Lecture 14: Green Chemistry and Technology

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Course code: CH 426

Credit: 6

Lecture 14:

Learning Objectives of the this Lecture:

To discuss four green chemistry principles: namely-

- **Renewable sources**
- **Derivative reduction**

Principle 7: Renewable Resources

This principle states that, "A raw material or feed stock should be renewable rather than depleting wherever technically and economically practicable."

The chemical industry in earlier times depended mostly on renewable resources such as wood, crops, animal excreta and others. The discovery of the effective distillation of crude oil led to our dependence on petroleum and natural gas. Starting materials for any synthesis are either obtained from non-renewable or renewable resources.

Principle 7: Renewable Resources

The demand for petrochemical and other materials is increasing due to increase in population and industrialization. These petrochemicals and materials are synthesized from fossil fuels, oils, coal, and natural gas, and these are depleting. Although vegetation is renewable, but it takes millions of years to convert it into fossil fuel along with animal remains. This is not practical, and time is the constraint, so these fossil fuels are considered to be depleting and non-renewable.

Principle 7: Renewable Resources

If we obtain starting materials from agricultural or biological produce, then these are referred to as renewable starting materials. CO_2 generated from natural resources and methane gas obtained from marsh gas, another natural resource, is available in the large amounts and also falls in the category of renewable resources.

Sustainability and Environmental Issues

Sustainability issue: As the fossil fuels are depleting, we have to find alternatives to fossil fuels to resolve sustainability issue. As our natural resources are depleting, we have to find ways to make these resources available for our future generations. This principle becomes important as we use renewable feed stock in the form of biomass making all our fuels, chemicals, and materials. This biomass is in the form of plants, trees, crops, algae, etc.

Sustainability and Environmental Issues

Although all living may be considered biomass, only non-animal renewable resources may be used for biomass economy. It is observed that about 170 billion tonnes of biomass is produced annually in nature. Out of this only 3.5% is used for everyday need. Only 25% is used for bio-based economy. It is the need of the hour to advance the research in this direction to develop fuels, chemicals, and renewable feed stock from biomass.

Sustainability and Environmental Issues

There are problems sometimes associated with biological feed stock, as they are seasonal. These feed stocks should be available as and when required. There are sometimes crop failures due to which there may not be continuous supply of starting materials for production. Another important aspect is availability of land to cultivate a large quantity of crops.

Sustainability and Environmental Issues

Environmental issue: The effects of fossil fuel are well known on human health and the environment. Air pollution due to refining, coal mining, oil spills, etc., is one of the problems associated with synthesis of petrochemicals. Other factors related to pollution includes oxidation of petroleum hydrocarbons to the other functional groups. These use heavy metals, such as, chromium, which are toxic. Generation of chromium compounds waste contributes to the human health and the environment.

Sustainability and Environmental Issues

Some examples of renewable raw materials are as follows:

(a) Ethanol from plants.

(b) Polyethylene can be made from ethylene, which is a product of bio-ethanol.

(c) Polyurethane can be synthesized from soya (polyhydroxy compounds known as *polyols*).

(d) Enzymes from biomass.

Sustainability and Environmental Issues

Some examples of renewable raw materials are as follows:

(e) Oils and carbohydrates from plants are used for surfactants.

(f) Starch-based plastics.

(g) Biodiesel from plant oil.

(h) 2-MeTHF as a solvent (under greener solvents).

Some Alternative Chemicals Derived from Natural Resources

Adipic Acid from Corn Starch

Almost 2 billion kg of adipic acid is needed every year to make nylon, polyurethane, lubricant, and plasticizers. Traditionally, it is made from benzene, which is carcinogenic. Now, glucose obtained from corn starch can make adipic acid. This is a green substituted for benzene.

Some Alternative Chemicals Derived from Natural Resources

- ***Bioethanol and Biodiesel***

During the last few years, significant progress has been made to develop fuel, chemicals, and materials from renewable resources. Sugarcane production in Brazil is very good and bioethanol production from it is helping them attain energy independence as well as in generating employment. Europe is producing biodiesel from rapeseed oil.

Some Alternative Chemicals Derived from Natural Resources

Biofuel Production from Microalgae

Interest in recent research is focused on microalgae. Lipid-extracted biofuel production from microalgae is due to high lipid and carbohydrate content. Also, there is increased productivity per unit land and water compared to higher plants. The raw material processing is a challenge among algae versus sugar versus lignocelluloses.

Some Alternative Chemicals Derived from Natural Resources

Green Plastic made from Corn

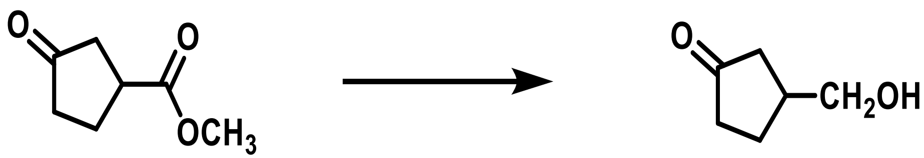
Annually, Nature Works LLC produces 300 million pounds of poly (lactic) acid (PLA) polymer from renewable resources. This process avoids the use of organic solvents common to the synthesis of petrochemical-based chemicals and helps in reducing to 40% less greenhouse gases (GHGs) released to the atmosphere. Degradation of PLA takes 47 days.

Principle 8: Derivative Reduction

"Unnecessary derivatisation (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible."

Derivative Reduction

- The derivatization principle is illustrated on an example from the beginning of organic chemistry. Starting from compound 1, which has a keto and ester groups, we need to make compound 2, in which the ester group is converted to alcohol, whereas the keto group is preserved.



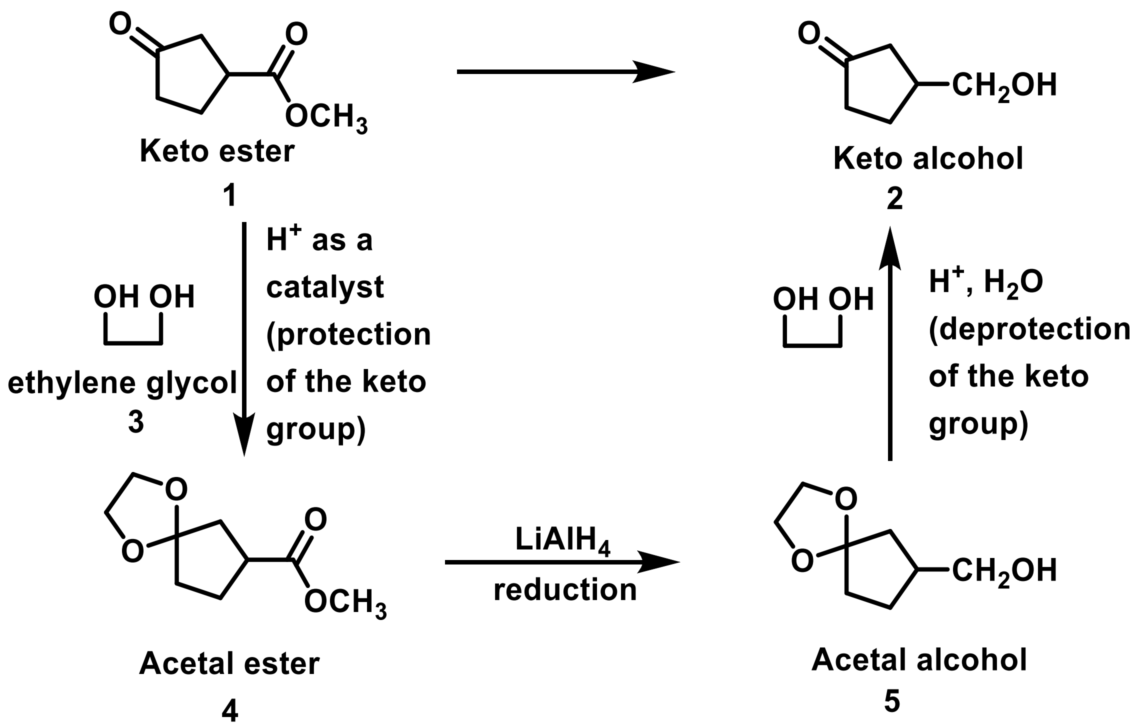
Keto ester 1 | Keto alcohol 2

- The reaction requires a reduction of the ester group to an alcohol. Two reducing agents that we are familiar with sodium borohydride ($NaBH_4$) and Lithium aluminium hydride ($LiAlH_4$). The latter will reduce the ester group, whereas the former will not. However, both reducing agents will reduce the keto group to alcohol, because keto function is more easily reduced than the ester.

Derivative Reduction

- To solve this synthetic problem, one can react 1 with ethylene glycol (3) under the acidic condition to give compound 4, in which the keto group is transformed to the acetal, whereas the ester group is unchanged (it does not react with 3). One can then reduce the ester group with $LiAlH_4$, which will convert it to the desired alcohol 5, while leaving acetal group intact. Finally, the acetal group is removed by an acid hydrolysis to give the desired product 2. The terms chemists use are that the keto group is protected against reduction by 'derivatisation' into an acetal, which is later removed to 'deprotect' the ketone.

Transformation of a keto ester 1 to a keto alcohol 2 via a protection/ deprotection scheme



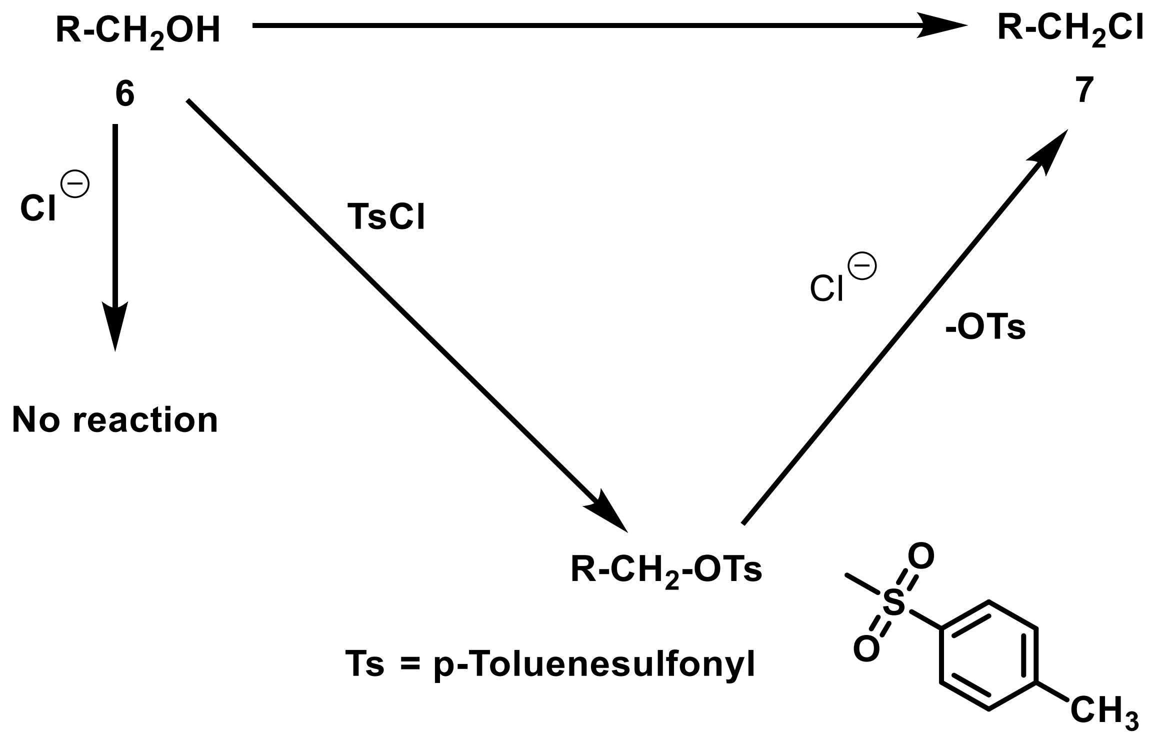
Why should we avoid protection and deprotection strategy?

- **A quick examination of the reaction sequence reveals a poor atom economy, because ethylene glycol will go to waste. Alternatively, a possible recycling of ethylene glycol would require an extraction from the aqueous waste and purification for its reuse, which may not be economical at all.**

Why protection and deprotection strategy is mandatory?

- Another type of derivatisation that the beginning organic students are familiar with is the introduction of a functional group that renders the molecule more reactive, and then replacement of this group is carried out with another group, which is desired. We wish to convert a primary alcohol RCH_2OH (6) to the corresponding chloride, RCH_2Cl (7) via a nucleophilic substitution S_N2 with Chloride ion. The reaction will fail, because the OH is a poor leaving group. However, if we derivatize the alcohol, by converting the OH group into a good leaving group such as tosylate, the reaction will occur.

Derivatization to facilitate the substitution reaction



Why should we look for greener alternatives?

- **In this example, we see also a poor atom economy because tosylate will go to waste.**