Green Chemistry

Slide 2

Twelve Principles of Green Chemistry

★ Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances.

★ Paul T. Anastas formulated the basic principles of Green Chemistry

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1. Prevention of waste/by-products.

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

What is the problem faced if by product is huge?

- The cost involved in the treatment and disposal of waste adds to the overall production cost.
- Even the unreacted starting materials (which mayor may not be hazardous) form part of the waste.
- The waste (or by-products) if discharged (or disposed off) in the atmosphere, sea or land not only causes pollution but also requires expenditure for cleaning-up.

E-Factor: Weight of byproducts/weight of desired product

E-Factor for the synthesis of Zeises salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$:

$$\underset{(4.5\ g)}{K_2PtCl_4} + \underset{\substack{(2\ g)\\ \text{(Approximately)}}}{C_2H_4} + \underset{(8.21\ g)}{HCl} \text{ (in water)} \xrightarrow[\text{(40 mg)}]{SnCl_2} \underset{(3.86\ g)}{K[PtCl_3(C_2H_4)].H_2O} + KCl + C_2H_4 \text{ (unreacted)}$$

Total amount of reactants: 4.5 g + 2 g + 8.21 g = 14.71 g [solvent (water) and catalyst ($SnCl_2$) have been excluded from this calculation].
Amount of final product: 3.86 g
Amount of waste: (14.71 – 3.86) g = 10.85 g

E-Factor = Amount of waste/Amount of product = 10.85/3.86 = 2.81

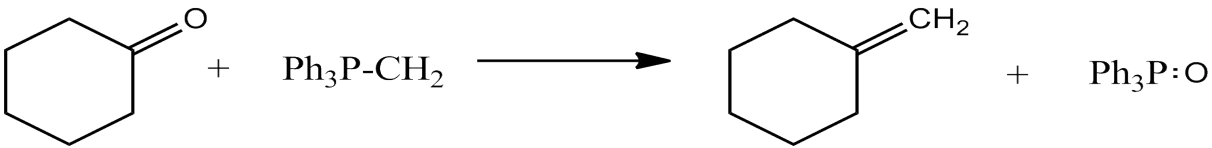
E- factor : Weight of byproducts/weight of desired product

Industry	Tonnes/annum	E-factor
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1–5
Fine chemicals	10^2–10^4	5 → >50
Pharmaceuticals	10–10^3	25 – >100

2. Maximum incorporation of the reactants (starting materials and reagents) into the final product.

The reaction or the synthesis is considered to be green if there is maximum incorporation of the starting materials and reagents in the final product.

Wittig Reaction



$$\% \text{ yield} = \frac{\text{Actual yield of the product}}{\text{Theoretical yield of the product}} \times 100$$

- **For the reaction % yield = 100%**
- **WHAT ABOUT THE SIDE PRODUCT FORMED? HOW IT SHOULD BE INCORPORATED IN CALCULATION?**

Atom Economy

1. ADDITION REACTION

$$\% \text{ atom economy} = \frac{\text{FW of atoms utilized}}{\text{FW of the reactants used in the reaction}} \times 100$$

DIELS-ALDER REACTION IS AN EXAMPLE OF 100% ATOM ECONOMY, WHILE WITTIG REACTION IS 35% ONLY

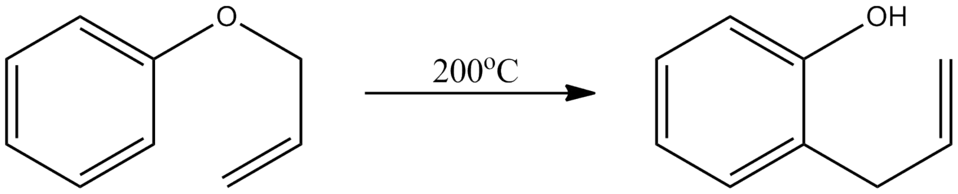
OTHER EXAMPLES OF ADDITION REACTION

$$\underset{\text{Propene}}{H_3C{-}CH{=}CH_2} + Br_2 \longrightarrow \underset{\text{1,2-Dibromopropane}}{H_3C{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}CH_2Br}$$

$$\underset{\text{Propene}}{H_3C{-}CH = CH_2} + H_2 \xrightarrow{\text{Ni}} \underset{\text{Propane}}{H_3C{-}CH_2{-}CH_3}$$

2. REARRANGEMENT REACTIONS

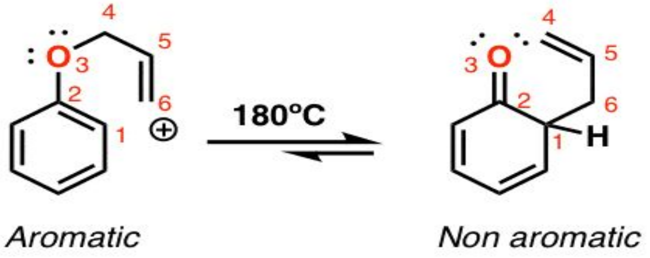
Rearrangement Reaction



CLAISEN REARRANGEMENT

Claisen Rearrangement of A Phenyl Allyl Ether

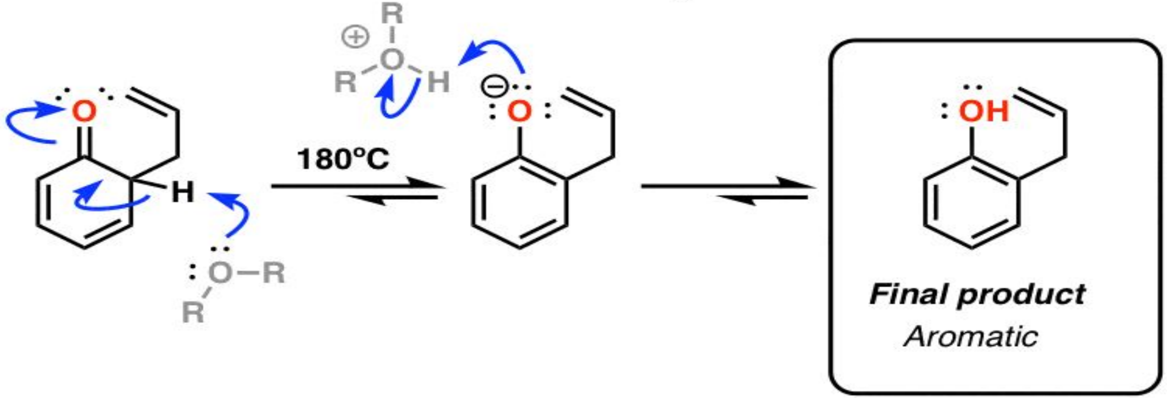
Part 1: Cope rearrangement (as before)



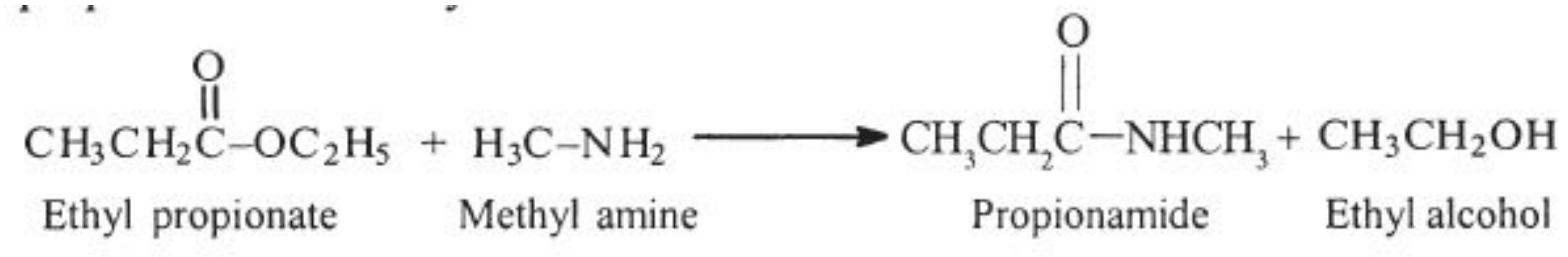
Bonds Formed	Bonds Broken
$C_1–C_6$	$C_1–C_2(\pi)$
$C_4–C_5(\pi)$	$C_5–C_6(\pi)$
$C_2–O(\pi)$	$C_4–O$

Same pattern as before

Part 2: Tautomerization to restore aromaticity



3. IS SUBSTITUTION REACTION AN ATOM ECONOMICAL REACTION?

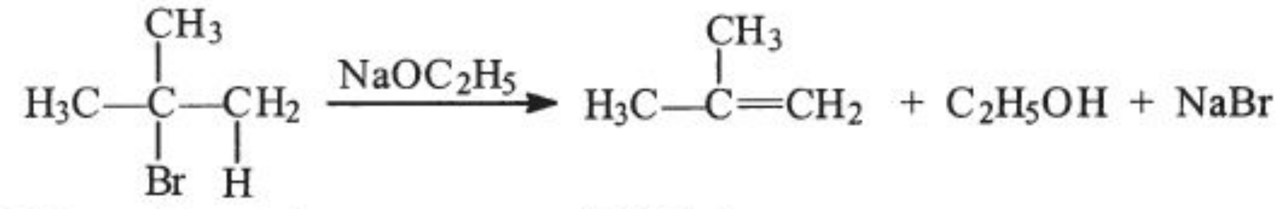


SUBSTITUTION REACTIONS DON'T HAVE 100% ECONOMY. IN PREVIOUS REACTION ETHYL ALCOHOL IS NOT A PART OF PRODUCT. ATOM ECONOMY = 65.4%

	Reactants		Utilised		Unutilised	
	Formula	FW	Formula	FW	Formula	FW
	$C_5H_{10}O_2$	102.132	C_3H_5O	57.057	C_2H_5O	45.061
	CH_5N	31.057	CH_4N	30.049	H	1.008
Total	$C_6H_{15}NO_2$	133.189	C_4H_9NO	87.106	C_2H_5OH	46.069

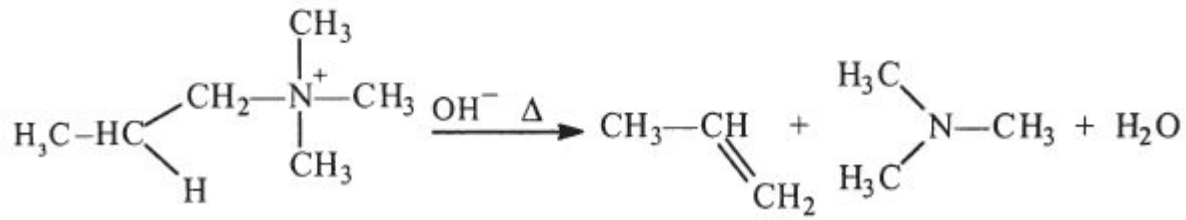
Therefore, the % atom economy = $\frac{87.106}{133.189} \times 100 = 65.40$ %.

4. ELIMINATION REACTIONS



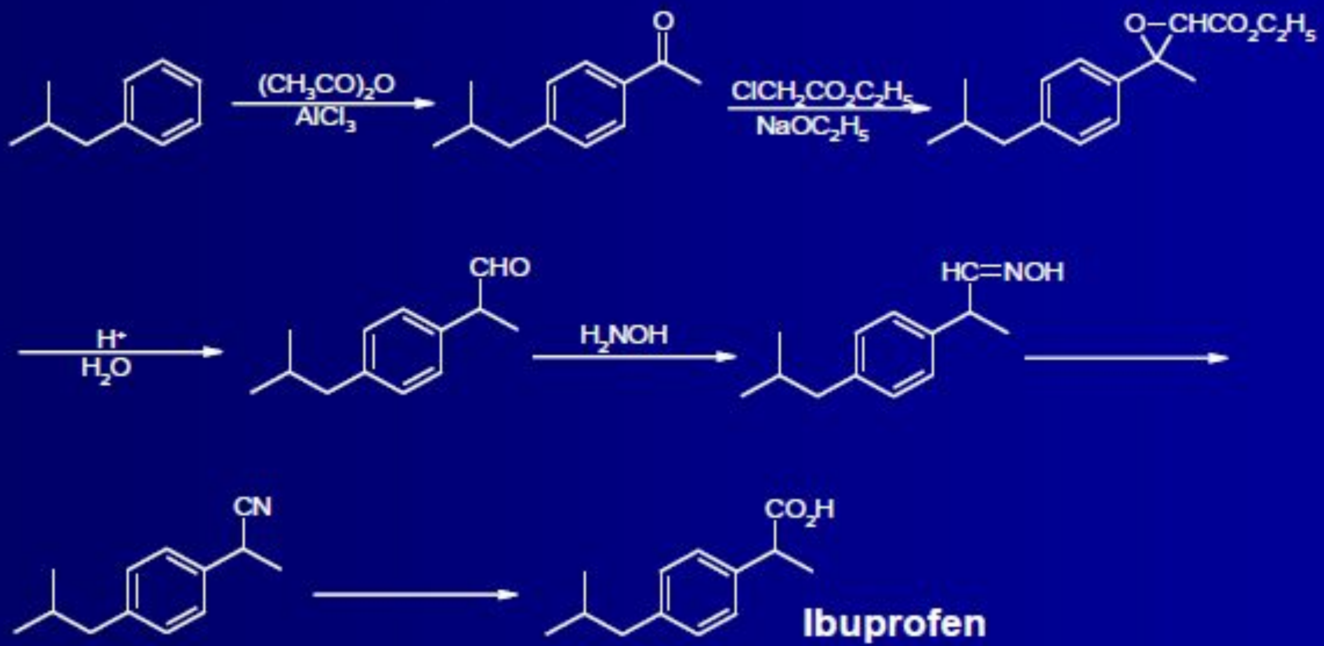
2-Bromo-2-methylpropane 2-Methylpropane

Elimination reaction= 27%



Hoffman elimination, Atom Economy = 35.30 %

- Traditional synthesis of ibuprofen
  - 6 stoichiometric steps
  - <40% atom utilization



- Catalytic synthesis of ibuprofen
  - 3 catalytic steps
  - 80% atom utilization (99% with recovered acetic acid)