"Green Chemistry"

. . .

Twelve Principles of Green Chemistry:

7. Maximize atom economy:

- Final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
- Relation between atoms in the products and atoms in the reagents
  - Addition – good atom efficiency
  - Elimination – not so good…

Atom Economy

- Concept introduced by Prof. Barry Trost, Stanford University
- Evaluate the efficiency of the chemical transformation

"Because an Atom is a Terrible Thing to Waste"

Atom Economy

How many of the atoms of the reactant are incorporated into the final product and how many are wasted?

How a reactions efficiency is measured?

Reaction Yield

$$\%\ \text{yield} = \frac{(\text{actual quantity of product obtained})}{(\text{theoretical quantity of product achievable})} \times 100$$

Atom Economy*

$$\%\ \text{atom economy} = \frac{(\text{MW of desired products})}{(\text{MW of all products})} \times 100$$

* B M Trost, Science 1991, 254, 1471

Atom Economy

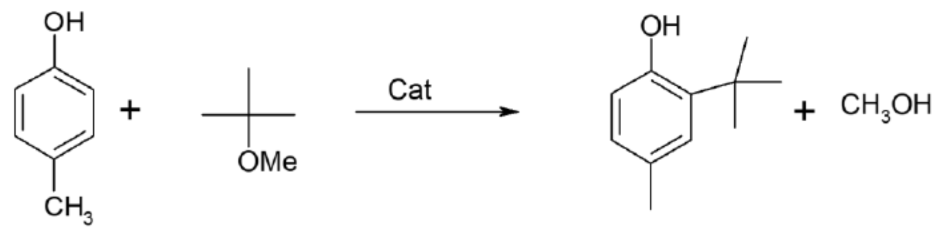
$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH + Na\text{-}Br + H_2SO_4 \rightarrow H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}Br + NaHSO_4 + H_2O$

1 2 3 4 5 6

Reagents Formula	Reagents FW	Utilized Atoms	Weight of Utilized Atoms	Unutilized Atoms	Weight of Unutilized Atoms
$H_3C\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}OH$	74	4C, 9H	57	OH	17
Na-Br	103	Br	80	Na	23
H_2SO_4	98	------	0	2H, 4O, S	98
Total 4C, 12H, 5O, Br, Na, S	275	4C, 9H, Br	137	3H, 5O, Na, S	138

% Atom Economy = (FW of atoms utilized/FW of all reactants) X 100 = (137/275) X 100 = 50%

% Yield vs. atomic economy



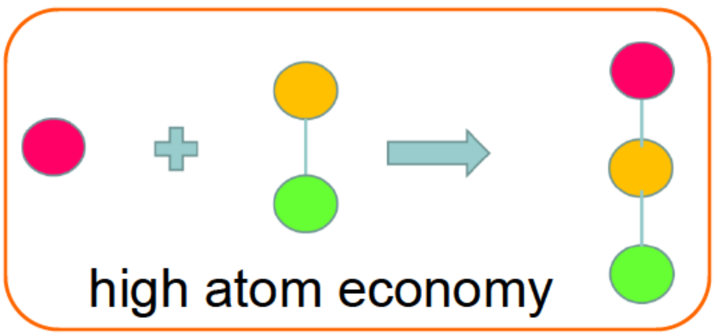
- % Yield = 43.7%
- %Atomic Economy = 83.6%

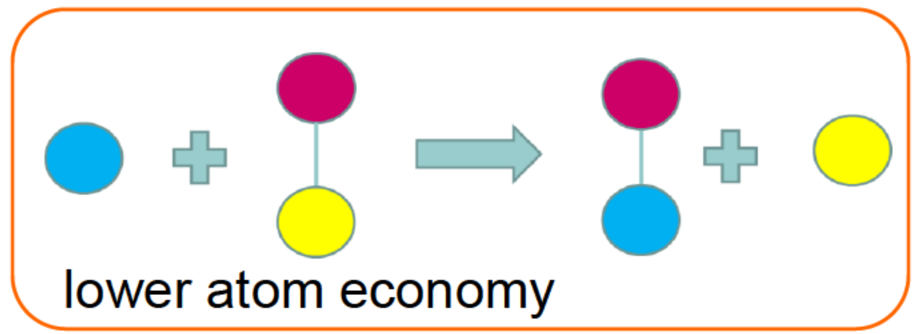
An Example: Hydrogen Production

- For example, what is the atom economy for making hydrogen by reacting coal with steam?
- Write the balanced equation:
  - $C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$
- Write out the A_r and M_r values underneath:
  - $C(s) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2(g)$
  - **12   2 × 18   44   2 × 2**
- Remember that the A_r or M_r in grams is one mole, so:
  - total mass of products = 44 + 4 = 48g (note that this is the same as the reactants: 12 + 36 = 48g)
  - mass of desired product (H_2) = 4g
  - % atom economy = $\frac{4}{48} \times 100 = 8.3\%$
- This process has a low atom economy and is therefore an inefficient way to make hydrogen. It also uses a non-renewable resource: coal.

Chemical Reactions and Atomic Economy

- Addition > Substitutions > Eliminations (decreasing order of atom economy)

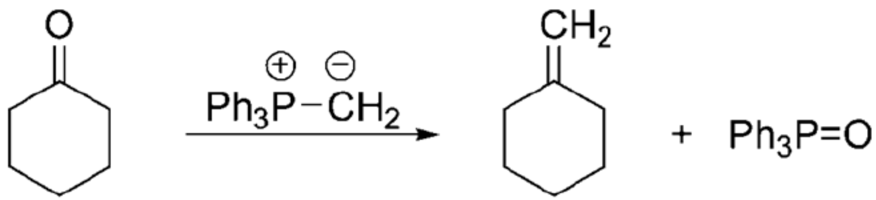




- Cycloadditions: 100 % atom efficient
  - Example: Diels-Alder

Chemical Reactions and Atomic Economy

e.g Wittig reaction:



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

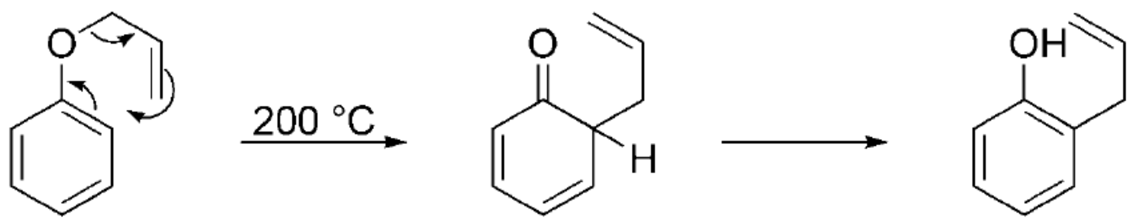
Claisen Rearrangement

112 g/mol **112 g/mol**

$$\textbf{Atom economy} = \frac{112}{112} = 100\ \%$$

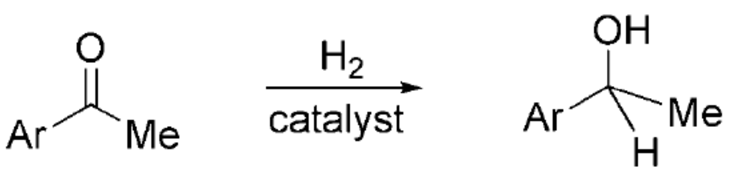
Chemical Reactions and Atomic Economy

❑ Rearrangements (100% atom economy)

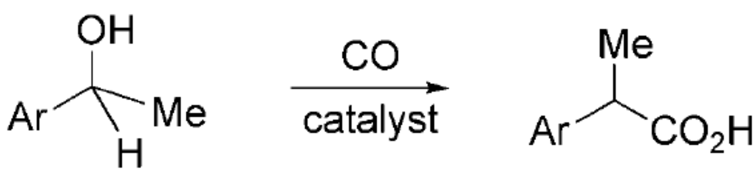


Claisen rearrangement

❑ Additions (100 % atom economy)



Hydrogenation

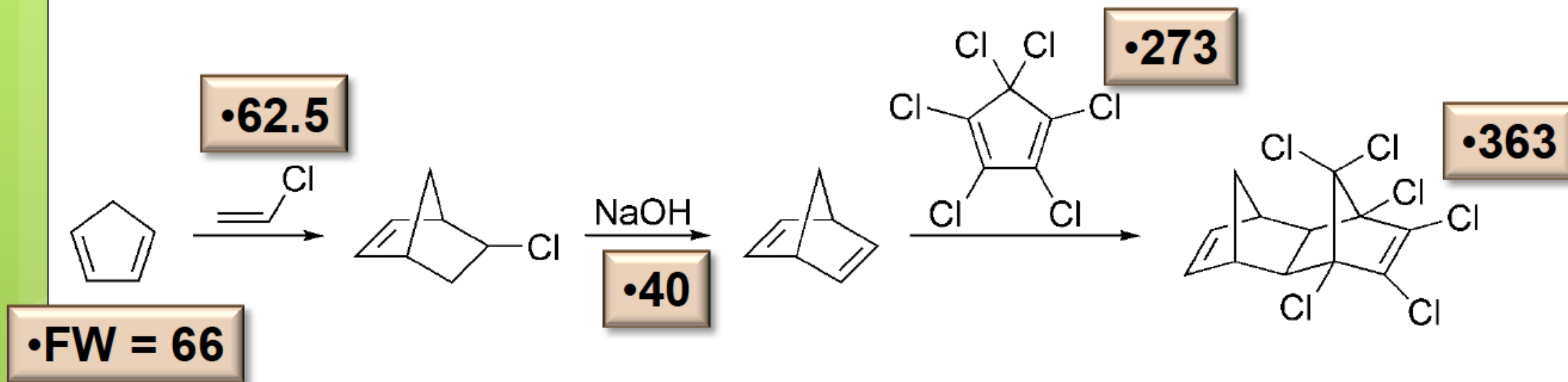


Carbonylation

❑ **Other examples include: additions to alkenes, Michael additions etc**

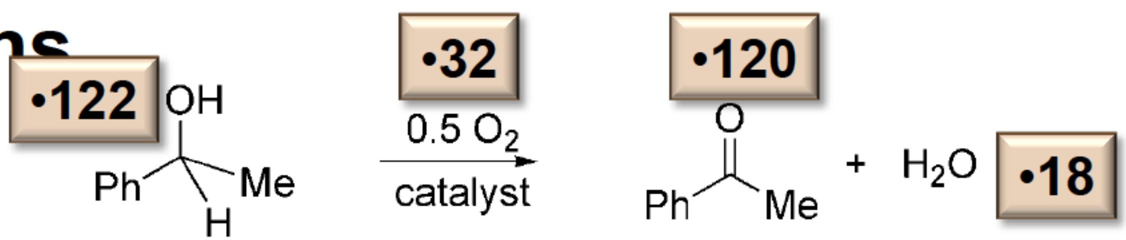
❑ Atom efficient reaction classes

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



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

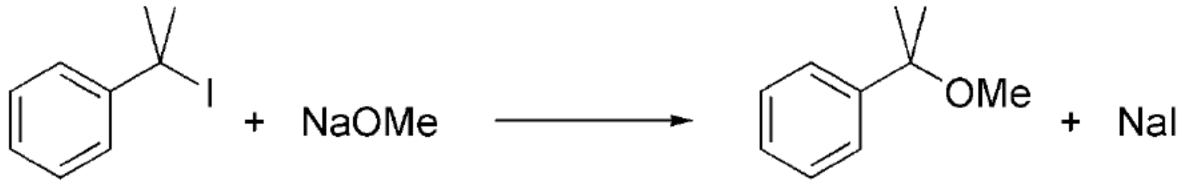
•Oxidations



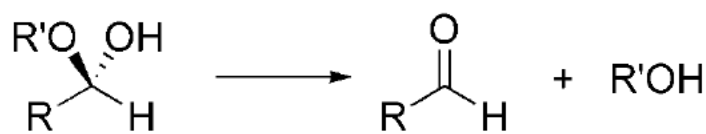
Atom economy = 120 / (122 + 16) = 87.0 %

Atom inefficient reaction classes

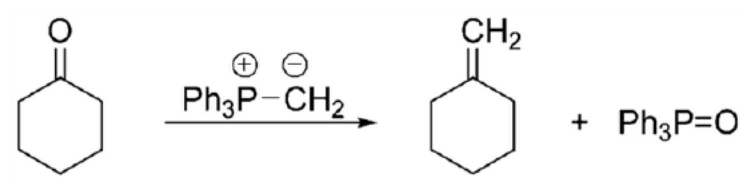
Substitutions



Eliminations



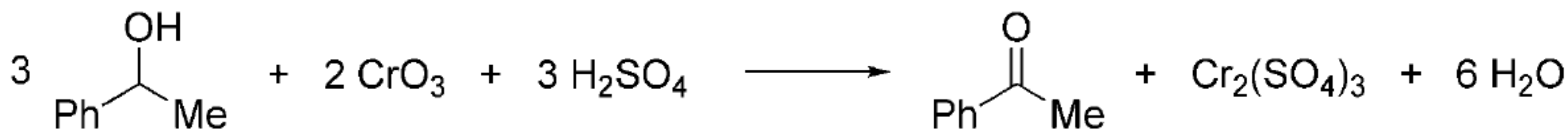
Wittig reaction



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

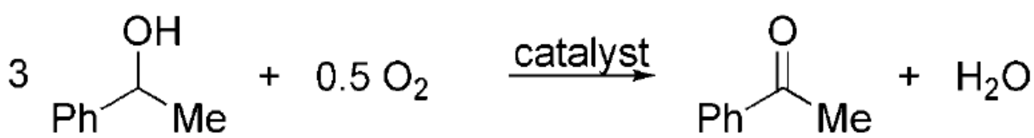
❑ Some transformations can be atom efficient if performed under different conditions

❑ 1. Stoichiometric oxidation (Jones Reagent)



atom economy = 42 %

❑ 2. Catalytic oxidation



atom economy = 87 %

- We will later that this uses another principle of Green Chemistry

•Principles of Green Chemistry: No. 9:

•"Catalytic reagents are superior to stoichiometric ones."

Twelve Principles of Green Chemistry:

8. Use safer solvents and reaction conditions

- Avoid:
  - solvents,
  - separation agents,
  - other auxiliary chemicals.
- USE: innocuous chemicals.

Solvents

- Organic solvents = high VOC's
- Alternatives
  - Synthesis without solvents
  - Water
  - Supercritical fluids (CO_2)
  - Ionic Liquids

Dry Cleaning – Greener…

- Initially gasoline and kerosene were used
- Now use PERC
- Future use Supercritical CO_2 and CO_2 surfactants

Twelve Principles of Green Chemistry:
9. Increase energy efficiency:

- Run chemical reactions at ambient temperature and pressure whenever possible. (Avoid reactions that involve excessive heating and cooling as it requires energy and also increases cost)

Twelve Principles of Green Chemistry:

10. Design chemicals and products to degrade after use:

- Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

Twelve Principles of Green Chemistry:

11. Analyze in real time to prevent pollution:

- Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

PAT:
Process Analytical Technologies

- Measure quality and execution properties DURING manufacturing
- Information is gather continuously to improve process

Pre - PAT

- Analysis of raw materials, intermediates and final products
- In case of problems identified at a later stage, the WHOLE lot will be rejected = A LOT OF WASTE!... A LOT OF $$$$!!

PAT: Process Analytical Technologies

- Helps to:
  - Understand the process
  - Make corrections in the moment, without waiting for the final product
  - Develop mitigation strategies.

Twelve Principles of Green Chemistry:

12. Minimize the potential for accidents:

- Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents:
  - explosions,
  - fires, and
  - Release of chemicals to the environment.