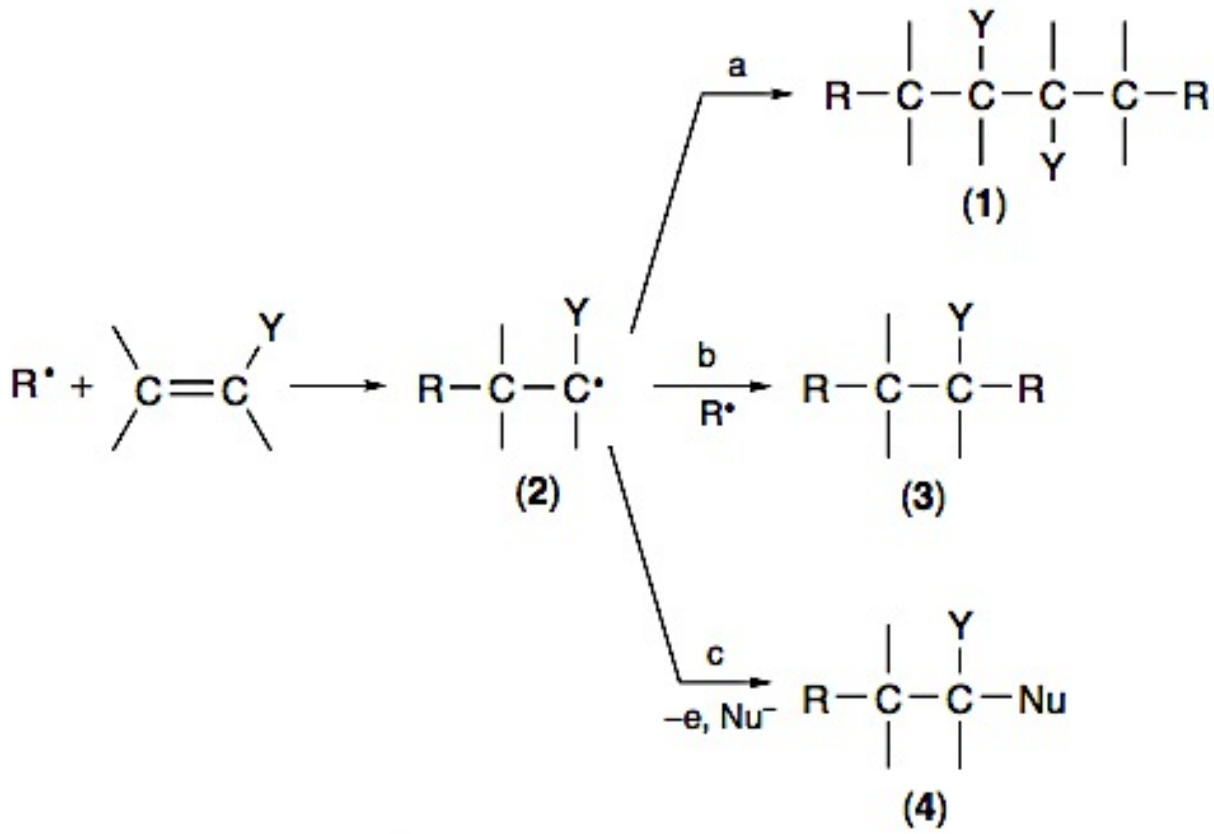
Fig. 10 Examples of parallel-plate and frame designs for laboratory flow-through cells (a) cell chamber for strong mixing and (b) various parts of a cylindrical cell. A: anode (with preelectrode); G: sealing gaskets; AC: anode compartment (glass ring, reduced mixing requirements); M: membrane (diaphragm); CC: cathode compartment (three tubes for gas outlet, sufficient mixing by gas evolution); C: cathode (current feeders outside the cell at the four corners).

Introduction



Scheme 1 Electrochemical generation of reactive intermediates for polar reactions.

Introduction



Scheme 2 Reactions of electrogenerated radicals.

Introduction

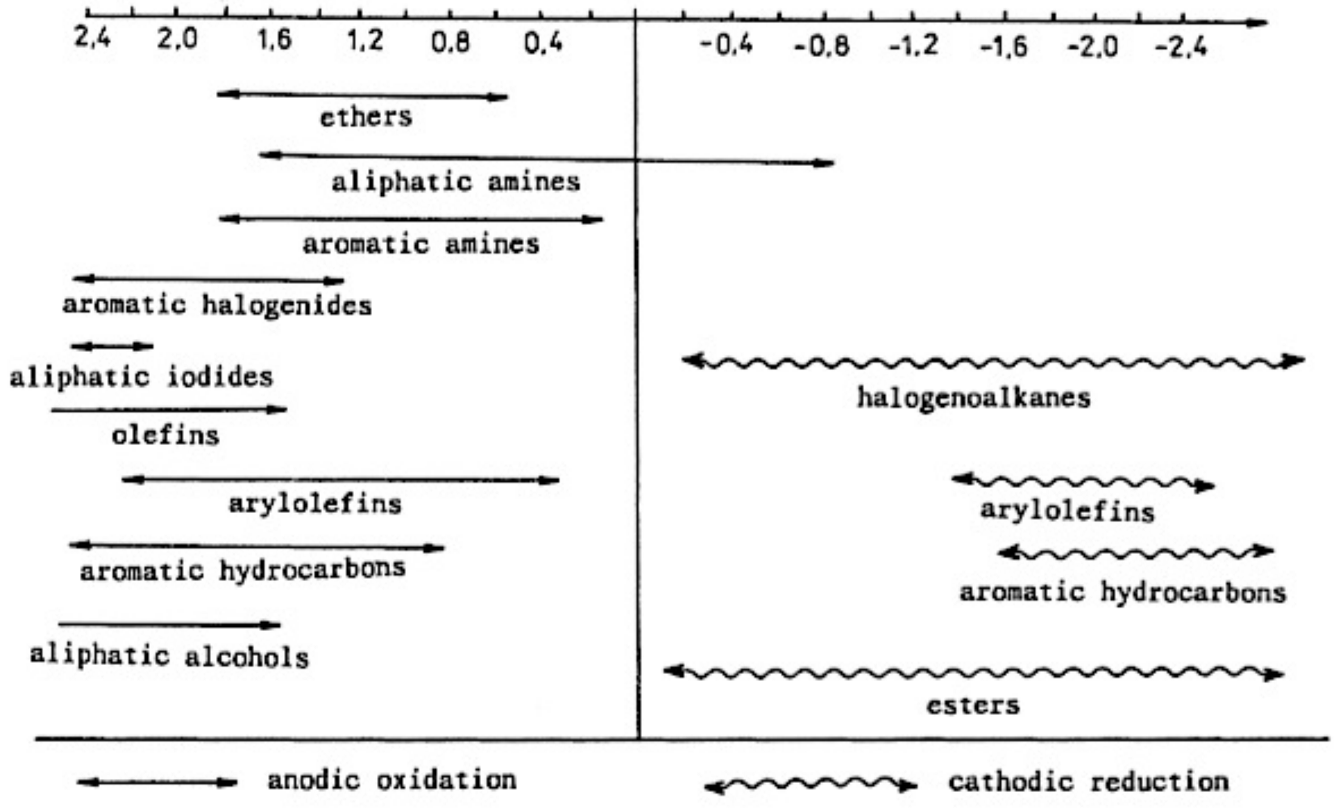
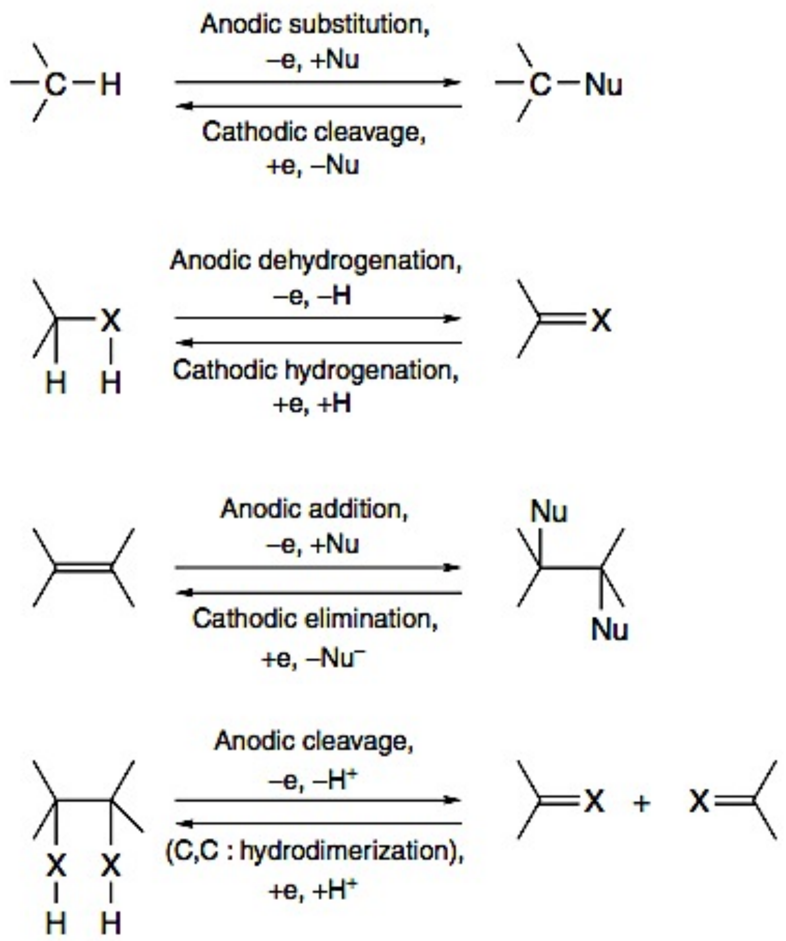


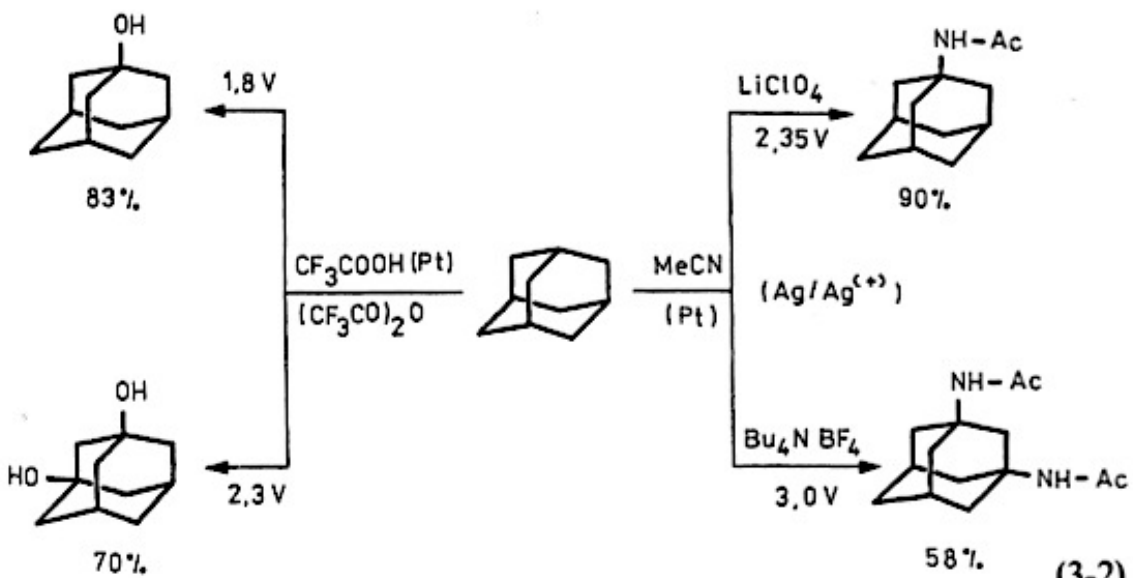
Fig. 3.1. Potential range of oxidation and reduction of some electrophors (vs SCE)

Introduction



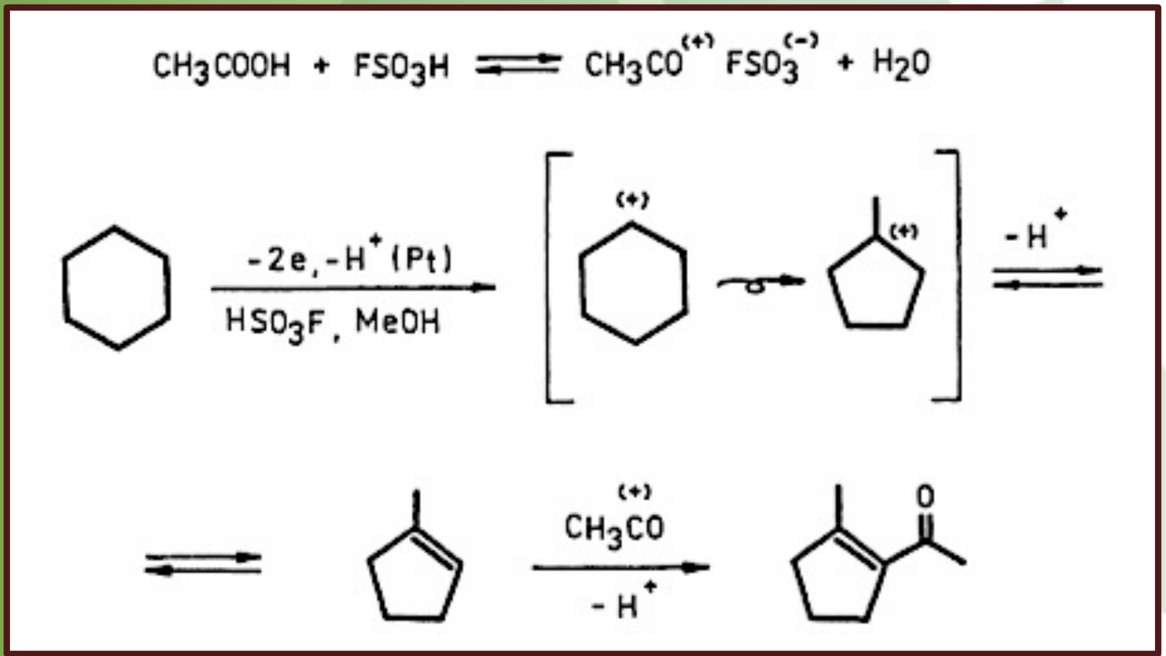
Scheme 3 Classification of electrochemical functional group interconversions (FGI's).

Direct Anodic Oxidation



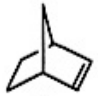
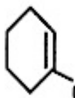
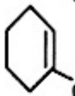
(3-2)

Direct Anodic Oxidation

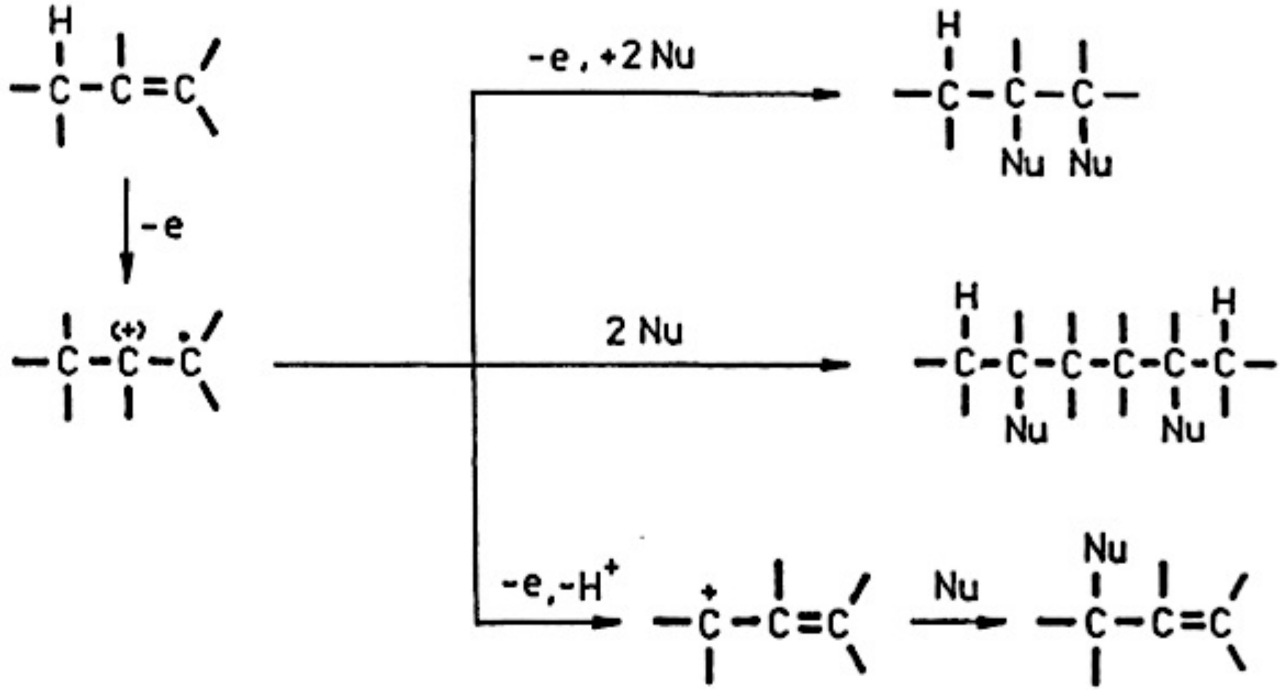


Direct Anodic Oxidation

Table 3.1. Oxidation potentials of selected unsaturated compounds

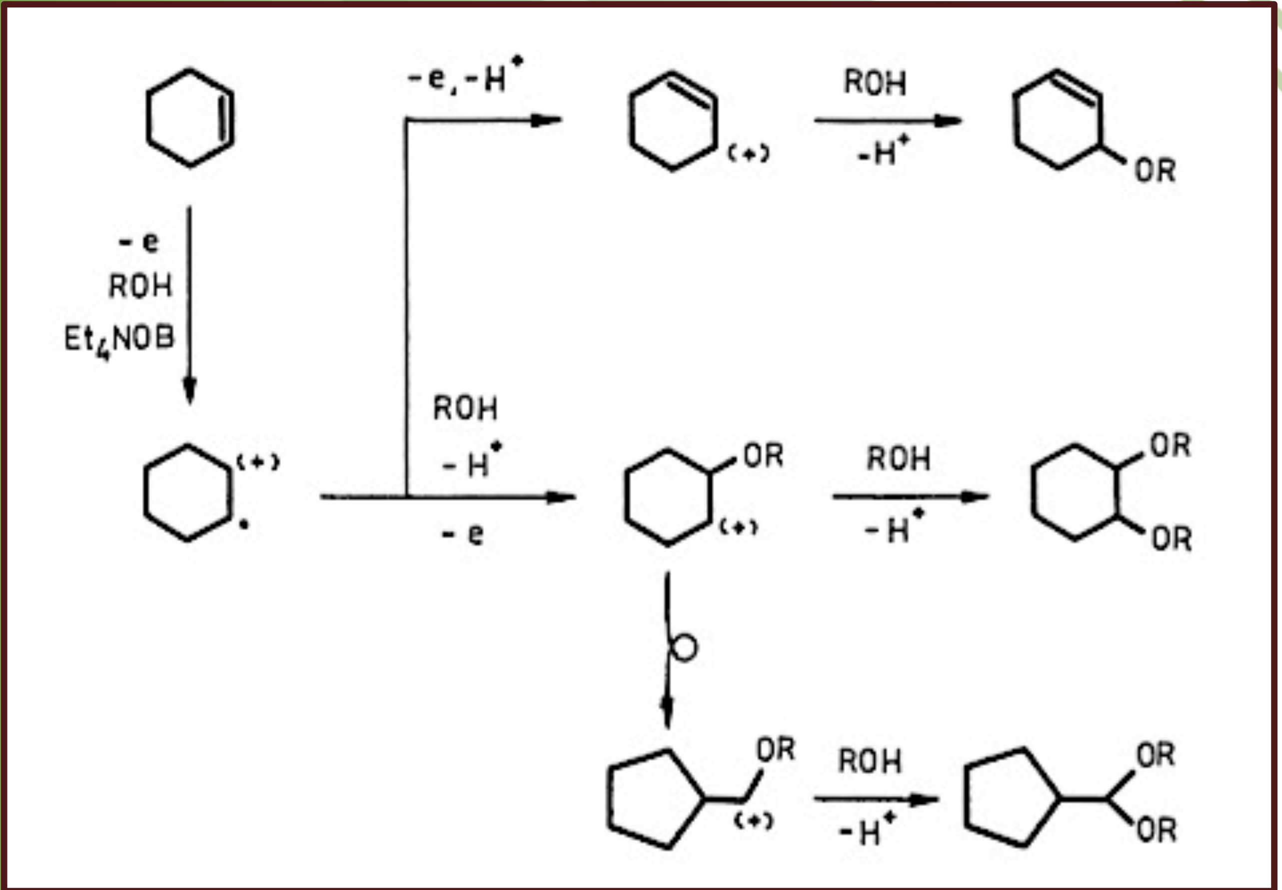
Compound	$E_{1/2}$ (E_p)	Reference electrode	Supporting electrolyte	Solvent	Electrode
C_6H_{13}–CH=CH_2	2.8	SCE	$LiClO_4$	CH_3CN	Pt
C_5H_{11}–CH=CH–CH_3	2.3	SCE	$LiClO_4$	CH_3CN	Pt
$(C_2H_5)_2C$=CH_2	2.17	SCE	$LiClO_4$	CH_3CN	Pt
	2.14	SCE	$LiClO_4$	CH_3CN	Pt
	2.02	SCE	$LiClO_4$	CH_3CN	Pt
	1.54	SCE	$LiClO_4$	CH_3CN	Pt
	1.36	SCE	$LiClO_4$	CH_3CN	Pt
					
X=H	1.54	SCE	$LiClO_4$	CH_3CN	Pt
X=$COOC_2H_5$	1.85	SCE	$LiClO_4$	CH_3CN	Pt
X=CN	1.99	SCE	$LiClO_4$	CH_3CN	Pt
CH_2=CH–O–C_2H_5	1.72	Ag/Ag^+	$NaClO_4$	CH_3OH	Pt
	1.28 (1.63)	Ag/Ag^+	$NaClO_4$	CH_3OH	Pt
	1.93	SCE	$LiClO_4$	CH_3CN	Pt

Direct Anodic Oxidation

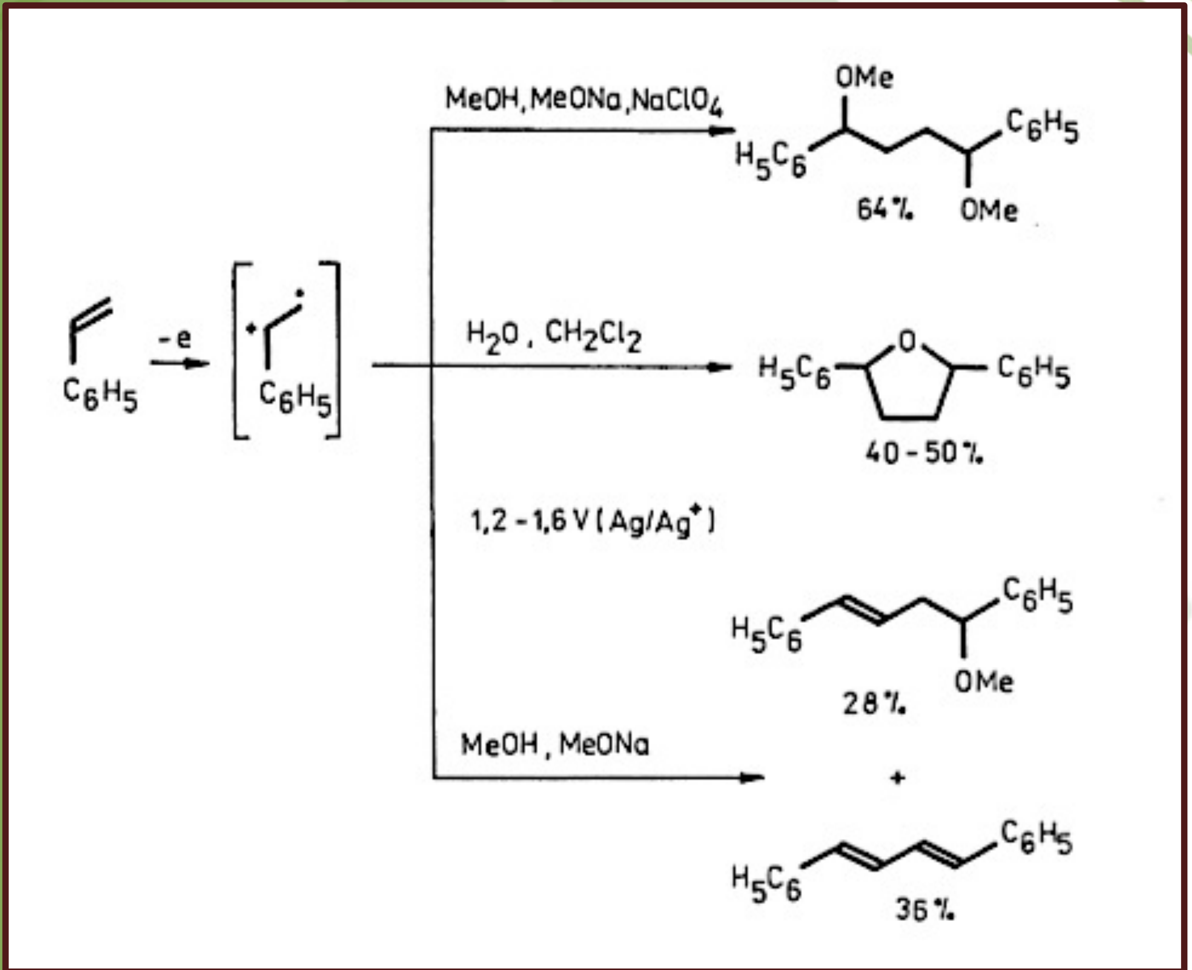


(3-7)

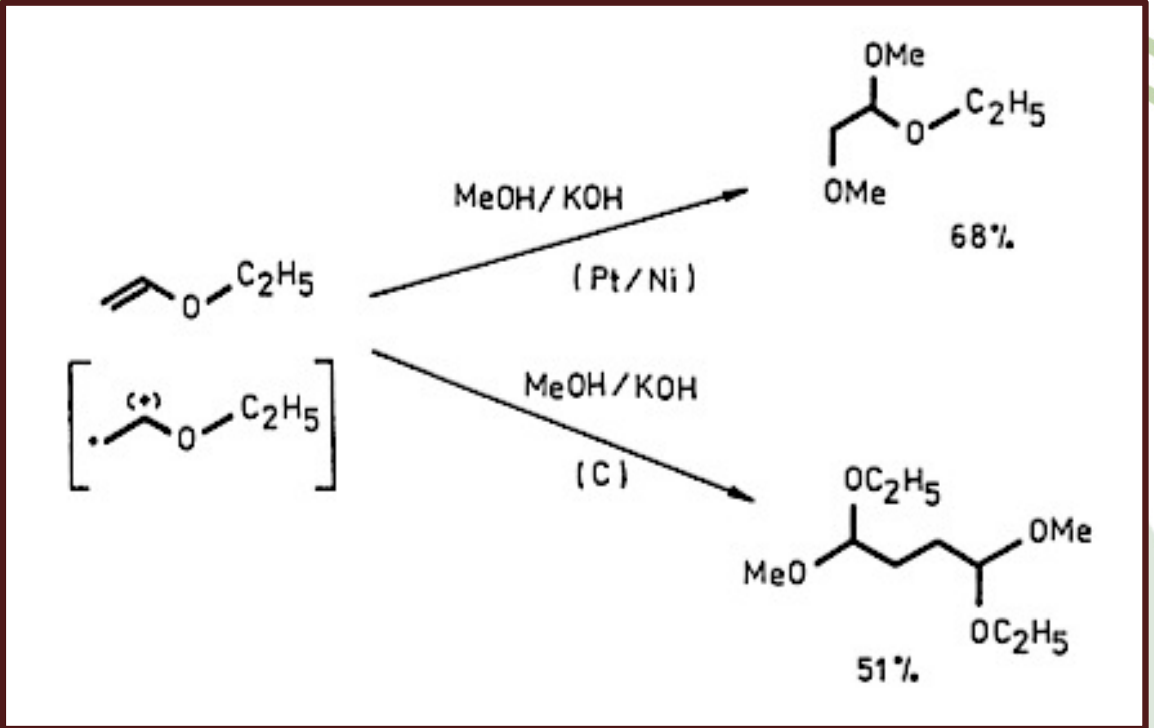
Direct Anodic Oxidation

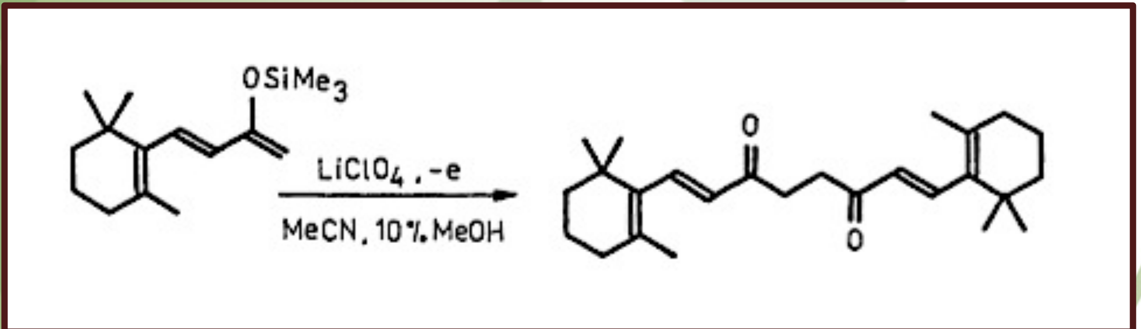


Direct Anodic Oxidation



Direct Anodic Oxidation





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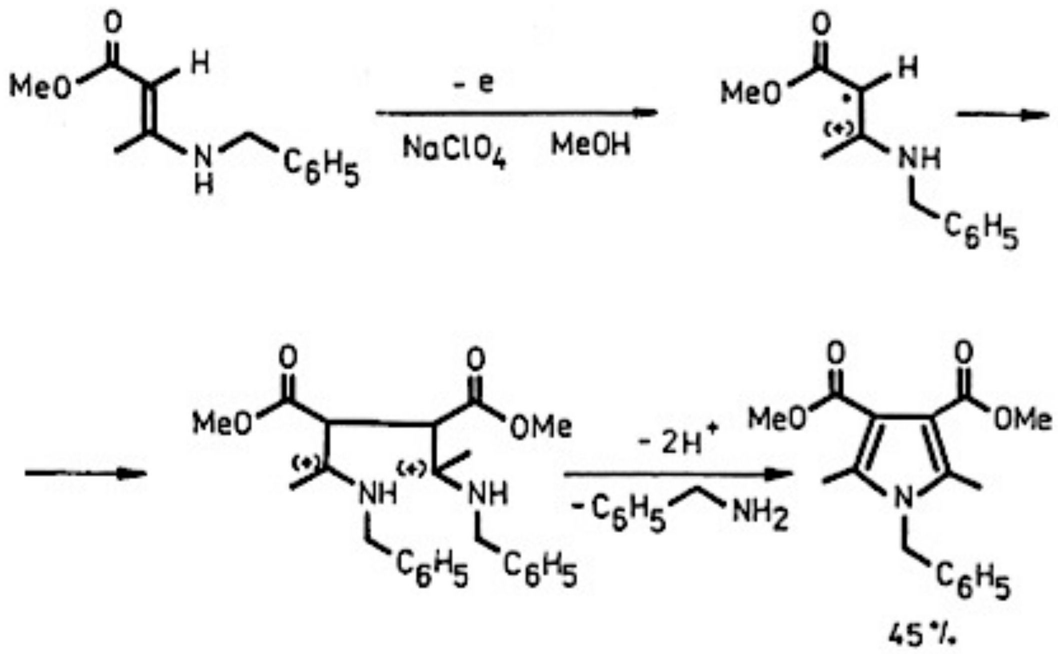

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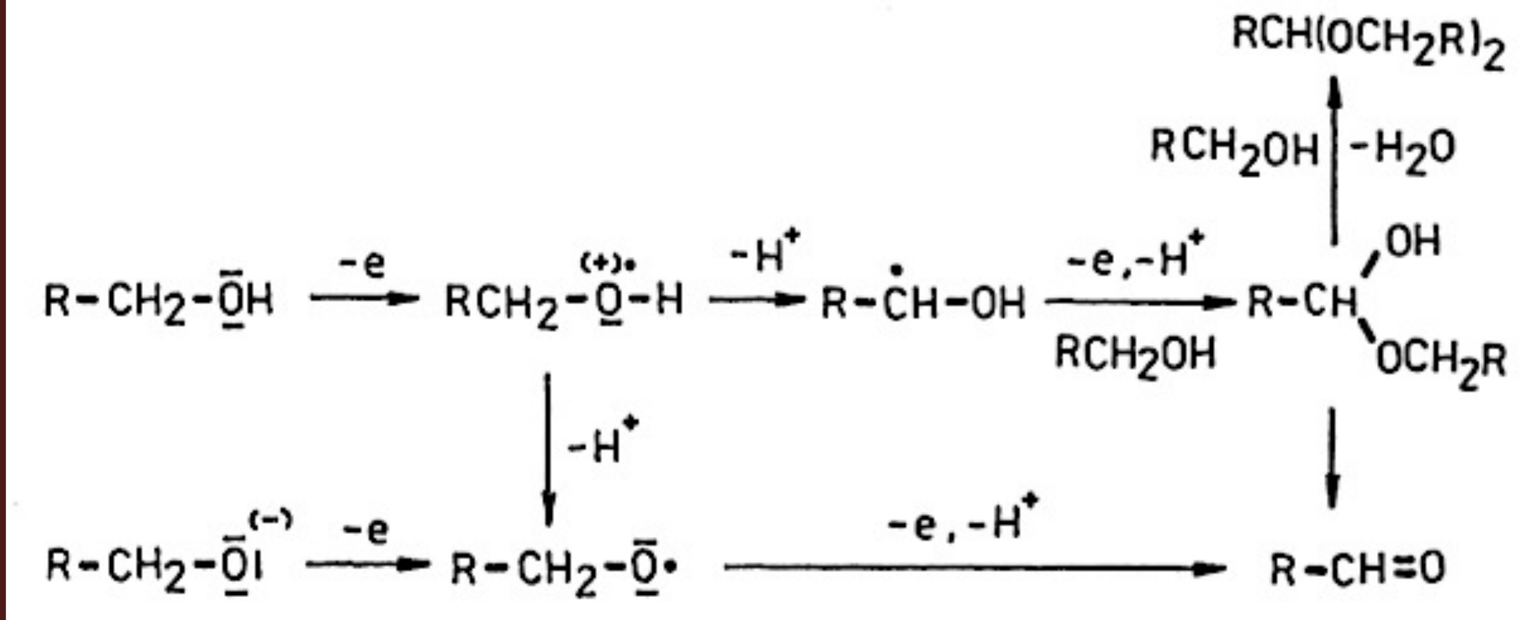
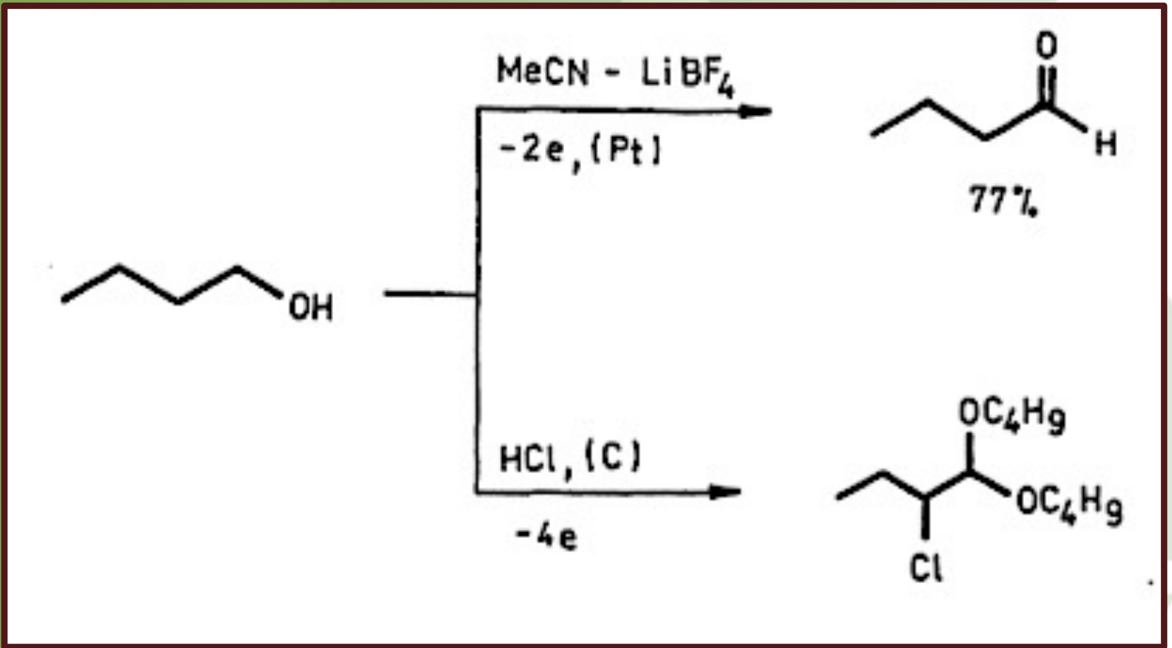


(3-28)

Direct Anodic Oxidation



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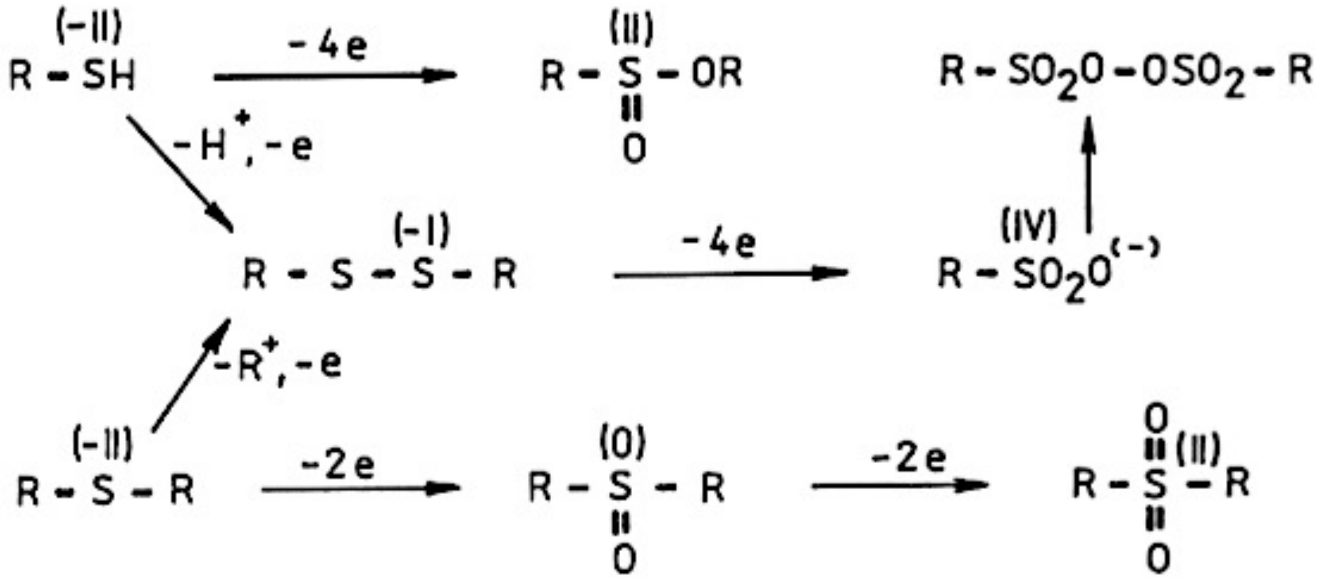
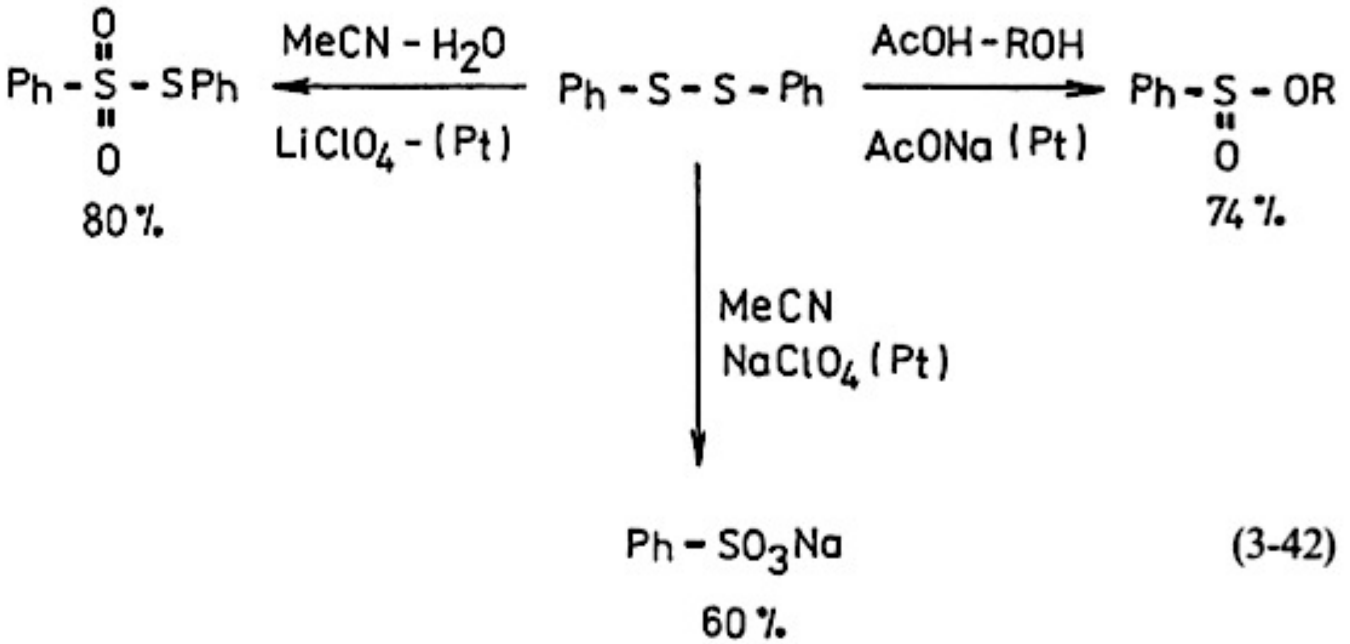


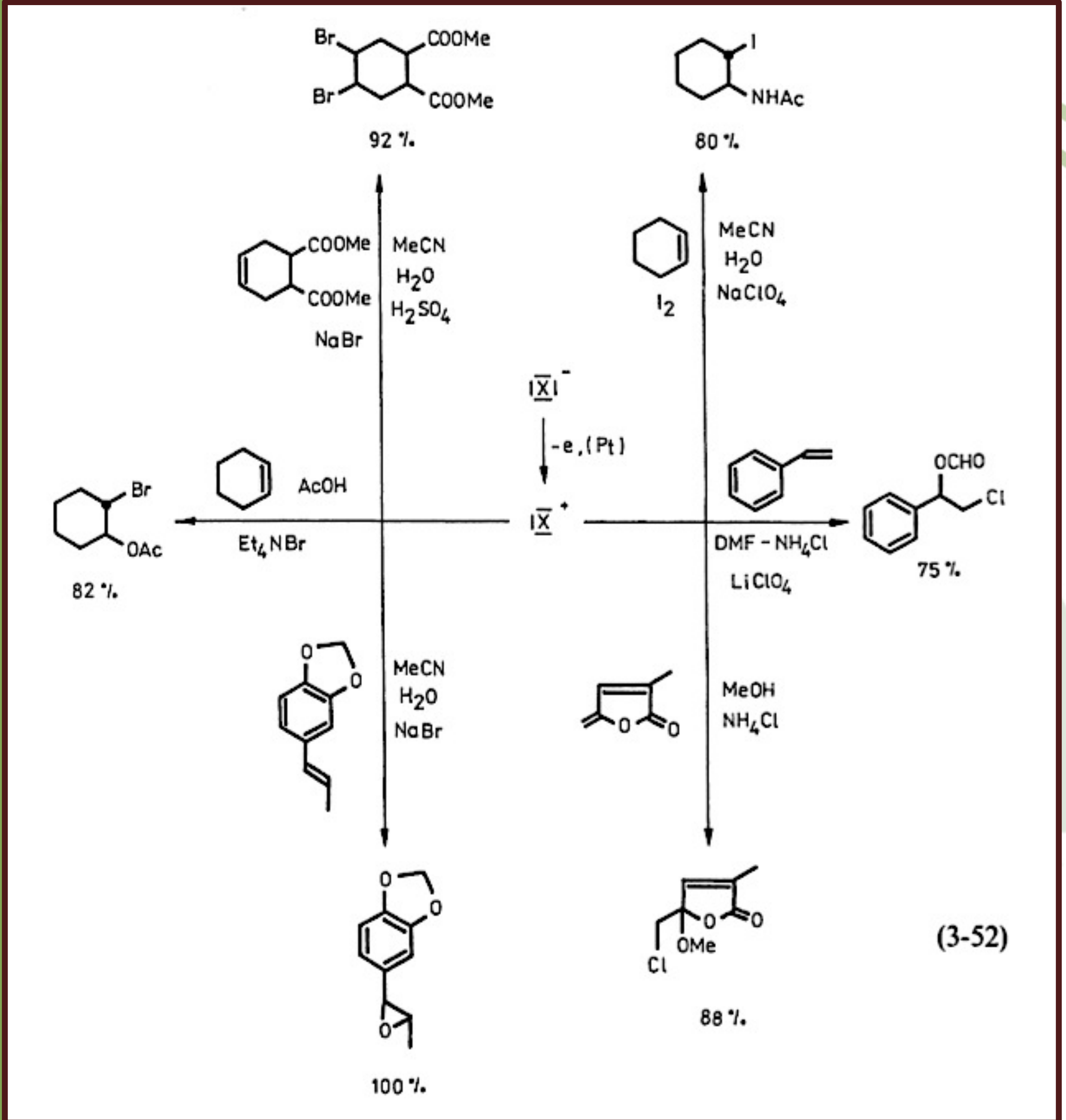
(3-39)

Direct Anodic Oxidation

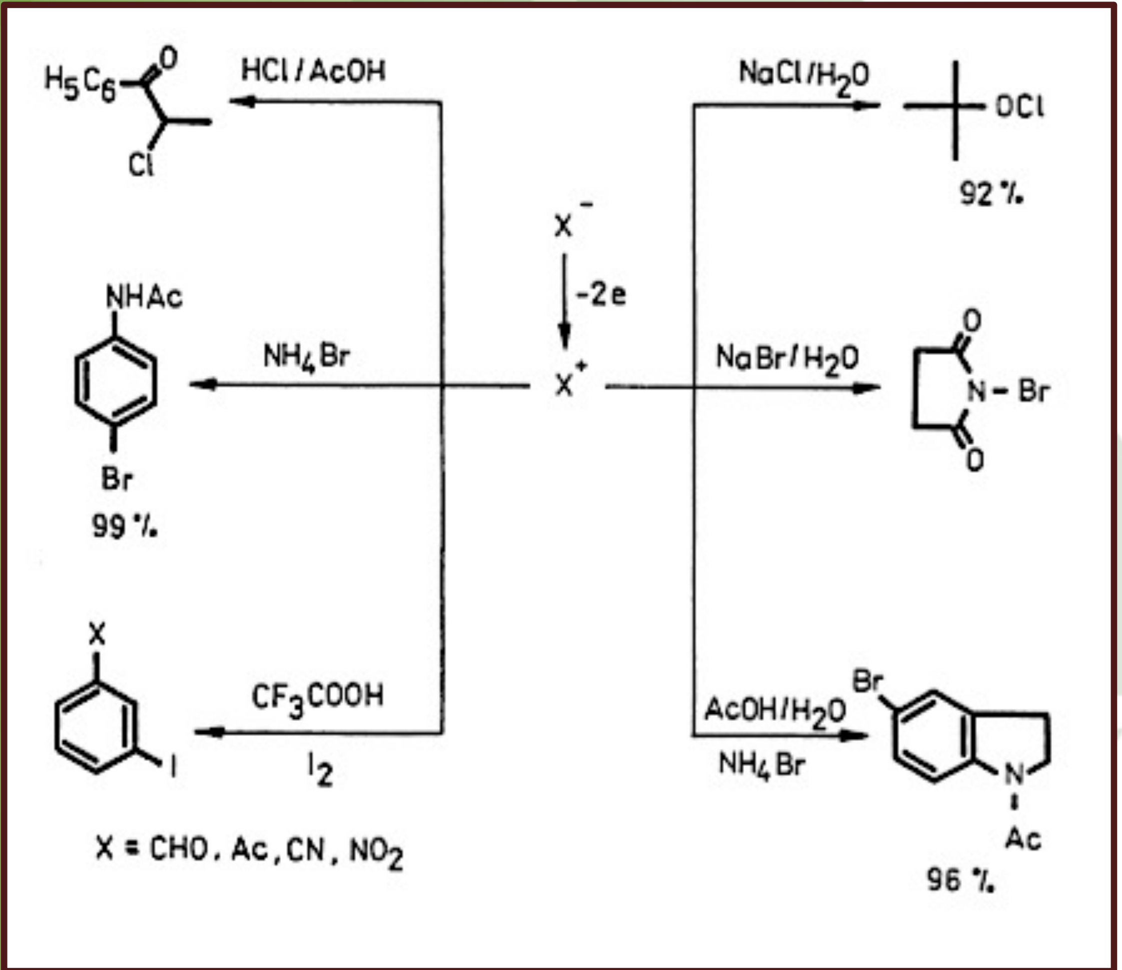


(3-42)

Direct Anodic Oxidation



Direct Anodic Oxidation



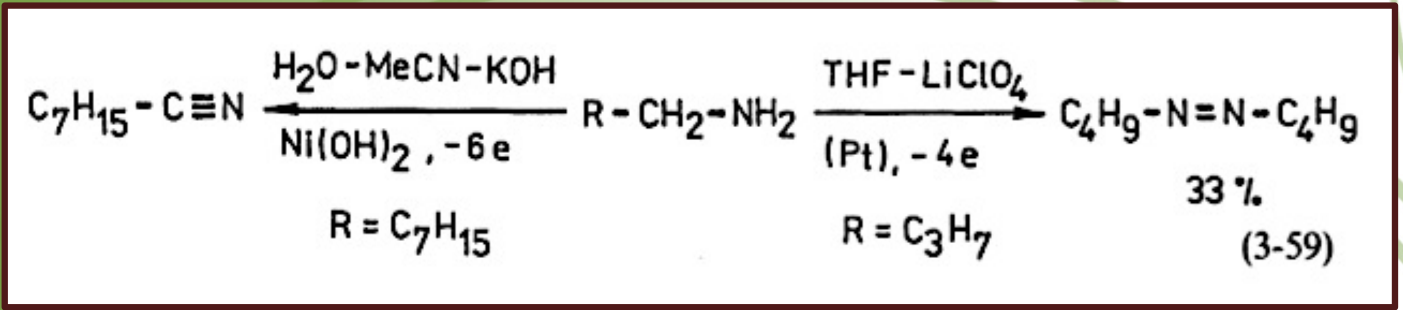
Direct Anodic Oxidation

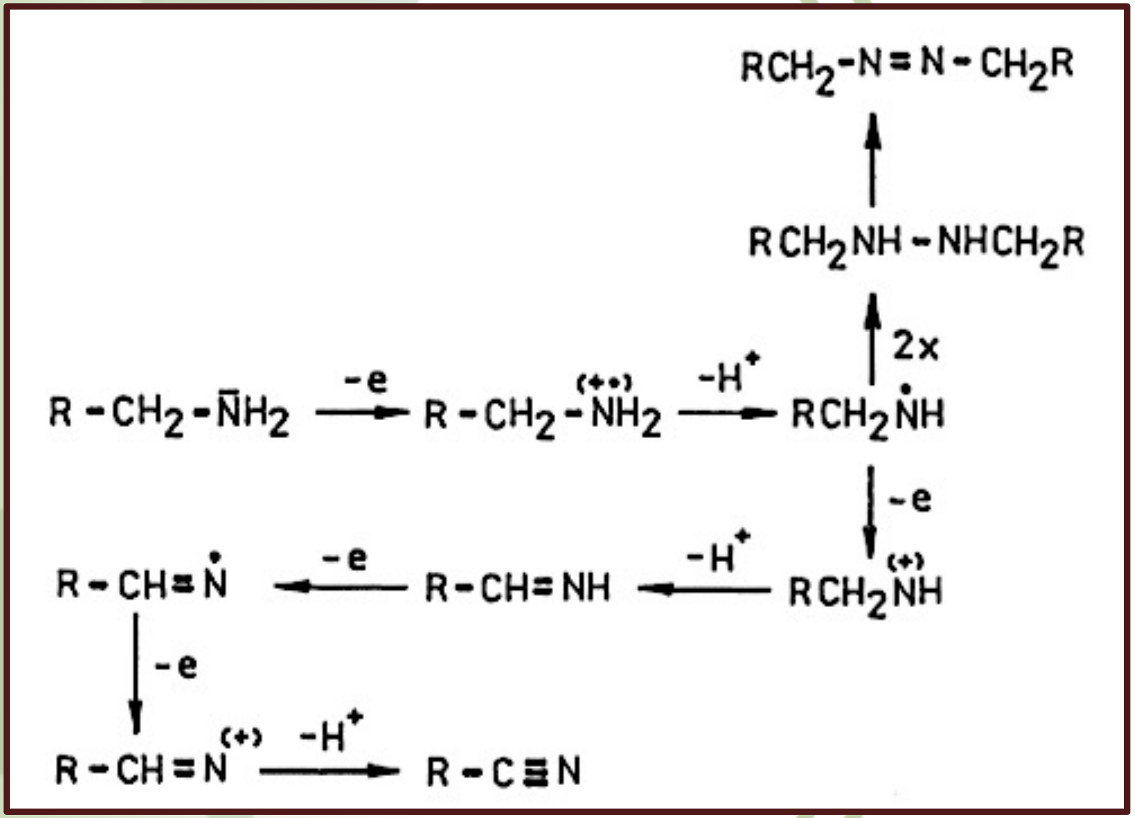
$$(R-CH_2)_3N \xrightarrow{-e} (R-CH_2)_3N^{(+\bullet)} \xrightarrow{-H^+} (R-CH_2)_2N-\dot{C}H-R \xrightarrow{-e}$$

$$(R-CH_2)_2N-\overset{(+)}{C}H-R \rightleftharpoons (R-CH_2)_2\overset{(+)}{N}=CH-R \xrightarrow[-H^+]{H_2O}$$

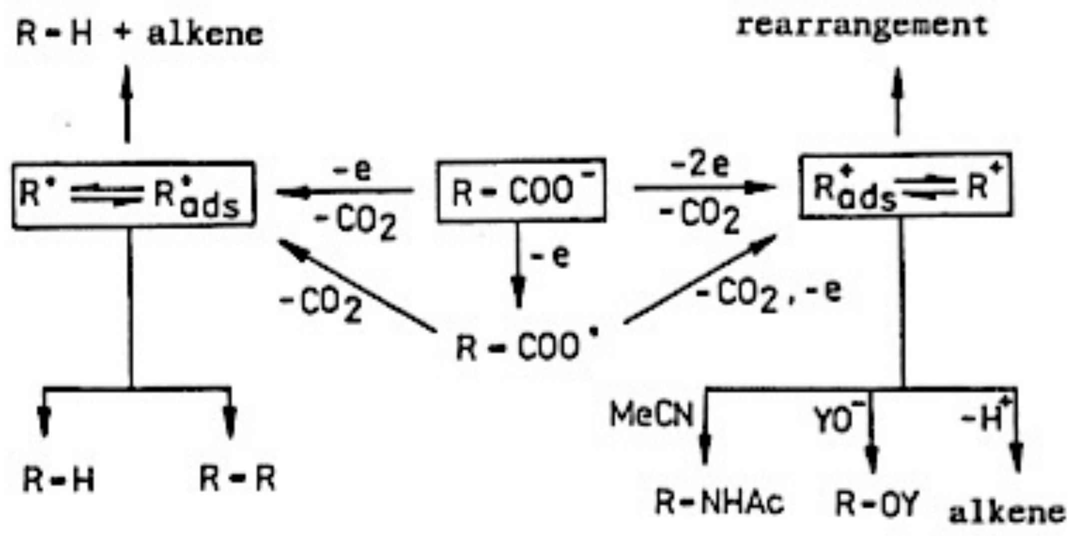
$$\longrightarrow (R-CH_2)_2NH + R-CH=O \qquad (3\text{-}57)$$

Direct Anodic Oxidation



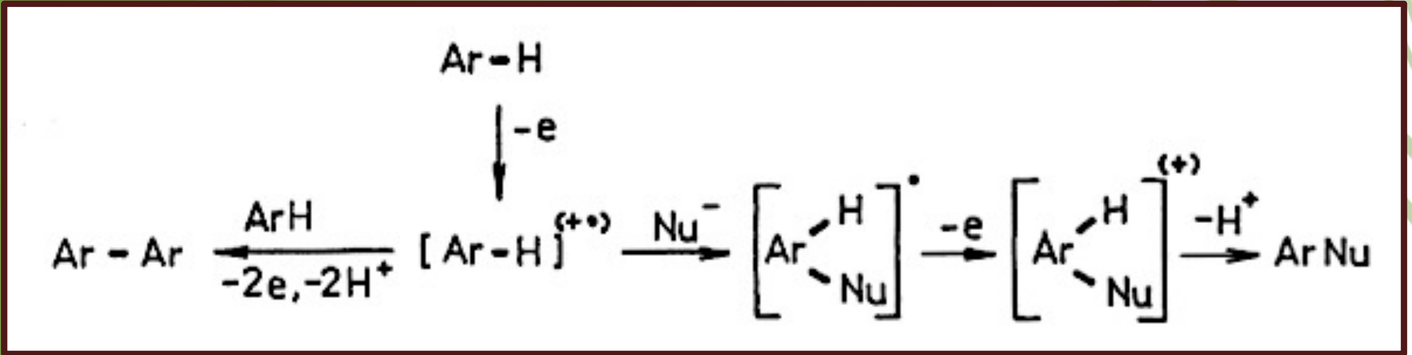


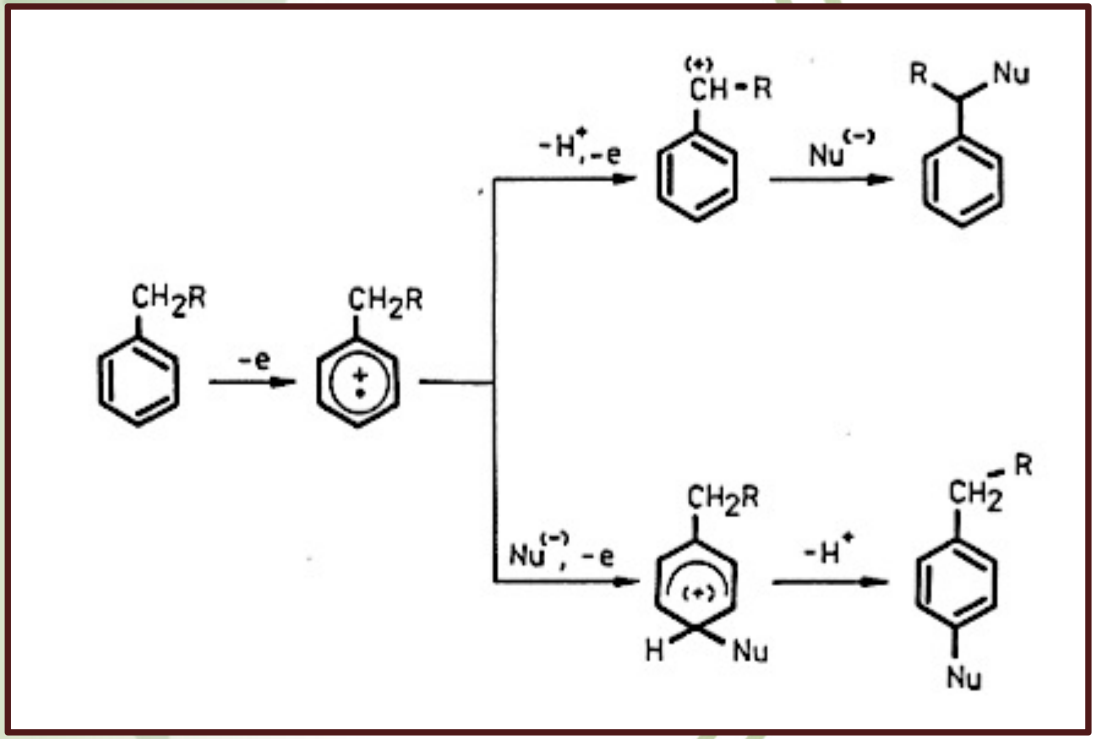
Direct Anodic Oxidation



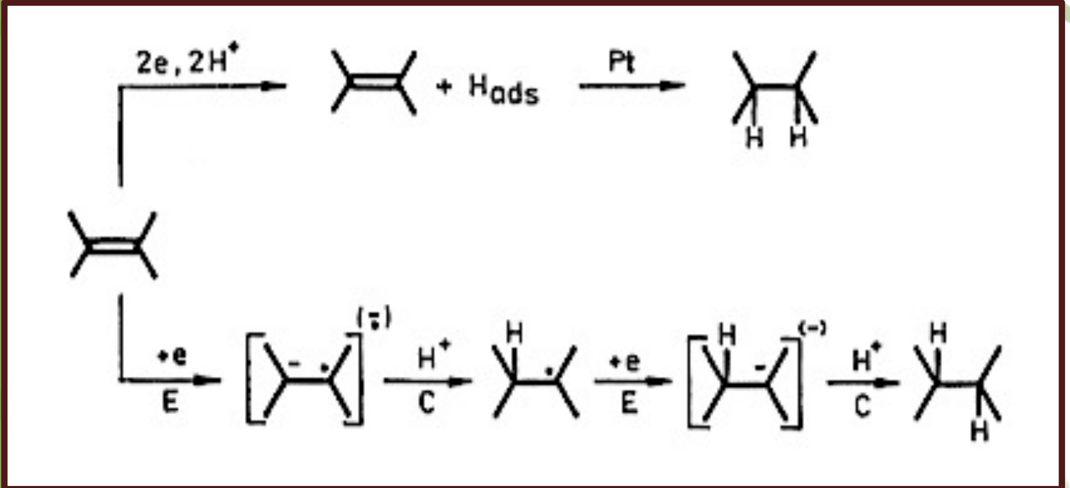
$$R-COO^{(-)} \xrightarrow{-e} R-COO^{\bullet} \xrightarrow{-CO_2} R^{\bullet} \xrightarrow{-e} R^{(+)}$$

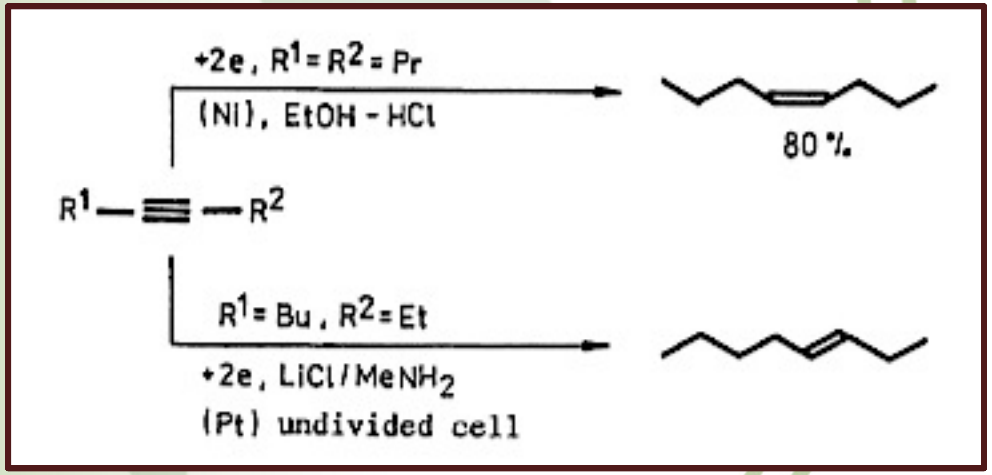
Direct Anodic Oxidation





Direct Cathodic Reduction





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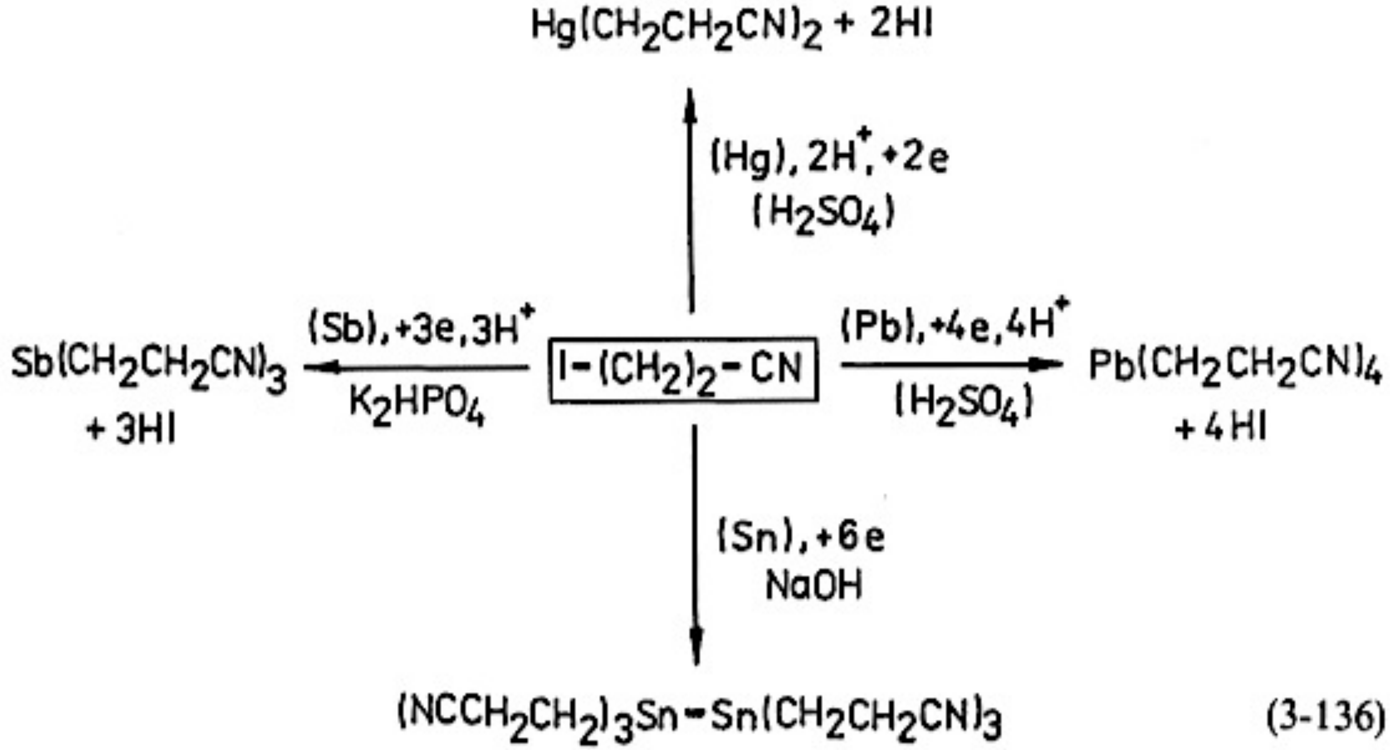
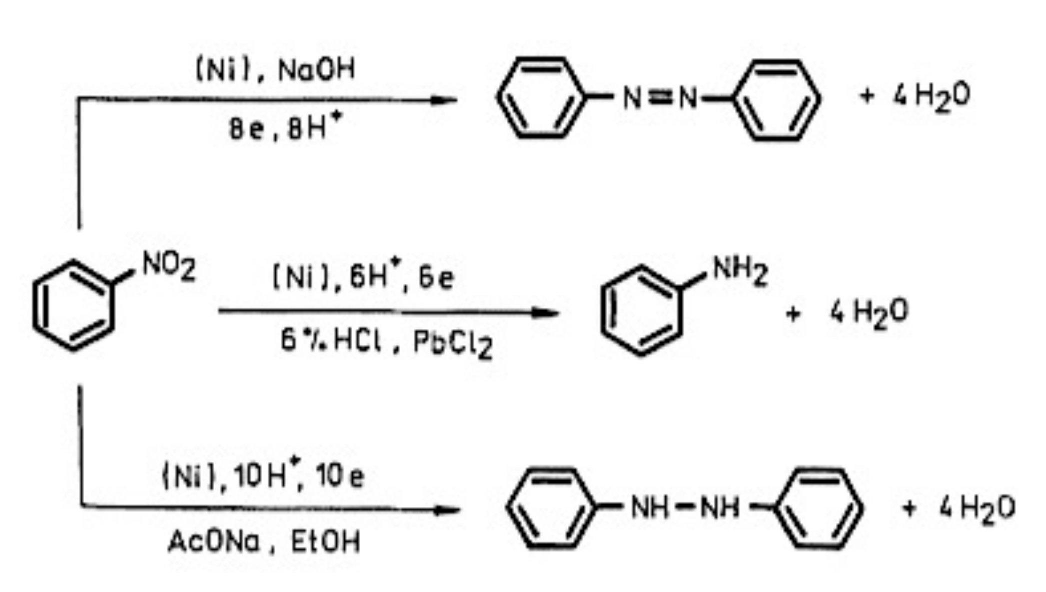
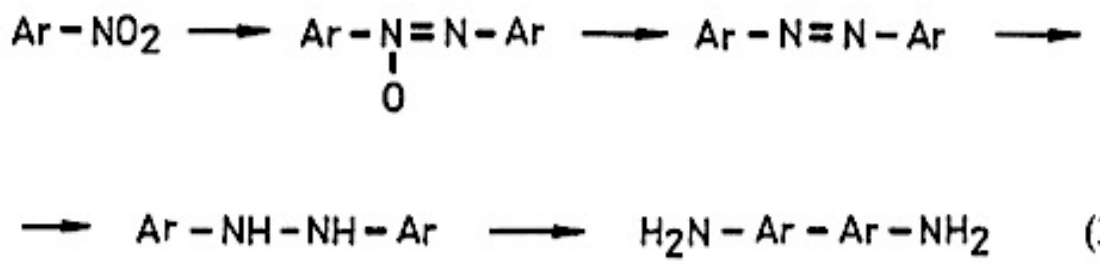


(3-136)

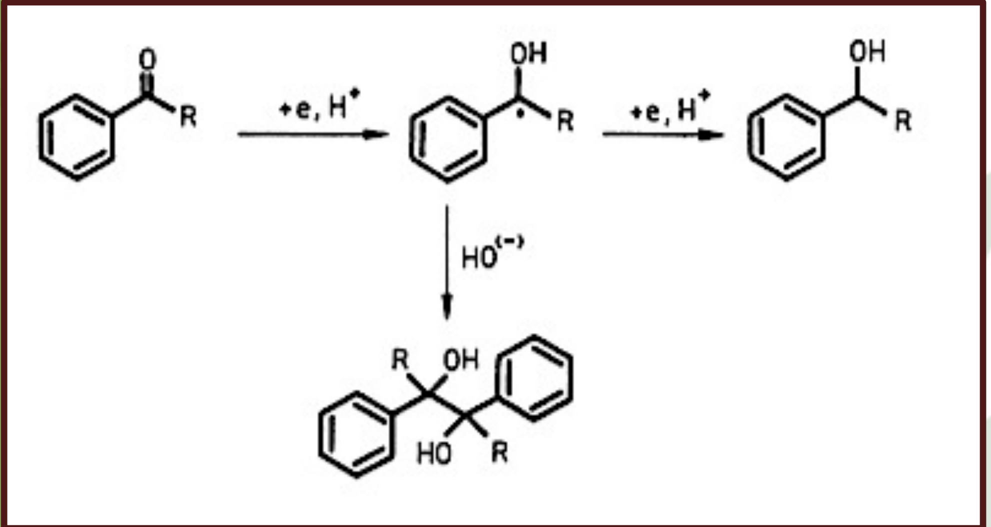
Direct Cathodic Reduction

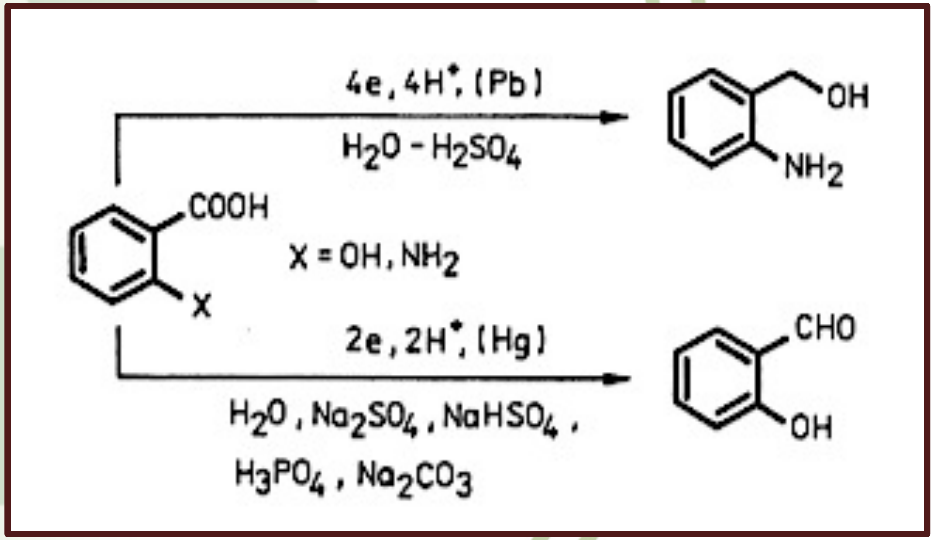




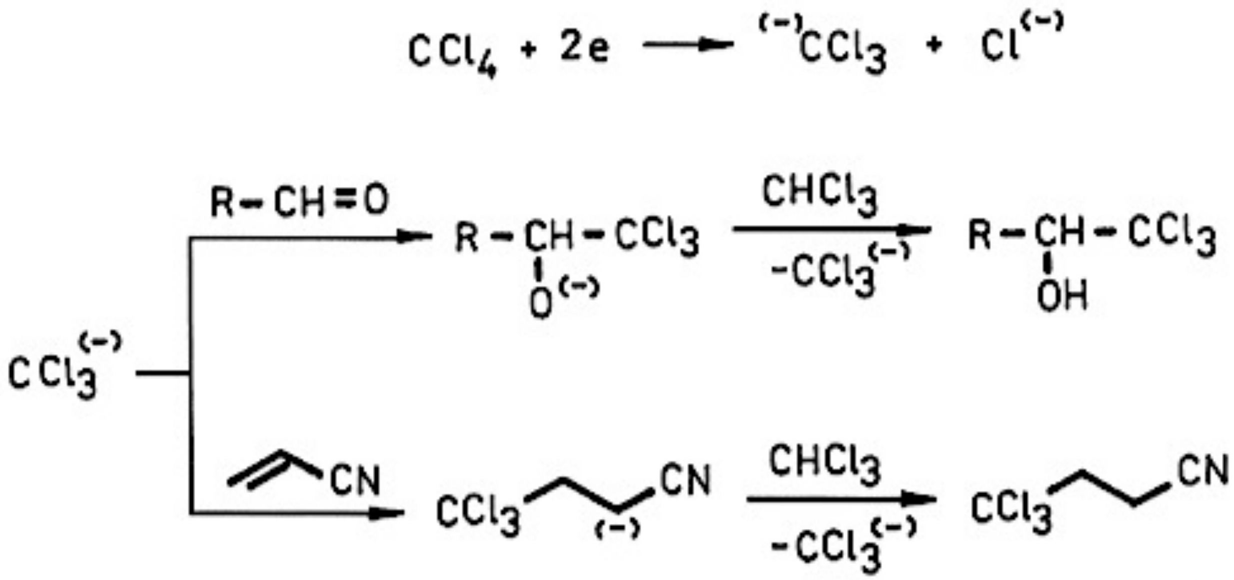
(3-141)

Direct Cathodic Reduction





Direct Cathodic Reduction



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