CHAPTER 7

Green Chemistry

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Qualitative principles that can be used identify green chemistry alternatives

7.3 Quantitative/Optimization-Based Frameworks for Design of Green Chemistry Synthesis Pathways

- Quantitative, optimization-based approaches that have been used to identify environmentally preferable reaction pathways.

7.4 Green Chemistry Expert System Case Studies

- US EPA’s Green Chemistry Expert System, which provides case studies of many of the principles

7.1 Green Chemistry

Chemical products can be manufactured a wide variety of synthesis routes. The chemical engineer who design a chemical process must choose

- Alternative raw materials
- Solvent
- Reaction pathways
- Reaction conditions

Design Choice

These design choices can have a significant impact on the overall environmental performance of a chemical process.

7.1 Green Chemistry

Ideal chemical reactions would have attributes such as

- simplicity
- safety
- high yield and selectivity
- energy efficiency
- use of renewable and recyclable reagents and raw materials

In general, chemical reactions cannot achieve all of these goals simultaneously and it is the task of chemical engineers to identify pathways that optimize the balance of desired attributes

7.1 Green Chemistry

- Identification of environmentally preferable pathways requires creative advances in chemistry as well as process design.

- Because the number of choices in selecting reaction pathways is so large and implications of those choices are so complex, systematic and quantitative design tools for identifying green chemistries are not available.

- Nevertheless, an extensive body of knowledge concerning green chemistry exists and some qualitative and quantitative design tools are emerging.

- ***Green Chemistry*** : the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

7.2 Green Chemistry Methodologies

- Designing chemical manufacturing process involves
  - selection of feed-stock
  - selection of solvents, catalysts and other materials
  - selection of reaction pathways

- This selection describes some of alternatives that are available in making these design decisions and suggests a set of principles that process designers can use to identify alternatives. Specially, the following issues are addressed:
  - alternative feed-stocks
  - green solvents
  - synthesis pathways
  - inherently safer chemistry

7.2 Green Chemistry Methodologies

7.2.1 Feedstocks

In many cases, the selection of a starting materials from which the final product will be the most significant factor in determining the impact of a chemical manufacturing process on the environment. There are a number of criteria that can be used in evaluating the potential environmental impacts of materials.

7.2 Green Chemistry Methodologies

7.2.1 Feedstocks

The criteria for a starting material include

- its persistence in the environment
- its bioaccumulation
- potential
- its ecotoxicity
- human toxicity
- scarcity of materials
- renewable or non-renewable

How do we identify alternative raw materials can improve environmental performance ?

Case Studies *for identifying alternative raw materials*

✿ **Adipic Acid manufacturing *(Fig. 7.2-1)***

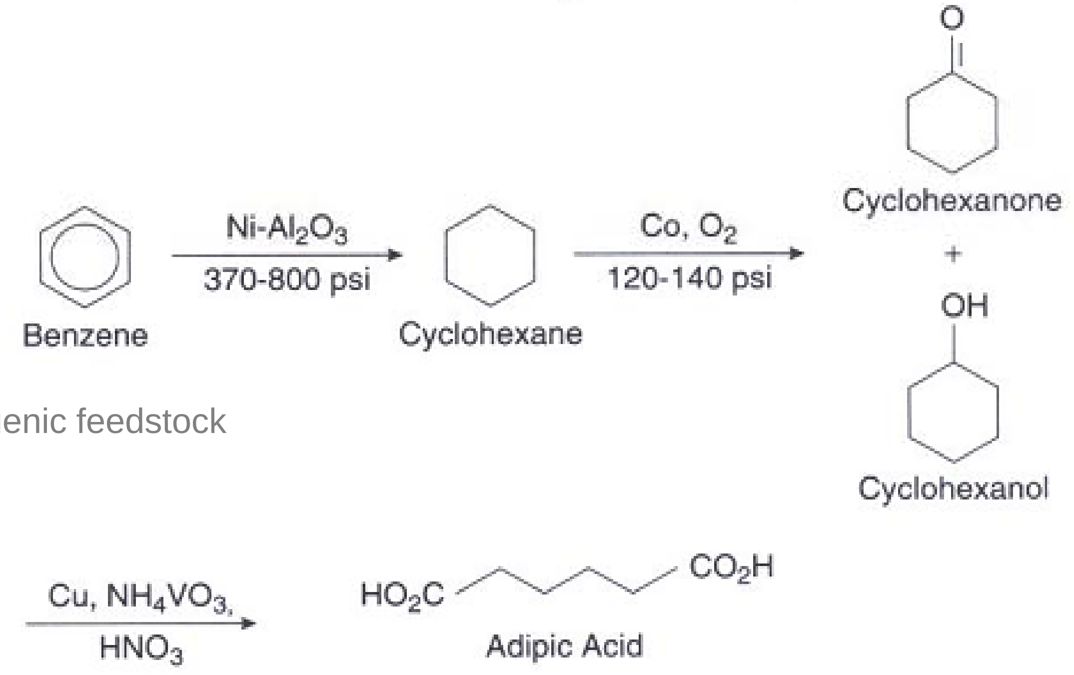
- Traditional method for adipic acid manufacture uses benzene, a fossil-fuel based, carcinogenic feedstock *(Designer may wish to consider feed-stocks which are renewable or less toxic)*
- One potentially environmentally preferable alternative uses glucose, a renewable feedstock which is innocuous.
- Thus, adipic acid pathway using glucose (Draths and Frost, 1998), shown in Figure 7.2-1, has some advantages.
- However, a complete evaluation would need to consider the environmental issues associated with glucose and benzene production and purification. (Chap. 13 and 14)

How do we identify alternative raw materials can improve environmental performance ?

Second example of the use of less hazardous materials is provided by the synthesis of disodium iminodiacetate.

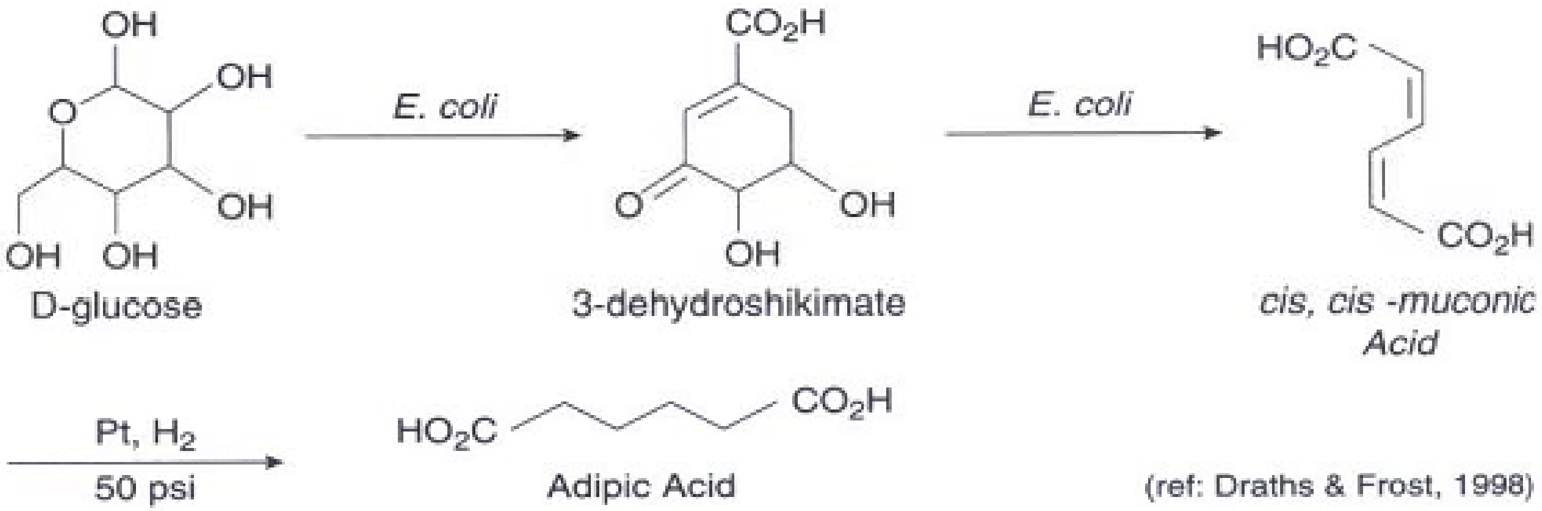
- **Synthesis of disodium iminodiacetate *(Fig. 7.2-2)***
  - traditional synthesis uses hydrogen cyanide
  - alternative route uses diethanolamine to avoid using HCN

Traditional Feedstock used in the synthesis of Adipic acid



carcinogenic feedstock

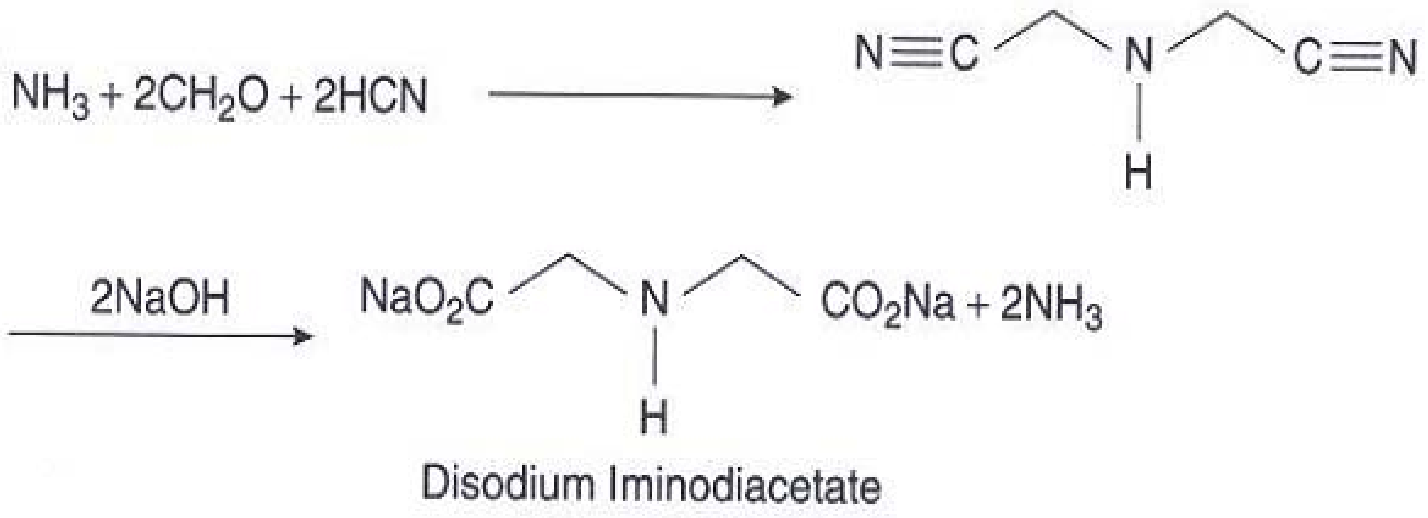
Alternative Feedstock used in the synthesis of Adipic acid



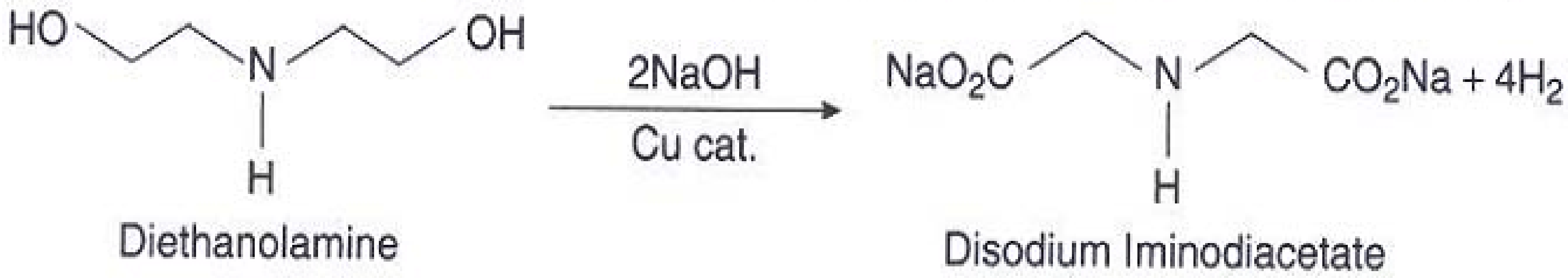
(ref: Draths & Frost, 1998)

Fig. 7.2-1 Traditional and alternative synthesis pathways for adipic acid.

Traditional Synthesis of Disodium Iminodiacetate (Strecker Process)



Alternative Synthesis of Disodium Iminodiacetate (Catalytic Dehydrogenation)



(ref: Anastas & Warner, 1998)

Fig. 7.2-2 Traditional and alternative synthesis pathways for disodium iminodiacetate

General Principles and Guidelines for Selection of Feedstocks

These few examples can be expanded into a set of more general principles and guidelines, which are described below.

- **Innocuous**
- **Generates Less Waste**
- **Selective**
- **Efficient**

General Principles and Guidelines for Selection of Feedstocks

❀Innocuous (무해한)

- The selection of starting materials should start with an evaluation the material themselves, using methods described in Chap. 5 & 6, to determine if they possess any hazardous

- Inherent to this analysis is determining whether the process or reaction step requiring hazardous material is necessary or whether the final target compound be obtained from an alternative pathway that uses a less hazardous material

General Principles and Guidelines for Selection of Feedstocks

❁ Generates Less Waste

- An important consideration associated with the use of a particular raw material is whether it is responsible for the generation of more or less waste than other materials.

- The amount of waste either generated or eliminate, however, cannot be the only consideration.

- The type of waste generated must also be assessed. Just as all chemical products are not equal in terms of their hazard, neither are chemical waste streams. Waste streams therefore must also be assessed for any hazardous properties that they possess.

General Principles and Guidelines for Selection of Feedstocks

✿ Selective

- Utilizing a raw material or reaction pathway that is more selective means that more of the starting material will be converted into the desired product. High product selectivity does not always translate into high product yield (and less waste generated). Both high conversion and high selectivity must be achieved for a synthetic transformation to generate little or no waste.

- Using highly selective reagents can mean that separation, isolation, and purification of the product will be significantly less difficult. Since a substantial portion of the burden to the environment that chemical manufacturing processes incur result from separation and purification processes, highly selective materials and reaction pathways are very desirable.

General Principles and Guidelines for Selection of Feedstocks

❁ Efficient

- Reaction efficiency, much like product selectivity, has long been a goal of synthetic design, and even prior to the advent of green chemistry principles, has offered benefits. When th overall yield of a process is increases by 10 or 20 %, less material ends up in waste streams and more is converted into product.

- However, yield and selectivity are not entirely adequate as a measure of reaction efficiency. Synthetic transformation can achieve 100% selectivity to produce and still generate a substantial amount of waste if the transformation is not "atom economical".

- Atom economy, a ratio of the molecular weight of the starting materials and regents to the molecular weight of the target molecule, provides a measure of the intrinsic efficiency of the transformation.

7.2.2 Solvents

- In 1991, the production of 25 most commonly used solvents was more than 26 million tons per year.

- According to Toxic Release Inventory (TRI), 5 of the top 10 chemicals released or disposed were solvents; methanol, toluene, xylene, MEK, dichloromethane.

- The total quantity of these chemicals released was over 687 million lbs, which accounts for 27 % of the total quantity of TRI chemicals in 1991

- With increasing regulatory pressure focusing on solvents, there is significant attention being paid to the use of alternatives to traditional solvents.

General Guiding Principles
in selection of solvents

- **Less Hazardous**

Examine to explode, ignite, and health and environmental effects

- **Human Health**

Solvents are of particular concern:
Significantly high exposure (high vapor pressure + large volume)
Carcinogens (Halogenated solvent: CCl_4, $CCl_2=CCl_2$, $CHCl_3$)
Neurotoxicological effect (Other solvents)

- **Environmental (Local and Global)**

The use of solvents has caused both global and local env. concerns.
CFCs (Stratospheric ozone depletion)
Other solvents (Global warming potential)
VOC (Local air pollution)

Alternative to Traditional Solvents

- Supercritical solvents
- Aqueous applications
- Polymerized/immobilized solvents
- Ionic liquids
- Solvent-less systems
- Reduced hazard organic solvents

Supercritical solvents

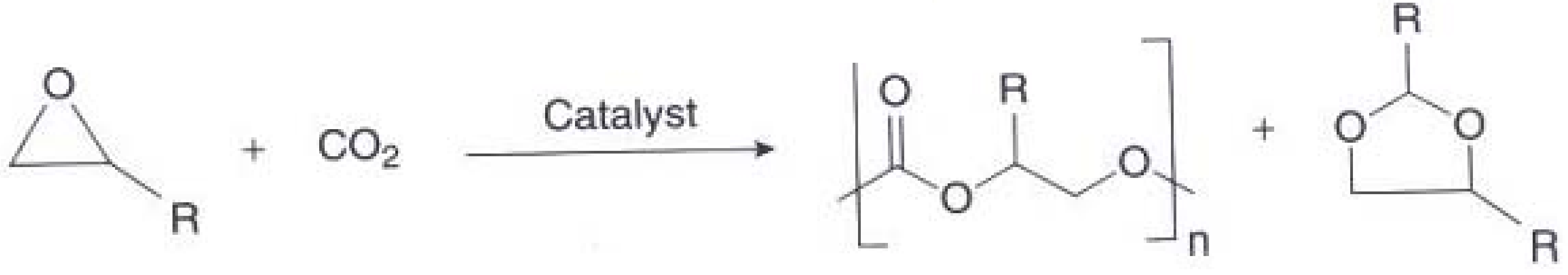
SCF-CO_2 as reaction medium

- CO_2 : non-toxic, non-flammable, renewable, inexpensive, (numerous SFE applications of solvating power at the SCF state) properties can replace conventional toxic organic solvents in separation / purification applications

- New reaction chemistry : solvents play a role in chemical synthesis (rxns occur in a solvent, SCF may enhance or inhibit desired rxn)

- As demonstrated in **Fig. 7.2-3**, reaction and selectivity in SC-CO_2 are comparable or superior to those achieved in conventional solvents (new research tip of iceberg)

Catalytic Co-polymerization of CO_2 with Epoxides



Asymmetric Catalytic Hydrogenation of Enamides

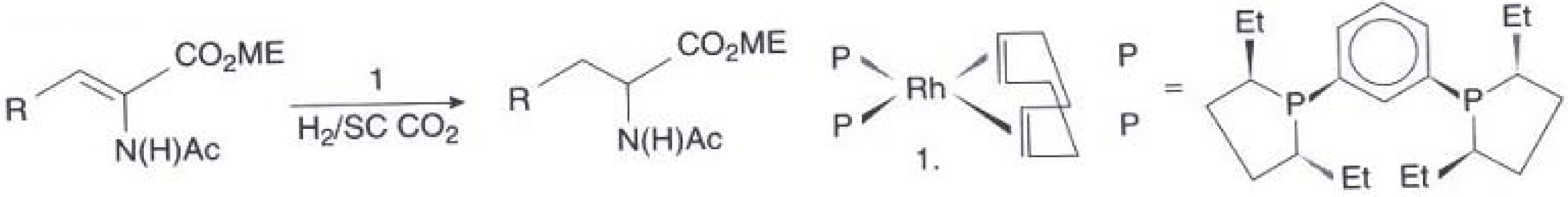


Fig. 7.2-3 Examples of the use of SC-CO_2 to replace conventional solvents

1. A co-solvent is used along with the SC-CO_2 to allow a polymerization rxn to take place;
2. The use of SC-CO_2 enhances the selectivity of a catalytic reaction

Water as an Alternative Solvent

- Water : non-toxic, non-flammable, renewable, inexpensive, (innovative use of water as a reaction medium)

- As demonstrated in **Fig. 7.2 - 4**, water with an alcohol co-solvent is used in ***Diels-Alder*** reaction (dimerization of 1,3 cyclopentadiene, are accelerated in water due to favorable packing of hydrophobic surfaces in the reaction transition state)

- Many other organic reactions that have traditionally been carried out in organic solvents have now been carried out in aqueous media (**Barbier-Grignard** reaction, pericyclic reactions, transition metal catalyzed reactions)

Aqueous Conditions for the Diels-Alder Reaction

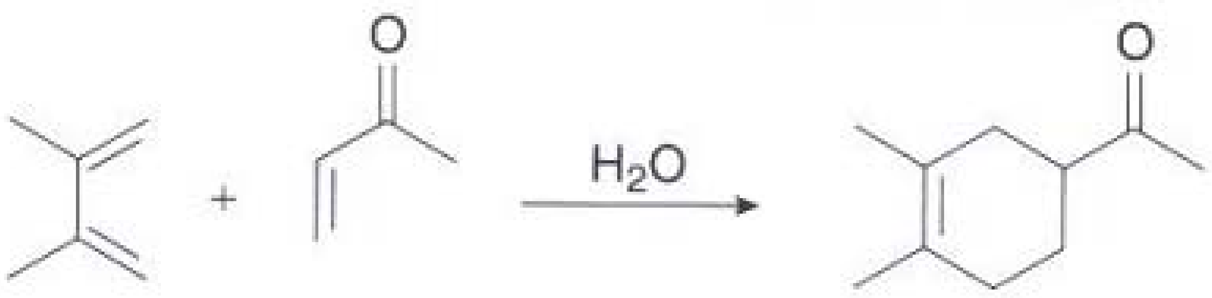


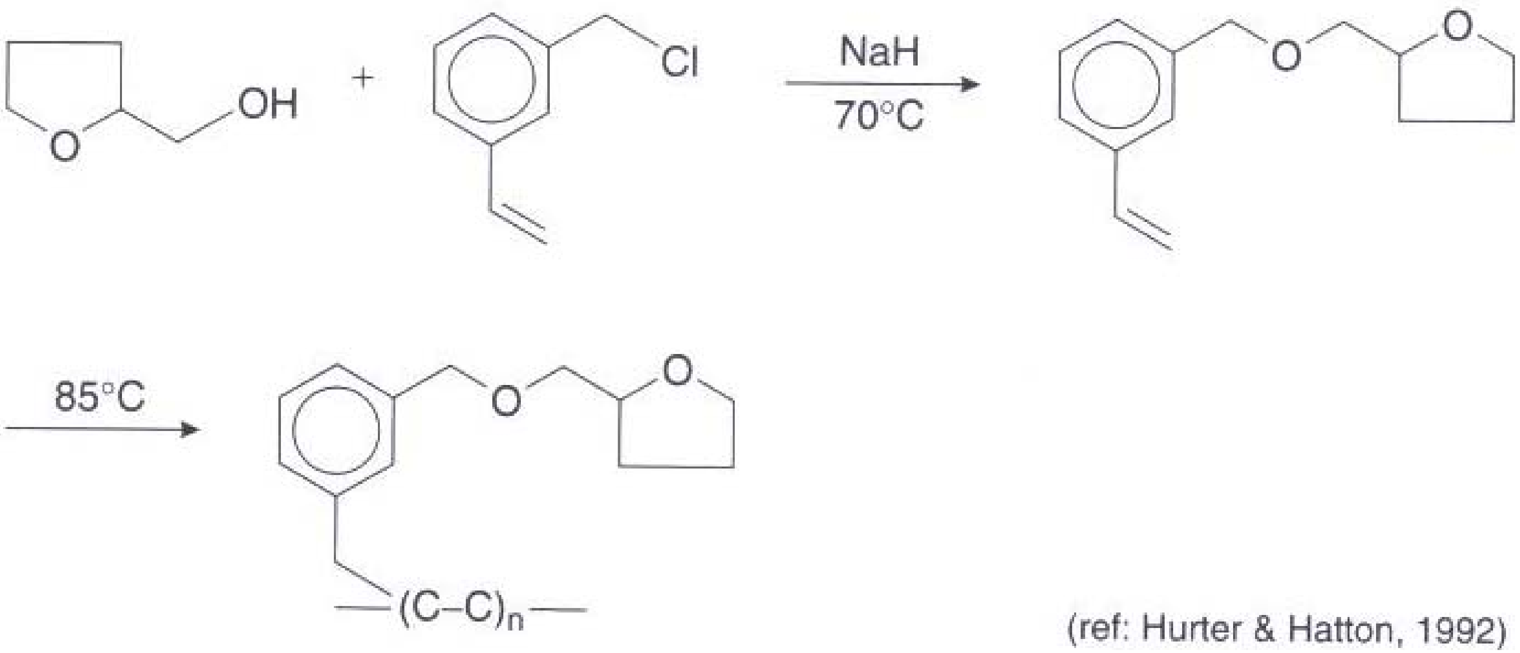
Fig. 7.2-4 When water is used as a solvent for certain Diels-Alder reaction, rates can be accelerated

Derivatized, Immobilized Solvent Use

- to reduce the emissions and promote the recovery of hazardous solvents by attaching the solvent to a hydrocarbon backbone

- as in Fig. 7.2 - 5, THF is attached to a polymeric backbone using chlorinated styrene derivatives (*THF remains relatively mobile, less likely volatilize and easily recover using ultra-filtration)*

Derivatized/Polymeric Solvent Replacement for THF



(ref: Hurter & Hatton, 1992)

Fig. 7.2-5 Use a solvent functionality (THF), attached to a large polymer backbone, to replace a volatile solvent, THF

Synthesis Pathways

- Identify chemical synthesis pathways may lead to superior environmental performance
  (complex and difficult task, beyond this lecture)

- Different reaction pathways can have different impact on health and environment :

  - **Addition reaction** **($A + B \rightarrow AB$)**
  - **Substitution reaction** **($AB + C \rightarrow AC + B$)**
  - **Elimination reaction** **($AB \rightarrow A + B$)**

Synthesis Pathways

- **Addition reaction (A + B → AB)**

  It incorporate starting materials into the final product.
  (It does not produce waste to treated and disposed)

- **Substitution reaction (AB + C → AC + B)**

  It necessarily generate stoichiometric quantity of substances as byproducts and wastes.

- **Elimination reaction (AB → A + B)**

  It does not require input of materials during reaction other than initial input of a starting material
  (They generate stoichiometric quantities of substances)

Friedel-Crafts Acylation

(substitution reaction)

- Friedel-Crafts reaction involves substitution reaction of acid chloride with aromatic substrate *(aluminum chloride catalyst)*

- Product forms a complex with catalyst, requiring a water wash, resulting in the formation of *HCl* and salt wastes

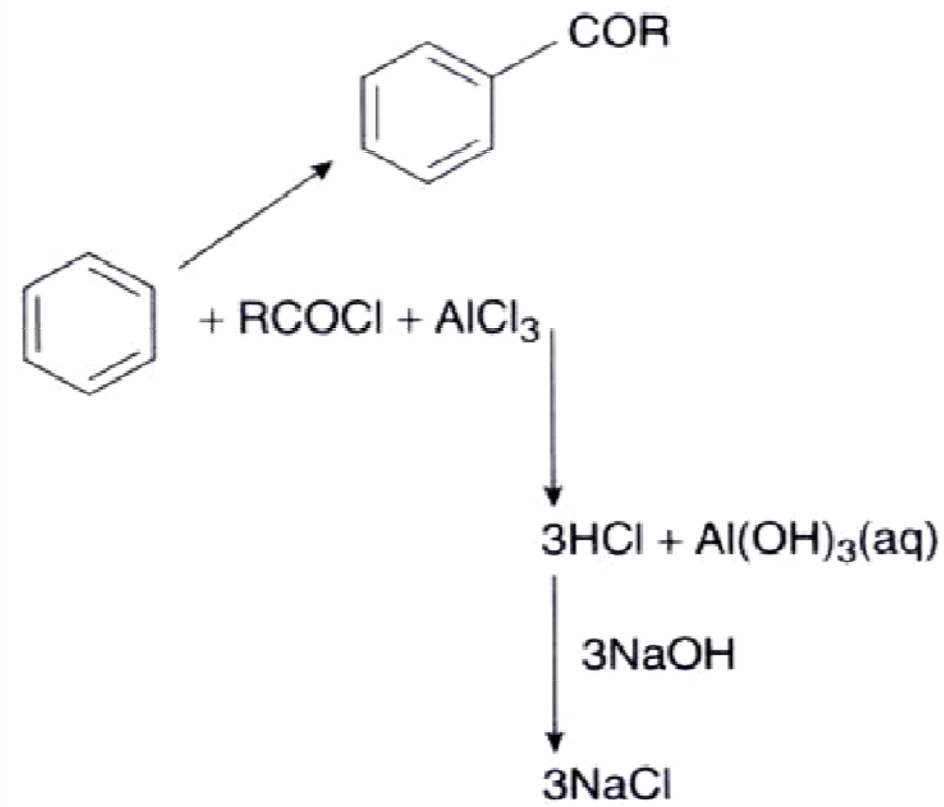


Fig. 7.2-6 Friedel Crafts acylation generates a relatively large amount of wastes, even if the reaction is carried out at 100 % yield and 100 % selectivity, because of the dissipative use of the aluminum chloride catalyst.

Environmental Improvements

(atom efficiency examination)

- Friedel Crafts acylations have atom efficiencies that are relatively low. A simplistic overall atom and mass balance suggest that only about 30% of the starting materials ends up in the product. Thus a simple calculation of atom efficiency identifies Friedel Crafts reaction as a potential target for environmental improvements.

- Retain the chemical pathway, but to regenerate and reuse the catalyst. In the synthesis of ethylbenzene via the alkylation of benzene with ethylene, approximately 1 ton of $AlCl_3$ waste is generated per 100 tons of product, a significant reduction in waste generation relative to the case of no catalyst recovery.

- Another alternative for improving environmental performance would be to identify an alternative catalyst such as acidic zeolites.

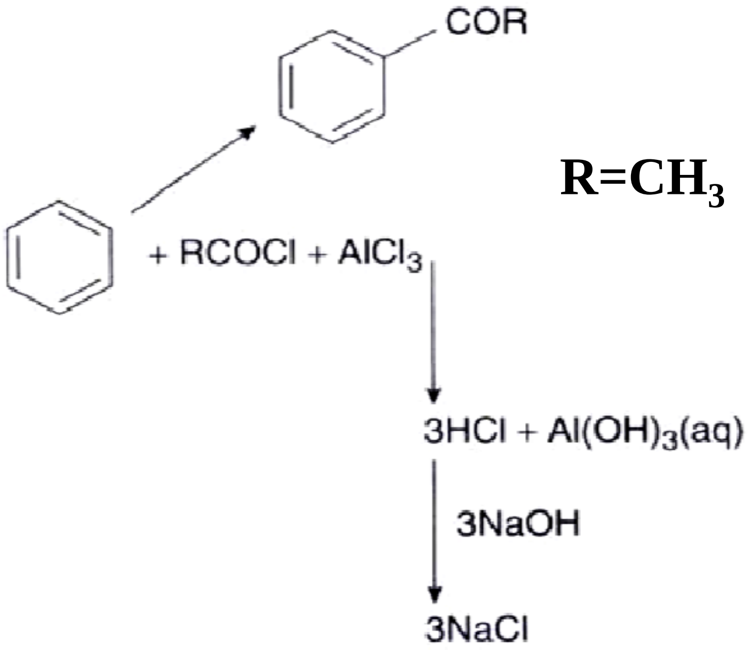
Ex. 7.2-1 Calculate atom and mass efficiencies

For the Friedel Crafts reaction

The atom efficiency:

- C = 100%
- H ~ 100%
- Al = 0%

- Cl = 0%
- Na = 0%
- O = 25%



R=CH$_3$

The mass efficiency=122/378=0.32

Mass input
= 8*12 (C)+16*1(H)+4*16(O)+1*27(Al)+3*35.5(Cl)+3*23(Na)=378
Mass in product
=8*12(C)+10*1(H)+1*16(O)=122

Partial Oxidation

- Industrially important reaction where atom utilization can be low **(Fig. 7.2-7)**

- In partial oxidations, the poor atom utilization can be due to the oxidizing agent (if molecular oxygen is used, then atom utilization may be high if selectivity is high)

- If oxidizing agents such as dichromate or permanganate are used, atom efficiency can be low as shown in **Table 7.2-1**

- Environmental performance can be improved in these cases by careful selecting the oxidizing agents

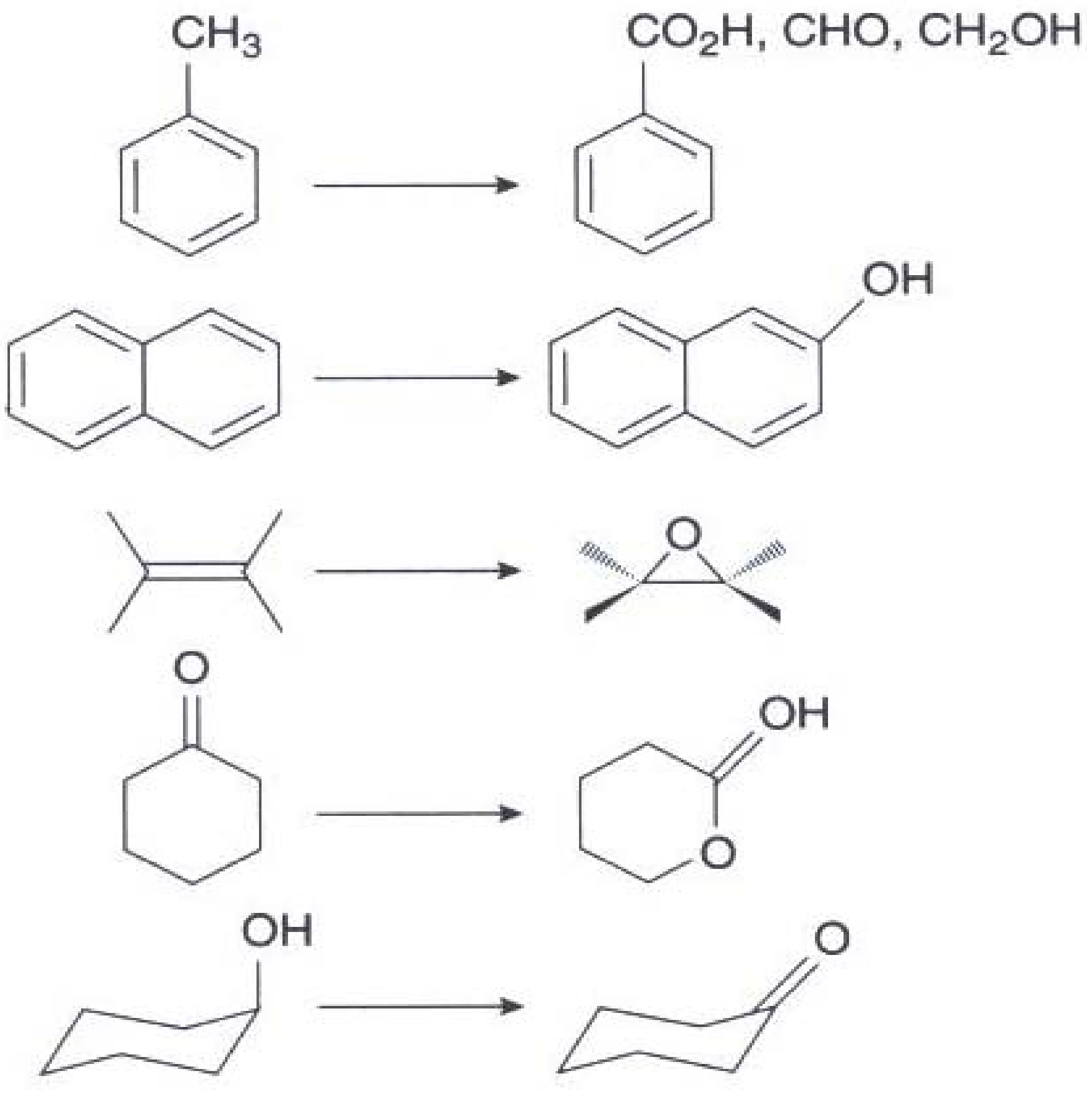
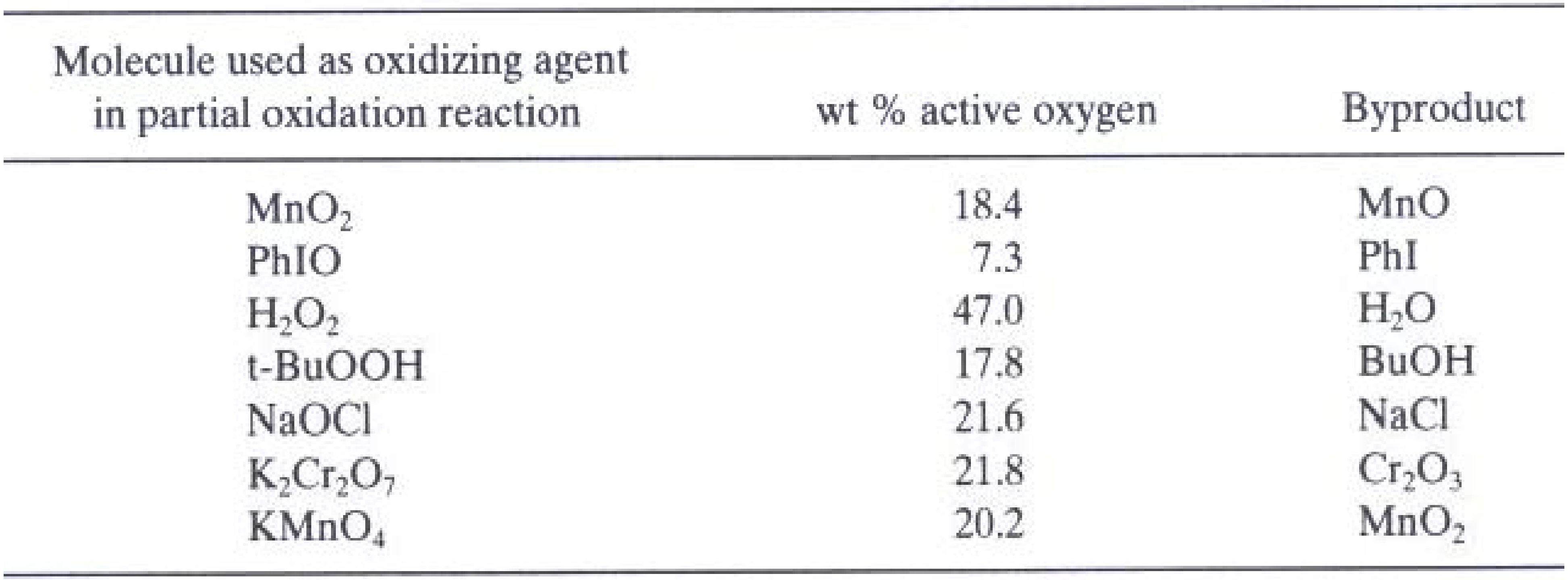


Fig. 7.2-7 Commercially important partial oxidation reactions

Partial Oxidation

Table 7.2-1 Atom utilization in oxidizing reagents



Molecule used as oxidizing agent in partial oxidation reaction	wt % active oxygen	Byproduct
MnO_2	18.4	MnO
PhIO	7.3	PhI
H_2O_2	47.0	H_2O
t-BuOOH	17.8	BuOH
NaOCl	21.6	NaCl
$K_2Cr_2O_7$	21.8	Cr_2O_3
$KMnO_4$	20.2	MnO_2

Simplifying Synthesis Pathways

(synthesis of Ibuprofen, an over-the counter pain reliever)

- wastes can be reduced by simplifying synthesis pathways (traditional method is shown in **Fig. 7.2–8)**
- An alternative synthesis, replacing the $AlCl_3$, acid catalyst with HF and reducing the number of subsequent transformations and solvent uses
- Atom utilization increased from less that 40 % in the traditional synthesis to approximately 80 % using the new pathway

Traditional synthesis of Ibuprofen

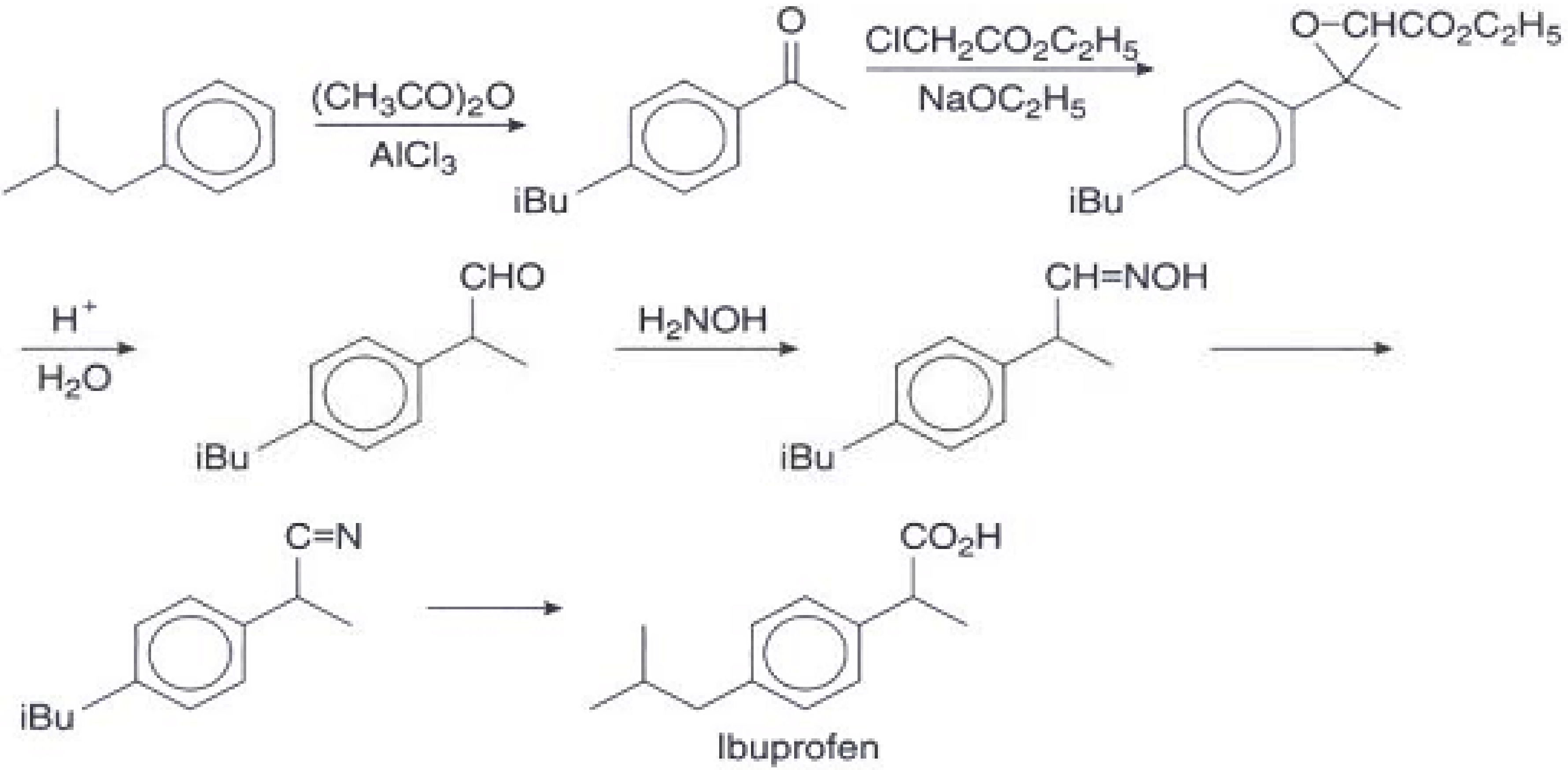
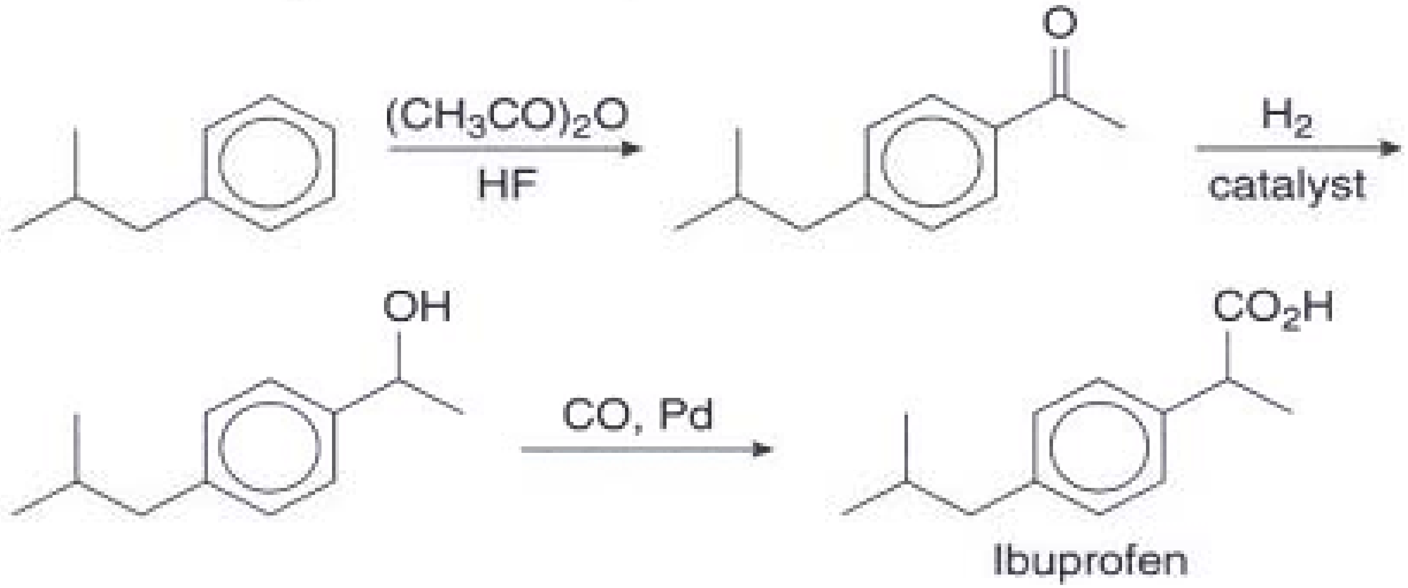


Fig. 7.2-8 Traditional synthesis of Ibuprofen involved a large number of steps, including a Friedel-Crafts reaction that generated byproducts of the type shown. The
new route is simpler and employs a recoverable strong acid as the catalyst.

Alternative Synthesis of Ibuprofen
Simpler can be better!



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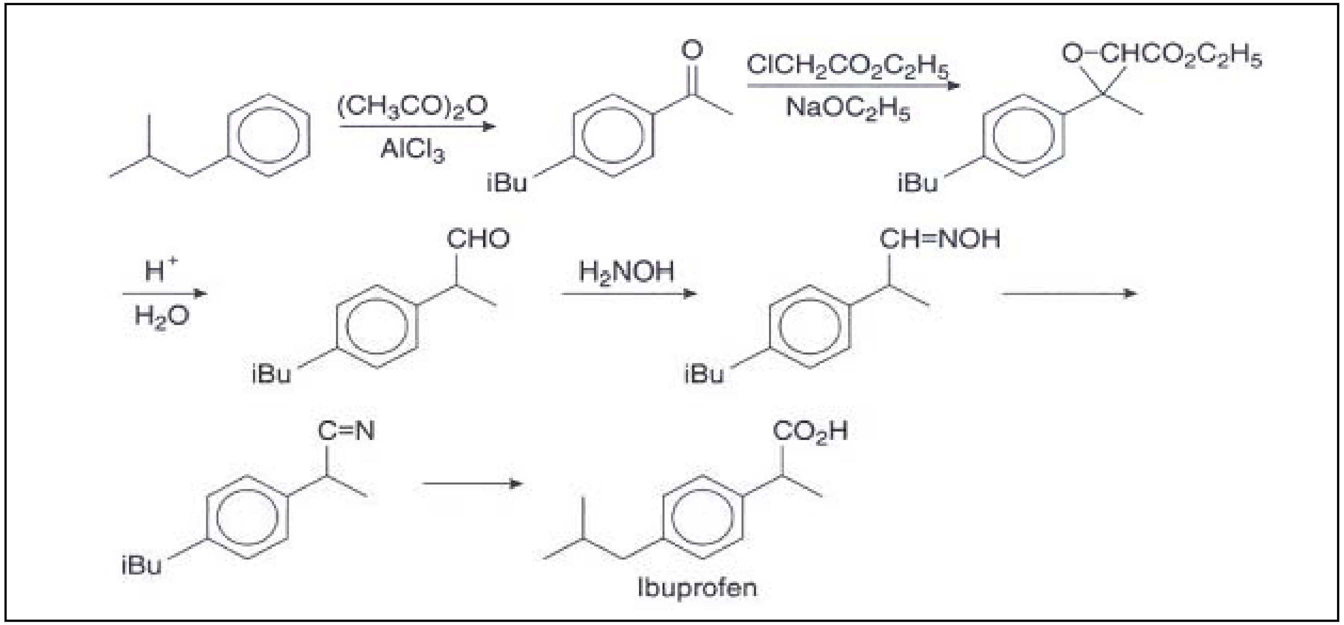
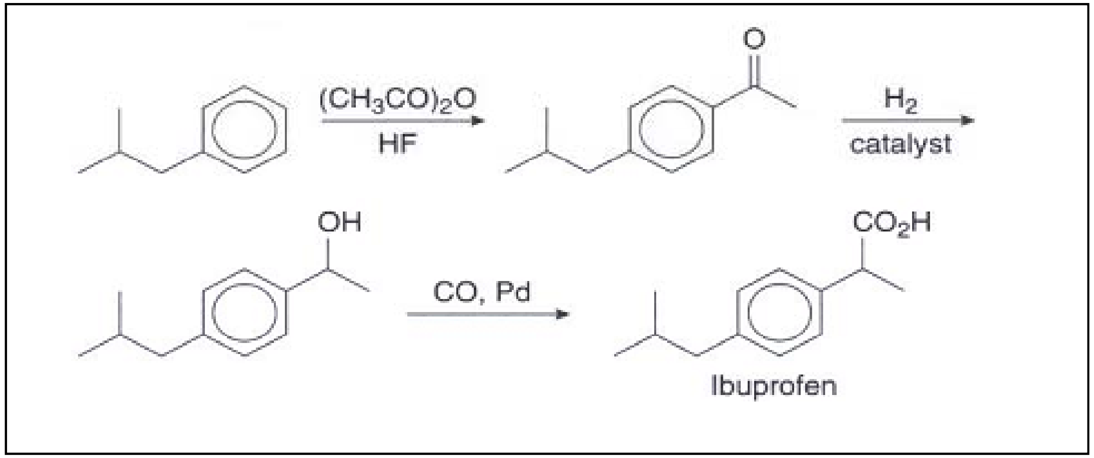




7.2.4 Functional Group Approaches

to Green Chemistry

A number of tools can be used in the design of more environmentally benign chemistries, including

- ***structural analysis relationship***
- ***identification and avoidance of toxic functional groups,***
- ***reducing bioavailability, and***
- ***designing chemicals for innocuous fate***

Structural Analysis Relationship (SAR)

Many times the mechanism of action may not be known, but structure activity relationships can be used to identify structural modifications that may improve a chemical's safety.

If methyl-substituted analog of a substance has very high toxic, and it decreases as the substitution moves from ethyl to propyl, it is reasonable to increase the alkyl chain length to design a safer chemical. Even in cases where the reason for the effect the alkyl chain length is not known, then the structure-activity relationship is certainly a powerful design tool.

Elimination of Toxic Functional Group

If information is not available about the specific chemical’s toxicity or the mechanism by which it produces that toxicity, the assumption that certain reactivity functional groups will react similarly within the body or in the environment is often a good one.

The design safer chemical could proceed by removing the toxic functionality. In some cases this is not possible because the functionality is what gives the molecule the properties that are required for the chemical to perform in the desired way. In these cases, there are still options such as masking the functional group to a non-toxic derivative from and only releasing the parent functionality when necessary.

Example: masking of vinyl sulfones, ***Fig. 7.2-9***

Masking of vinyl sulfones as hydroxylethylsulfones allows these relatively hazardous materials to be used more safely

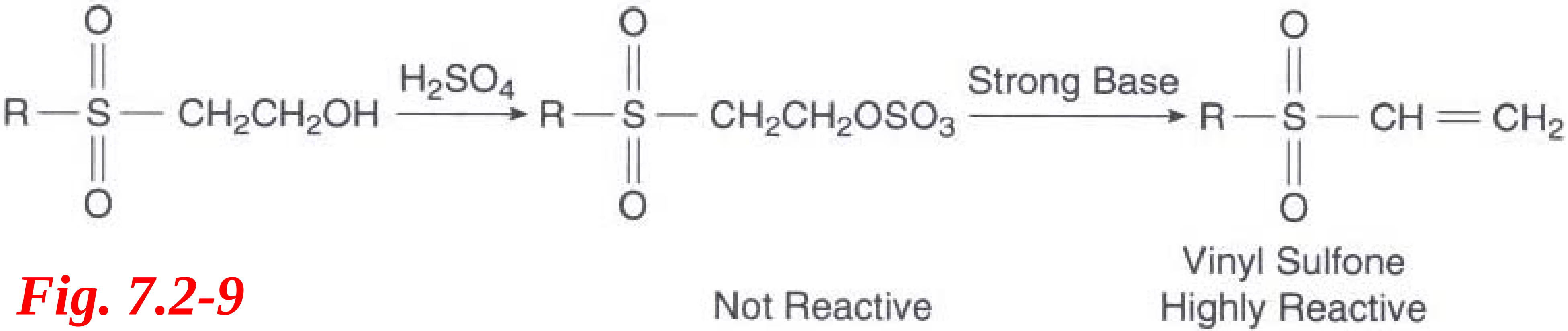


Fig. 7.2-9

The masking of vinyl sulfones provides an interesting example of this technique. The vinyl sulfone functionality is highly electrophilic and reacts with celluosic fibers, making it an effective component of dyes. There are, however, a variety of toxic effects associated with this functionality. Rather than manufacturing, storing, and transporting the relatively hazardous sulfone, the sulfone can be generated when and as needed by converting a hydroxyethylsulfone into a vinyl sulfone, using the chemistry shown in Figure 7.2-9 (De Vito, 1996)

Reduce Bio-Availability

If it is not known what structural features of the molecule need to be modified to make it less hazardous, then there is still option of making the substance less bioavailable.

This can be done through a manipulation of the water-solubility/lipophilicity relationships that often control the ability of substance to pass through biological membranes such as skin, lungs, or the gastrointestinal tract.

Design for Innocuous Fate

It is often the goal of the chemist to design substances which were robust and could last as long as possible. This philosophy has resulted in persistent, and at times bioaccumulative and toxic substances.

It is now known that it is more desirable to not have substances persist in the environment or a landfill forever, but that they should be designed to degrade after their useful life is over.

Therefore, the design of safer chemicals cannot be limited to only hazards associated with manufacture and use of the chemical but also that of its disposal and ultimate end of life cycle.

7.3 Quantitative/Optimization-Based Frameworks for Design of Green Chemical Synthesis Pathways

Previous general guidelines for improving environmental performance rely on knowledge and creativity of engineers

- More popular method is **"Combinatorial Approaches"** *(to identify green chemistry alternatives)*

1. To select a set of molecular or "functional group building blocks" from which a target molecule can be constructed

2. A series of stoichiometric, thermodynamic, economic, and other constraints can be identified. These constraints serve to reduce the number of possibilities that might be considered)

3. A set of criteria can be used to identify reaction pathways that deserve further examination

Systematic construction of alternative chemical pathways

The first step is to select a set of functional group building blocks.

Because the number and variety of pathways that are generated is strong function of the starting materials that are used, this is a critical step.

To keep the alternatives as varied as possible, it is desirable to include as many functional group building blocks as possible, yet to keep the search focused and tractable, the number of groups should be limited.

Systematic construction of alternative chemical pathways

Rules and guidelines in selecting a group of starting materials (Buxton, 1997)

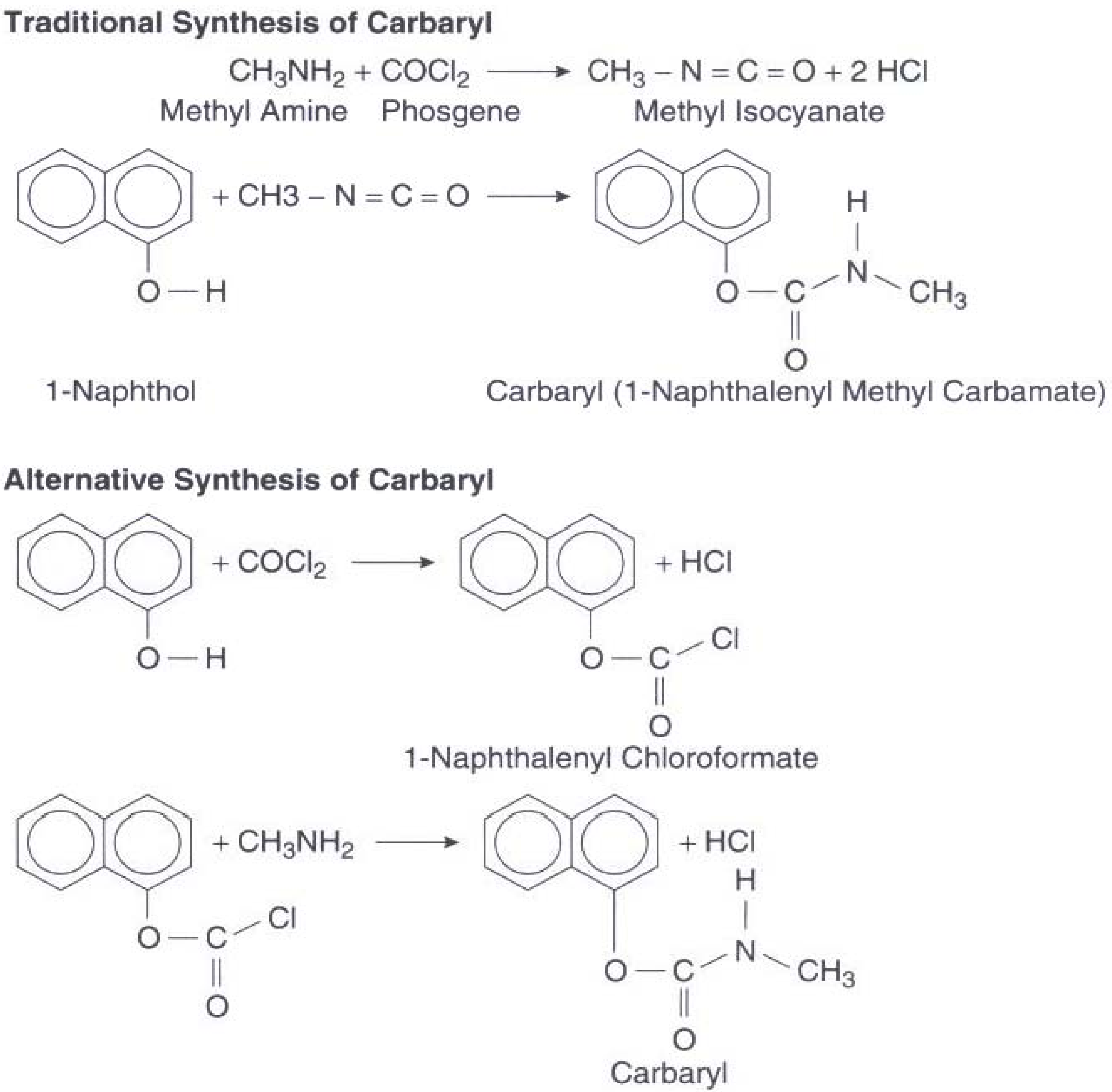
- Include the groups present in the product
- Include groups present in any existing industrial raw materials, co-products or byproducts
- Include groups which provide the basic building blocks for the functionalities of the product or similar functionalities
- select sets of groups associated with the general chemical pathway employed *(cyclic*, *acyclic*, *or aromatic)*
- reject groups that violate property restrictions

Systematic construction of alternative chemical pathways

Example

Consider the synthesis of 1-naphthyl-methylcarbamate (carbaryl), manufactured by Union Carbide. In 1984, a catastrophic release of methylisocyanate occurred at a carbaryl manufacturing facility in Bophal, India, killing thousands. α-naphthol and methylisocyanate were used as reactants to synthesize carbaryl **(Fig. 7.3-1)**.

Are other chemistries for the synthesis of carbaryl possible or desirable?



Traditional Synthesis of Carbaryl

Alternative Synthesis of Carbaryl

Fig. 7.3-1 Synthesis of carbaryl can be accomplished with a methylisocyanate intermediate. An alternative route, not involving methylisocyanate, is also shown

Systematic construction of alternative chemical pathways

The first step in identifying alternative pathway is to select a set of functional group building blocks that will be included in the analysis.

Since the product molecule contains **aromatic groups**, it is necessary to include a range of aromatic functionalities such as

- *aromatic carbon bound to hydrogen(ACH)*
- *aromatic carbon to other aromatic carbon (AC -)*
- *aromatic carbon bound to chlorine*
- *aromatic carbon bound to a hydroxyl group (ACOH)*

More aromatic functionalities could be chosen, if desired.

Systematic construction of alternative chemical pathways

Other groups appearing in the product molecule, or related to groups appearing in the product molecule are

$-CH_3$, $CH_3NH<$, CH_3NH_2-, $-COO-$, $-CHO$, $-CO_2H$, $-OH$, $-Cl$

These functional group building blocks can be used to identify a set of potential molecular reactants.

Going from a set of functional group building blocks to potential molecular starting materials can generate very large numbers of potential reactants, so constraints, based on chemical intuition, are generally imposed.

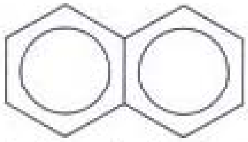
Systematic construction of alternative chemical pathways

For example, in identifying alternatives to the carbaryl synthesis,

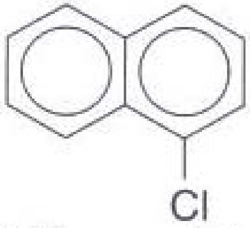
It is assumed that only mono-substituted aromatic molecules would be used, since the product is mono-substituted.

It is also assumed that reactants for which carbon skeleton would need to be altered would not be used (for example, benzene would not be used as a reactant since forming the product would require a ring condensation reaction).

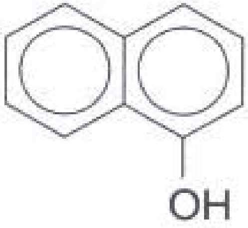
Using these and other assumptions, a limited set of reactants can be identified by Buxton. (Figure 7.3-2)



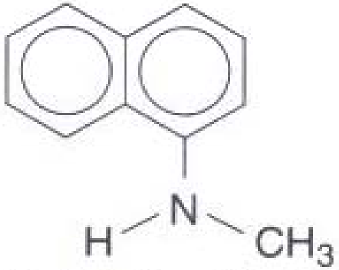
(a) Naphthalene



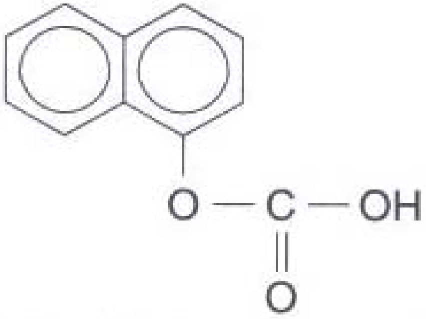
(b) 1-Chloronaphthalene



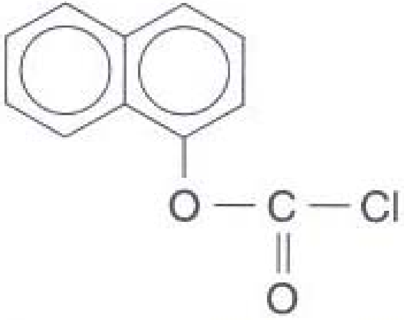
(c) 1-Naphthol



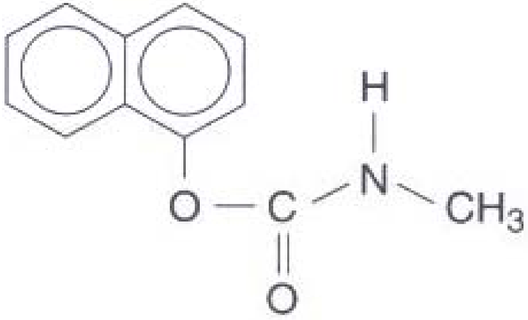
(d) N-Methyl-1-Naphthylamine



(e) 1-Naphthalenyl Hydroxformate



(f) 1-Naphthalenyl Chloroformate



(g) Carbaryl

Aromatic Molecules

Fig. 7.3-2 Potential reactants on carbaryl synthesis identified by Buxton

Cl_2

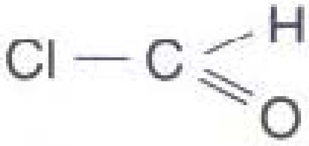
(a) Chlorine

CH_3Cl

(b) Chloromethane

CH_3OH

(c) Methanol



(d) Chloromethanal

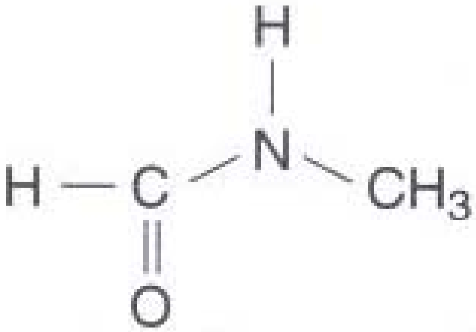
CH_3NH_2

(e) Methylamine

(f) Phosgene

$CH_3—N=C=O$

(g) Methyl Isocyanate



(h) Methyl Formamide

Aliphatic and Other Molecules

Fig. 7.3-2 Potential reactants on carbaryl synthesis identified by Buxton

Systematic construction of alternative chemical pathways

Once a set of potential reactants has been selected, as set of rules and constraints must be applied to describe how the reactants can interact to form molecules. The most obvious of constraints are stoichiometric.

For example, the product molecule contains 7 aromatic carbons bound to hydrogen and 2 aromatic carbons bound to other aromatic carbons. Thus, the reactants must provide sufficient aromatic carbons, of various types, to generate the product molecule. Similar stoichiometric constraints could be written for the other types of groups in the molecule. Some reaction pathway analysis methods assume that reactions, appropriately balanced for stoichiometry, can proceed 100% selectivity and yield. Other methods include thermodynamic constraints on selectivity

Systematic construction of alternative chemical pathways

Once constraints are established, pathways can be identified and ranked. Ranking schemes might include cost and environmental performance metrics. Buxton identified and ranked 13 different reaction pathways for the synthesis of carbaryl ***(Table 7.3-1).***

The **economic ranking** is based on the price difference between product and reactants

The **environmental ranking** is based on the assumption that a fixed percentage of the materials used is released to the environment

Table 7.3-1 Alternative pathways for the synthesis of carbaryl. The species numbers are listed below the Table and refer to the compounds shown in **Fig. 7.3-2.** The profit is the difference in value between reactants and products and environmental ranking is determined by assuming that a fixed fraction of the reactants and products are released to the environment

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	Profit	Env. Rank
−1								−1	1	1	−2								1.45	9
	1	1		−1	−1					1		−1							1.03	7
	2			−1	−1					1	−1								1.00	2
	1			−1						1		−1				1	−1		1.00	12
−1				−1	1					1	−1								1.00	1
		1			−1			−1		1		−1							0.976	13
				−1						1	−1					1		−1	0.967	4
	1				−1			−1		1	−1								0.952	8
								−1		1		−1				1	−1		0.952	11
		2				−1	−1		−1	1									0.604	5
	1	1				−1			−1	1								−1	0.543	6
1				−1					−1	1									0.503	3
								−1	−1	1									0.451	10

1=Oxygen; 2=Hydrogen; 3=Hydrogen chloride; 4=Naphthol chloroformate; 5=Methyl formamide; 6=Water; 7=Methylamine; 8=Phosgene; 9=Methyl isocyanate; 10=Naphthol; 11=Carbaryl; 12=Naphthalene; 13=Chloronaphthalene; 14=methyl-naphthylamine; 15=Naphthenyl hydroxyformate; 16=Chlorine; 17=Chloromethane; 18=Methanol; 19=Chloromethanal

Systematic construction of alternative chemical pathways

While the results of Table 7.3-1 are intriguing, it would be inappropriate to suggest that this type of analysis will yield the optimal reaction pathway. Rather, the point of these analysis methods is to inject systematic decision rules into the search for alternative pathways.

(1) Sets of starting materials are identified based on stoichiometry and chemical intuition. **(2)** Then, pathways can be identified and potential upper bounds for selectivity can be estimated using thermodynamics. **(3)** Finally, alternatives can be quickly ranked using economic and environmental criteria.

These systematic procedures may lead to a desirable alternative pathway, or they may merely lead to a clear definition of the constraints that should be considered in evaluating alternative pathway.

Homework #6

Problem 7-1

Due on April 30, 2011