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Lecture 2: Green Metrics

Green Chemistry is often said to be a 'cradle to grave' approach. Explain what this term means with specific reference to the industrial production of polyethylene.

5 marks

'Cradle to grave' describes the need to consider ALL factors in the production of a chemical from the source of the raw materials, to the disposal / recycle of the product once its useful lifetime has ended.

Possible factors might include:

- **ethylene is produced from petroleum feedstocks (is biomass an alternative, renewable source?)**
- **catalysts greatly reduce the temperature and pressure conditions**
- **no solvents are used (gas phase monomer passed over a solid catalyst)**
- **minimal waste**
- **polyethylene is non-degradable, therefore it contributes significantly to landfill; recycling is difficult and energy intensive**
- **energy requirements, transportation to market etc.**

Lecture 2: Learning Objectives

By the end of today's lecture you should be able to:

(i) discuss (but not memorise) the 12 Principles of Green Chemistry;

(ii) calculate Atom Economies, E-factors and Effective Mass Yields for chemical processes;

(iii) discuss the advantages and disadvantages of each approach;

(iv) describe the competing processes for the industrial production of

- **dimethyl carbonate**
- **lactic acid**

Today's lecture

How can we measure the 'greenness' of a chemical reaction?

OR, given two chemical processes, how can we decide which is most consistent with the Principles of Green Chemistry?

The Twelve Principles of Green Chemistry: 1-6

1) It is better to prevent waste than to treat or clean up waste after it is formed.

2) Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3) Wherever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4) Chemical products should be designed to preserve efficiency of function, whilst reducing toxicity.

5) The use of auxiliary substances (e.g. solvents, separating agents etc.) should be made unnecessary wherever possible and innocuous when used.

6) Energy requirements should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.

The Twelve Principles of Green Chemistry: 7-12

7) A raw material or feedstock should be renewable rather than depleting wherever technically and economically possible.

8) Unnecessary derivatisation (blocking group, protection/deprotection, temporary modification) should be avoided whenever possible.

9) Catalytic reagents are superior to stoichiometric ones.

10) Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation products.

11) Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.

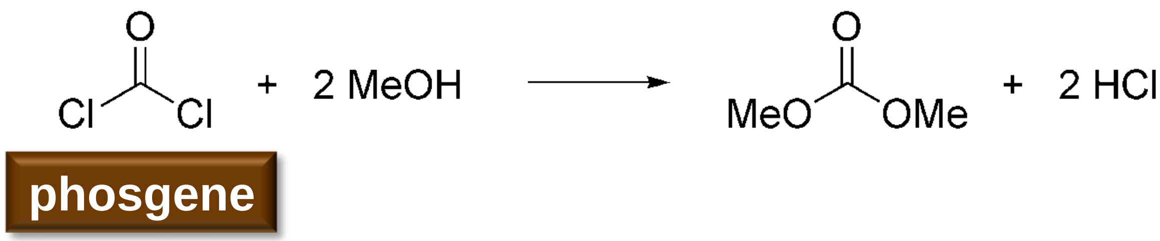
12) Substances used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions and fires.

The Twelve Principles of Green Chemistry: Summary

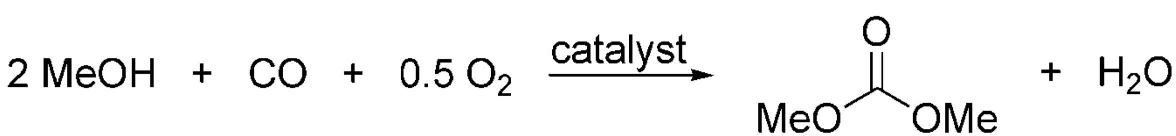
Reduction in:	1	2	3	4	5	6	7	8	9	10	11	12
Materials												
Waste												
Hazards												
Toxicity												
Environmental impact												
Energy												
Cost												

Two syntheses of dimethyl carbonate - which is greener?

1. Traditional synthesis from phosgene and methanol



2. Modern synthesis - methanol carbonylation

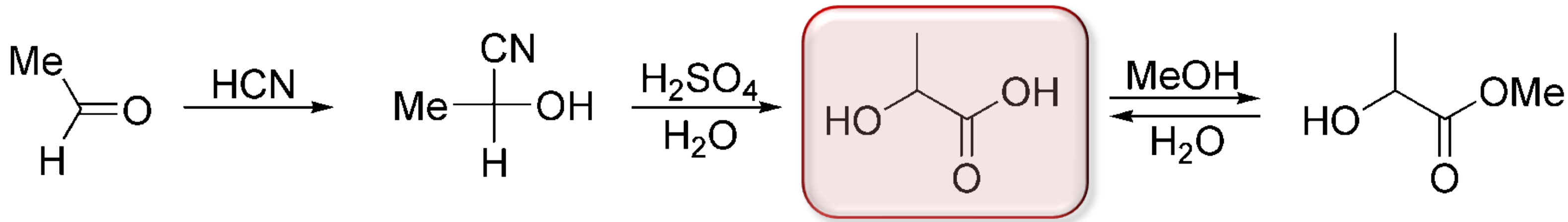


Route 2 is preferred since it avoids the use of phosgene and it gives less harmful side-products (route 2 also produces purer product, so energy intensive purification steps are eliminated).

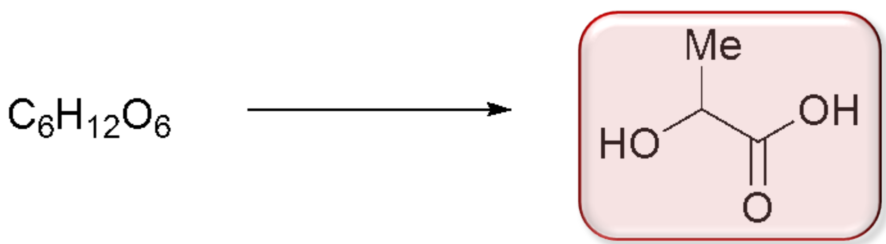
Some decisions are straightforward

Two syntheses of lactic acid ($HOCHMeCO_2H$) - which is greener?

1. Chemical – hydrocyanation of acetaldehyde



1. Biochemical – fermentation of sugars or starch



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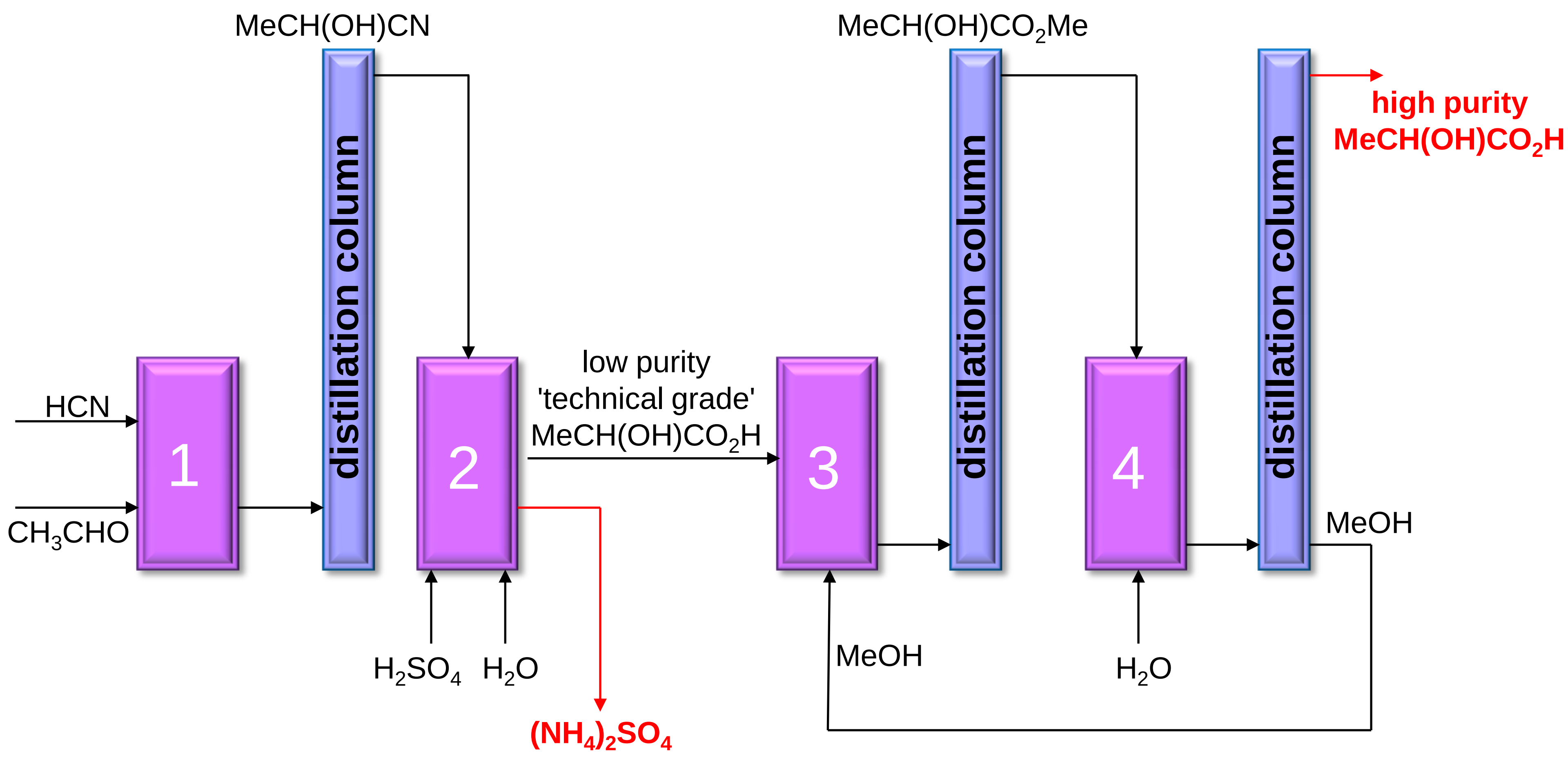
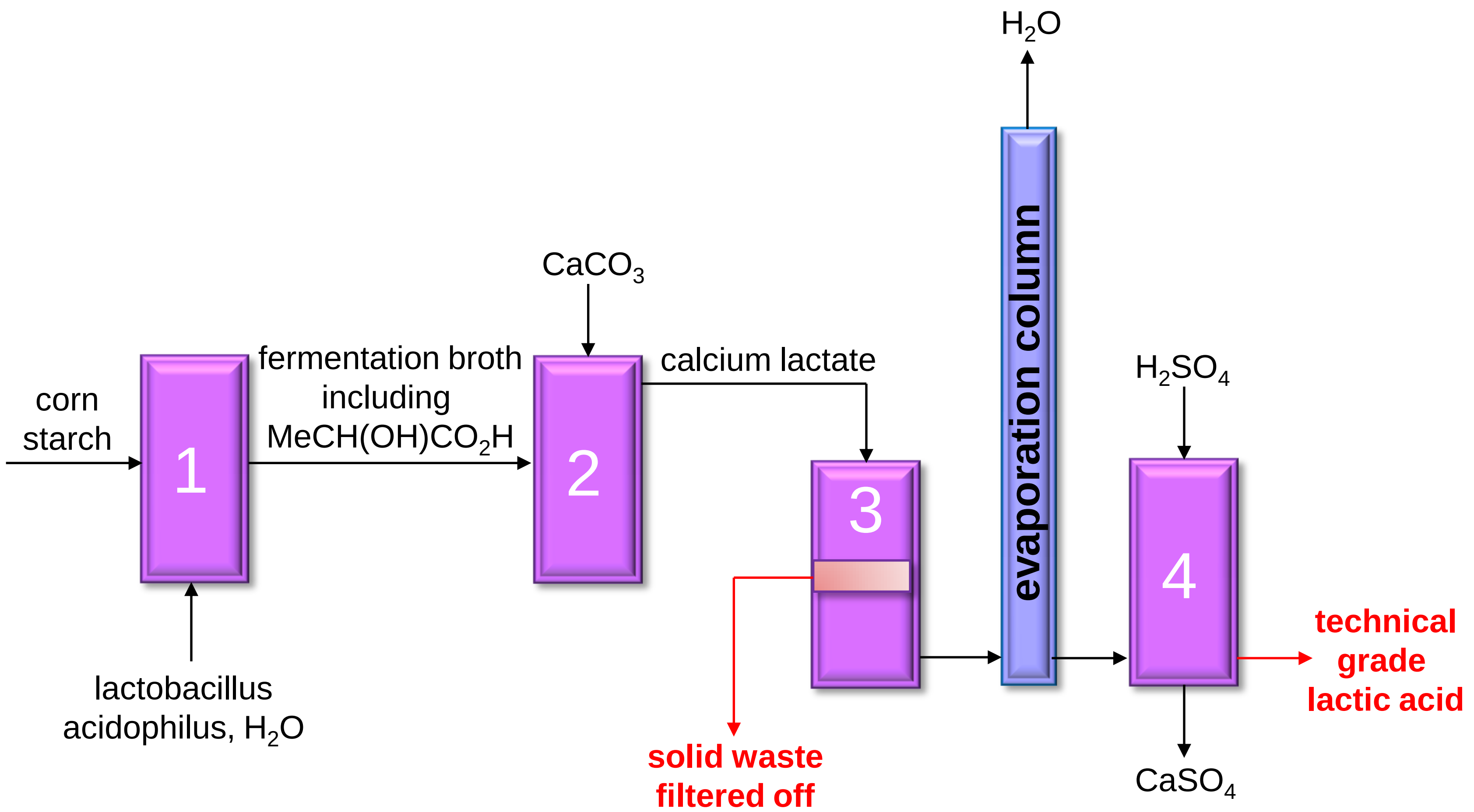
Chemical synthesis from CH$_3$CHO and HCN
Reactor 1: hydrocyanation; 2: hydrolysis; 3: esterification; 4: hydrolysis



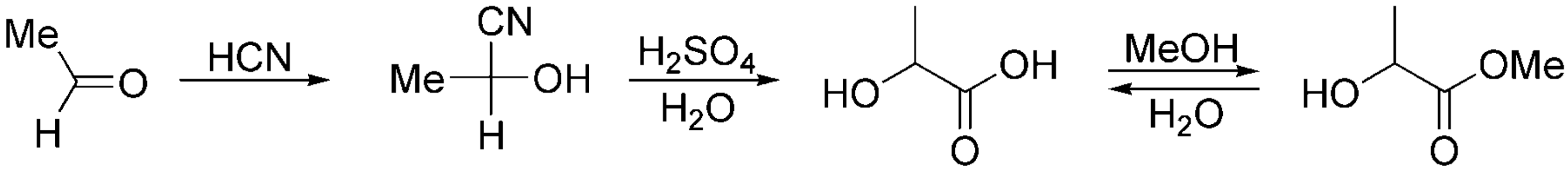
Biochemical (fermentation) route to lactic acid

Biosynthesis from starch

Reactor 1: fermentation; 2: salt formation; 3: filtration; 4: hydrolysis



Chemical synthesis of lactic acid



Advantages

- **Fast, high yielding reactions.**
- **MeOH generated in final step is recycled.**
- **Produces high purity lactic acid (> 99 %).**

Disadvantages

- **HCN is highly toxic; CH_3CHO and MeOH are also toxic.**
- **Waste stream of $(NH_4)_2SO_4$ produced (can be used as a fertiliser).**
- **Several energy intensive distillations required**

Biochemical synthesis of lactic acid

Advantages

- **Renewable feedstocks.**
- **Uses non-hazardous materials.**

Disadvantages

- **Slow (every cycle takes 4-6 days).**
- **Quantity of product per reactor volume is low.**
- **Evaporation is required (due to low salt concentration) - energetically intensive.**
- **Technical grade lactic acid (ca. 85 % purity) produced. In order to produce high purity product, the material still has to undergo the methanol transesterification process outlined on slide 10.**
- **Waste stream of $CaSO_4$ produced and very large quantities of waste water.**

Some decisions are more difficult!

So how can we make such decisions easier?

In order to try to decide which chemical process is greener, chemists have tried to develop ways of measuring ‘greenness’.

The two most common methods are called:

- Atom Economy;
- E-factor.

Both methods concentrate on reducing waste – other factors (e.g. toxicity, risks, energy consumption etc) are ignored.

The only true way to decide between two reactions is to perform a full life cycle analysis (e.g. the nappies question in lecture 1).

Traditional way of comparing reactions - percentage yields

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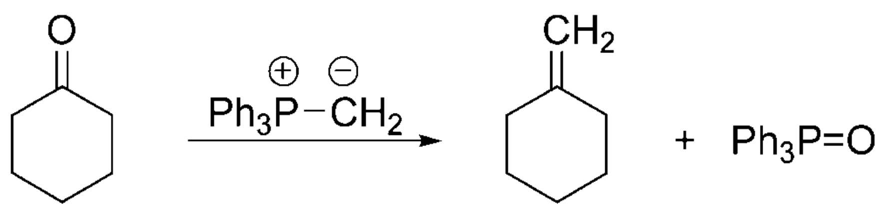
$$\text{Percentage yield} = \frac{\text{Isolated moles of product}}{\text{Theoretical maximum moles of product}} \times 100\ \%$$

However, percentage yield takes no account of by-products, e.g. Wittig reaction:



86 % yield

FW = 98 | **96** | **278**

$\therefore$ 1 kg $C_6H_{10}O$ (10.2 mol) ⟶ 842 g C_7H_{12} (8.8 mol) + **2446 g Ph_3PO (8.8 mol)**

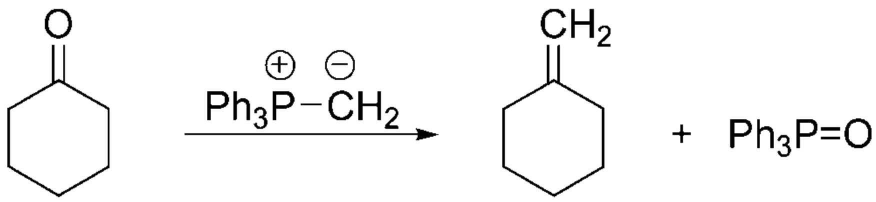
This reaction is high yielding but produces a large amount of waste

The Concept of Atom Efficiency and Atom Economy

Atom Efficiency:
Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

$$\text{Atom Economy} = \frac{\text{FW of desired product(s)}}{\text{Combined FW of starting materials}} \times 100\ \%$$

e.g Wittig reaction:



$$\text{Atom economy} = \frac{96}{98 + 276} = 25.7\ \%$$

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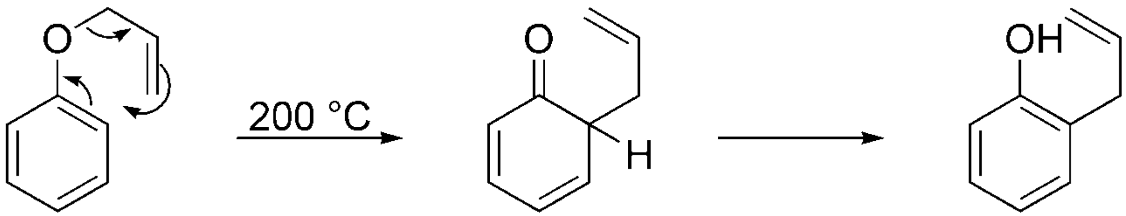
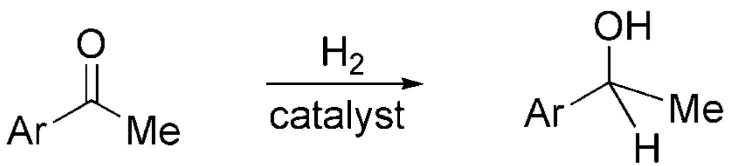
Rearrangements (100% atom economy)

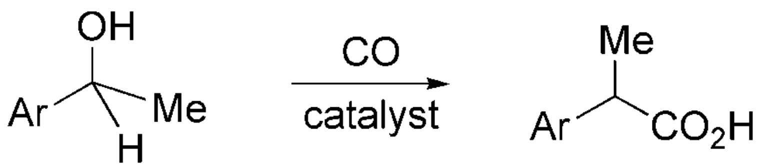


Claisen rearrangement

Additions (100 % atom economy)



Hydrogenation

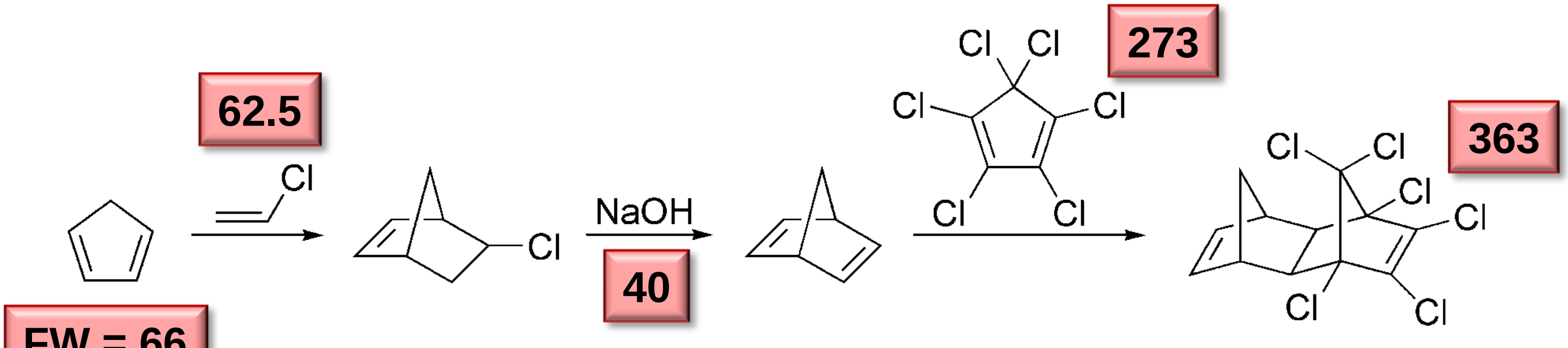


Carbonylation

Other examples include: Markownikoff additions, Michael additions etc

Atom efficient reaction classes

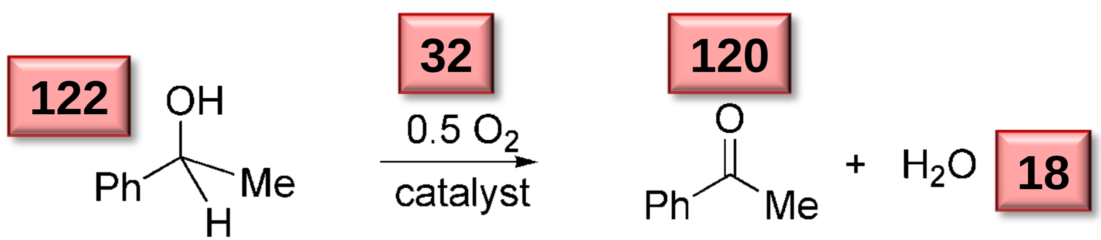
Cycloadditions, e.g. Diels-Alder (100% atom economy)



"Aldrin"

Overall atom economy = 363 / (66 + 62.5 + 40 + 273)
= 82.2 %

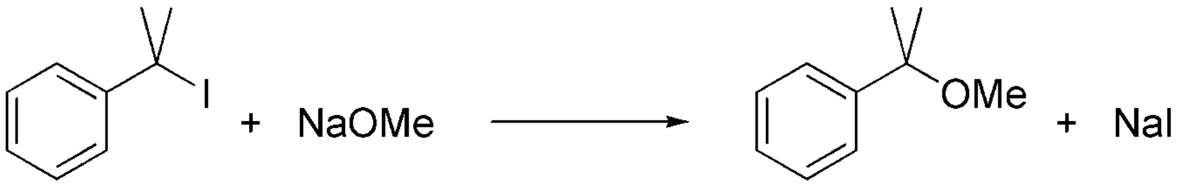
Oxidations



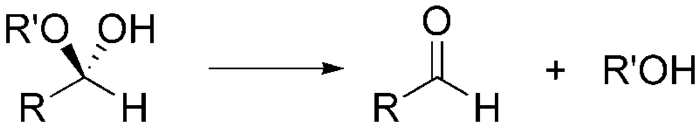
Atom economy = 120 / (122 + 16) = 87.0 %

Atom inefficient reaction classes

Substitutions



Eliminations



Wittig reaction

see earlier slides

E-Factors

$$\text{E-factor} = \frac{\text{kgs of waste produced}}{\text{kgs of desired product}}$$

Industry sector	Annual production (tonnes)	Total waste (tonnes)	E-Factor
Oil refining	10^6 - 10^8	10^6	ca. 0.1
Bulk chemicals	10^4 - 10^6	10^5	< 1-5
Fine chemicals	10^2 - 10^4	10^4	5 - >50
Pharmaceuticals	10 - 10^3	10^3	25 - >100

Advantages:

- take into account solvent use

Disadvantages:

- what if large volumes of solvent are water, or if the waste consists of dilute aqueous solutions of benign inorganics?
- still concentrates on waste rather than other Green factors

Atom economies and E-factors are usually in agreement

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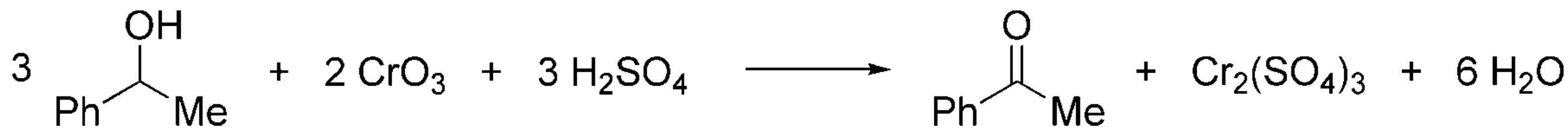
1. Stoichiometric oxidation (Jones Reagent)



atom economy = 42 %
E-factor = ca. 1.5

2. Catalytic oxidation

atom economy = 87 %
E-factor = ca. 0.1

Principles of Green Chemistry: No. 9:

"Catalytic reagents are superior to stoichiometric ones."

Defficiencies of atom economies and E-factors

Atom economies are a useful way of comparing the waste production of alternative pathways, but other factors should still be considered.

- **Atom economies are theoretical and tell us nothing about reaction yield or selectivity, or the nature (toxic / benign) of the waste stream.**
- **Atom economies only take into account stoichiometric reagents - what about catalysts and solvents?**
- **Clearly, atom economies also tell us nothing about other green chemistry concerns, e.g. energy, toxicity.**

Effective Mass Yield - EMY

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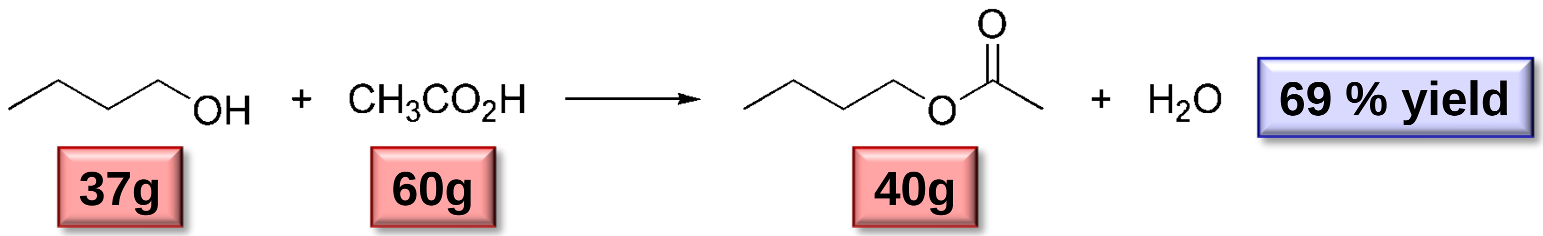
$$EMY = \frac{\text{mass of desired product}}{\text{mass of non-benign reagents}} \times 100\,\%$$

e.g. esterification of n-butanol with acetic acid

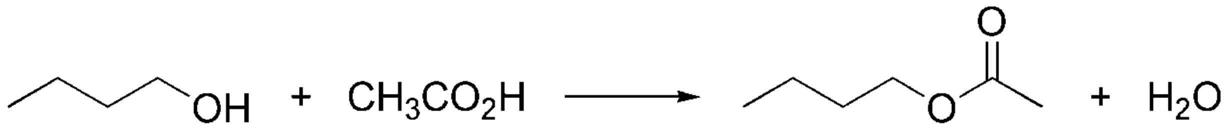


EMY = (40 / 37) x 100 % = 108 %

The main disadvantage of this approach:
How do we judge if a reagent is non-benign?

A final example

e.g. esterification of n-butanol with acetic acid



Typical procedure: 37g butanol, 60 g glacial acetic acid and 3 drops of H_2SO_4 are mixed together. The reaction mixture is then poured into 250 cm^3 water. The organic layer is separated and washed again with water (100 cm^3), saturated $NaHCO_3$ (25 cm^3) and more water (25 cm^3). The crude ester is then dried over anhydrous Na_2SO_4 (5 g), and then distilled. Yield = 40 g (69 %).

Metric	Value	Greenness
yield	69 %	Moderate
atom economy	85 %	Good (byproduct is water)
E-factor	502 / 40 = 12.6	Moderate
EMY	40/37 x 100 = 108 %	Very good

EMY indicates that this reaction is very 'green'

Lecture 2 learning objectives - you should now be able to:

(i)discuss (but not memorise) the 12 Principles of Green Chemistry

(ii) calculate Atom Economies, E-factors and Effective Mass Yields

$$\text{Atom Economy} = \frac{\text{FW of desired product(s)}}{\text{Combined FW of starting materials}} \times 100\ \%$$

$$\text{E-factor} = \frac{\text{kgs of waste produced}}{\text{kgs of desired product}}$$

$$\text{EMY} = \frac{\text{mass of desired product}}{\text{mass of non-benign reagents}} \times 100\ \%$$

Lecture 2 learning objectives - you should now be able to:

(iii) discuss the advantages and disadvantages of each approach

Atom economies – simple to calculate, but focus too much on waste

E-factors – account for solvent use, but still focus principally on waste

EMY – account for toxicity of reagents, but the calculation is open to abuse

(iv) describe the competing processes for the industrial production of dimethyl carbonate and lactic acid.

Dimethyl carbonate: phosgene versus methanol carbonylation
Lactic acid: chemical versus biosynthesis

Recall the question of disposal versus renewal nappies from Lecture 1. Trying to evaluate an entire production process is often an enormous and complex task.

Instead, when questioning the sustainability of competing chemical reactions we tend to compare the nature of five individual components:

- **raw materials**
- **reaction types (e.g. additions, eliminations etc)**
- **reagents (e.g. catalysts)**
- **reaction conditions (including solvents)**
- **toxicity of products (including waste by-products)**

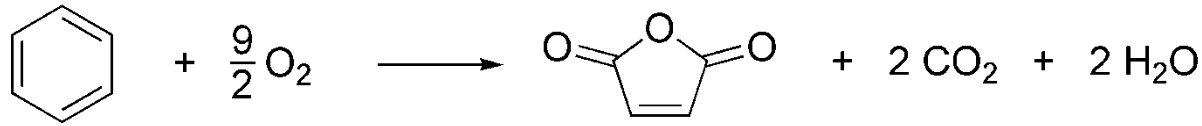
The only complete answer comes from a life cycle analysis

Remember Lecture 1 - "Green Chemistry is not easy!"
The difficulties encountered in trying to measure 'greenness' are a major reason.

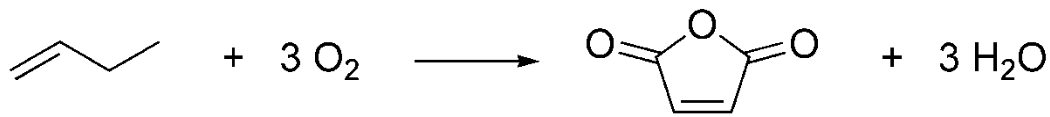
Exam style question - answer next time

Maleic anhydride may be prepared using two routes:

Oxidation of benzene:



Oxidation of but-1-ene:



The benzene oxidation route typically occurs in 65 % yield, while the but-1-ene route only gives yields of 55 %.

(a) Assuming that each reaction is performed in the gas phase only, and that no additional chemicals are required, calculate (i) the atom economy and (ii) the effective mass yield of both reactions. You should assume that O_2, CO_2 and H_2O are not toxic.

(b) Which route would you recommend to industry? Outline the factors which might influence your decision.