Organic Chemistry

Alcohols and Ethers

by

Nurlin Abu Samah, Dr. Md. Shaheen & Dr. Nadeem Akhtar
Faculty of Industrial Sciences & Technology
nurlin@ump.edu.my

Chapter Description

- Aims
  - The students should **understand** the fundamental of organic chemistry in terms of alcohols and ethers
  - The students should be able to **explain** the fundamental of organic chemistry in terms of alcohols and ethers

- Expected Outcomes
  - Explain the basic knowledge in alcohols and ethers
  - Describe the chemical reactions and conditions for alcohols and ethers reactions
  - Describe the alcohols and ethers used in certain industrial application

- References
  - Janice Gorzynski Smith (2008), Organic chemistry,Mc Graw-Hill
  - T. W. Graham Solomons. (2008). Organic chemistry, 9th ed, Mc Graw-Hill
  - K. Peter C. Vollhardt, Neil E. Schore, (2009). Organic chemistry, Fourth Edition: Structure and Function, Pub Chem

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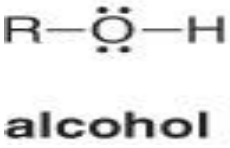
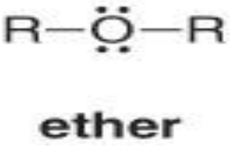
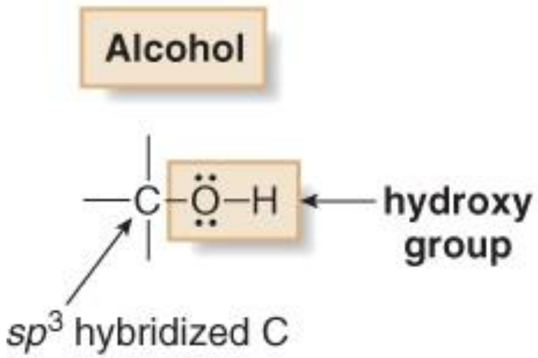
Introduction—Structure and Bonding


alcohol


ether

- **Alcohols** contain a hydroxy group (OH) bonded to an *sp*^{3} hybridized carbon.



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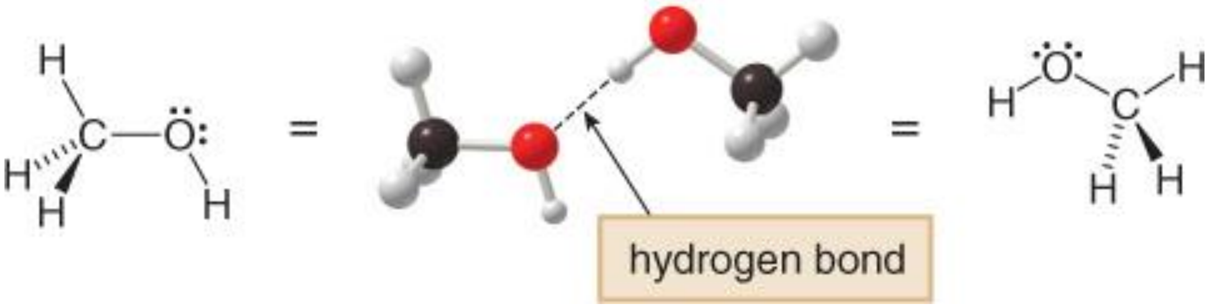
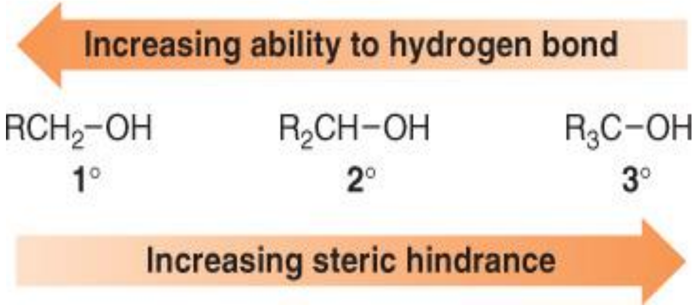
Physical Properties

- **Alcohols and ethers exhibit dipole-dipole interactions because they have a bent structure with two polar bonds.**
- **Alcohols are capable of *intermolecular hydrogen bonding*. Thus, alcohols are *more polar* than ethers.**



- **Steric factors affect hydrogen bonding.**



Increasing ability to hydrogen bond

RCH_2-OH 1°

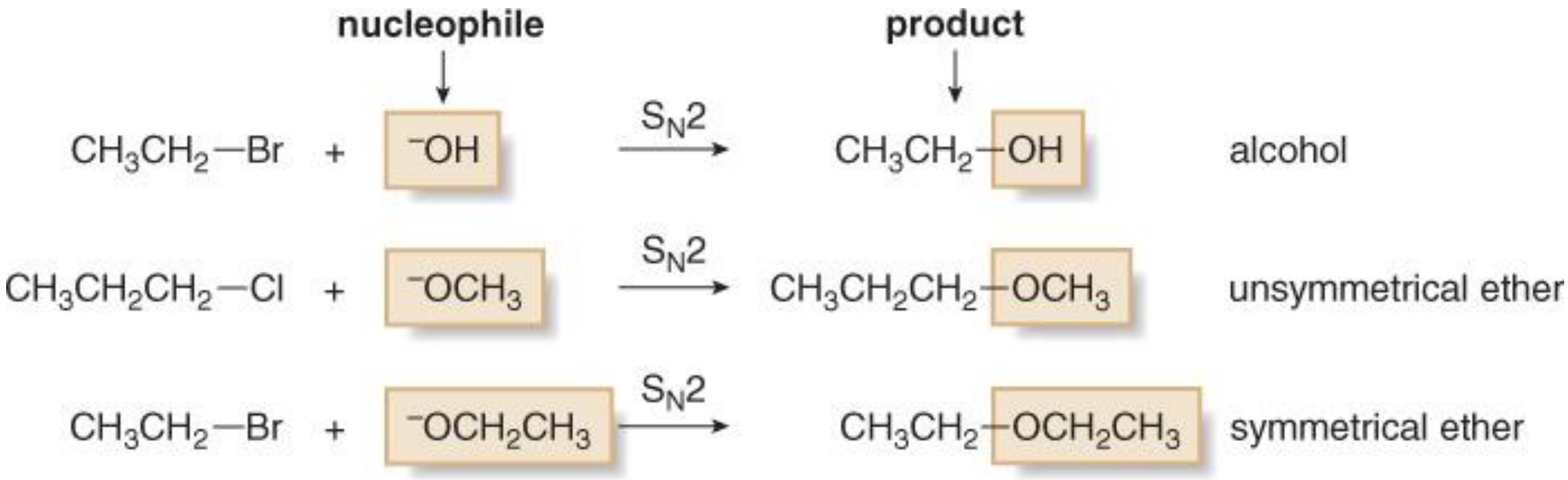
R_2CH-OH 2°

R_3C-OH 3°

Increasing steric hindrance

Preparation of Alcohols and Ethers

- Alcohols and ethers are both common products of **nucleophilic substitution**.



$CH_3CH_2{-}Br + {}^{-}OH \xrightarrow{S_N2} CH_3CH_2{-}OH$ alcohol

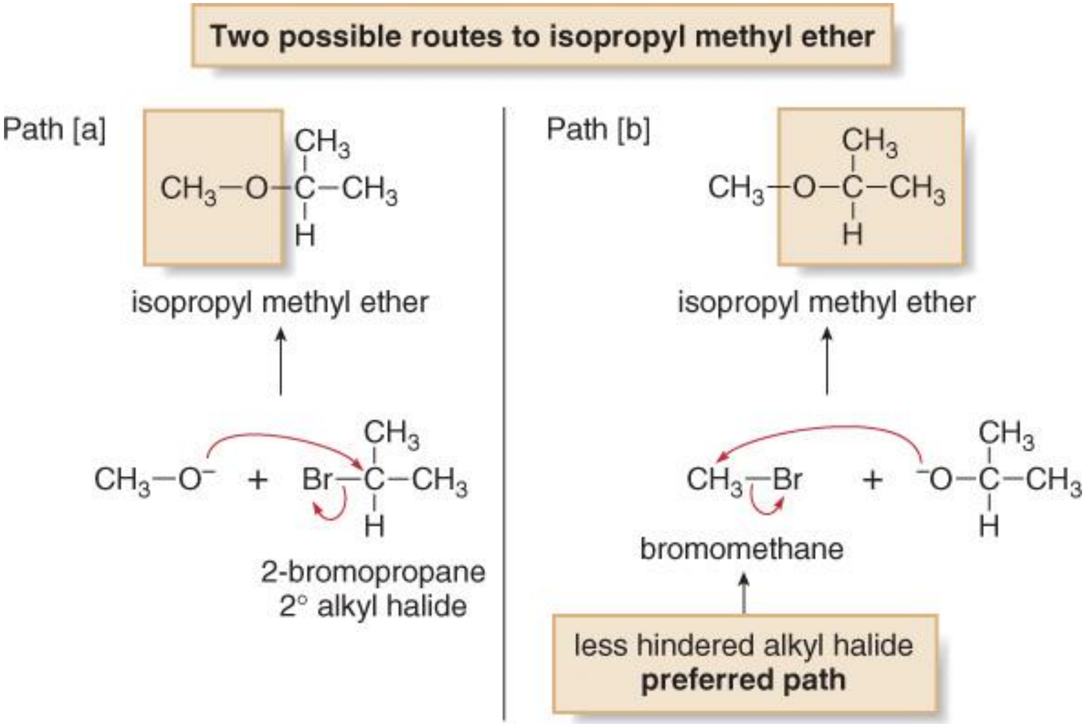
$CH_3CH_2CH_2{-}Cl + {}^{-}OCH_3 \xrightarrow{S_N2} CH_3CH_2CH_2{-}OCH_3$ unsymmetrical ether

$CH_3CH_2{-}Br + {}^{-}OCH_2CH_3 \xrightarrow{S_N2} CH_3CH_2{-}OCH_2CH_3$ symmetrical ether

- The preparation of ethers by this method is called the **Williamson ether synthesis.**

Preparation of Alcohols and Ethers

- **Unsymmetrical ethers can be synthesized in two different ways, but often one path is preferred, Why?.**



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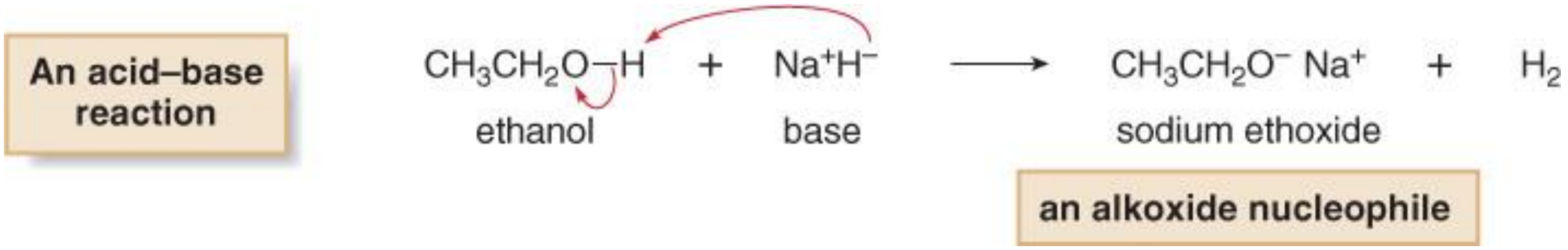
Preparation of Alcohols and Ethers

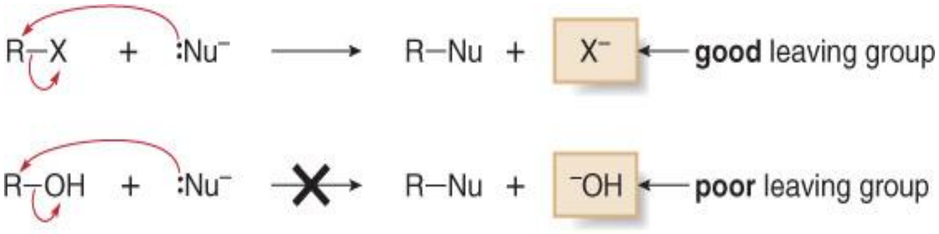
- **An alkoxide salt is needed to make an ether.**
- **Alkoxides can be prepared from alcohols by a BrØnsted-Lowry acid—base reaction. For example, sodium ethoxide ($NaOCH_2CH_3$) is prepared by treating ethanol with NaH.**



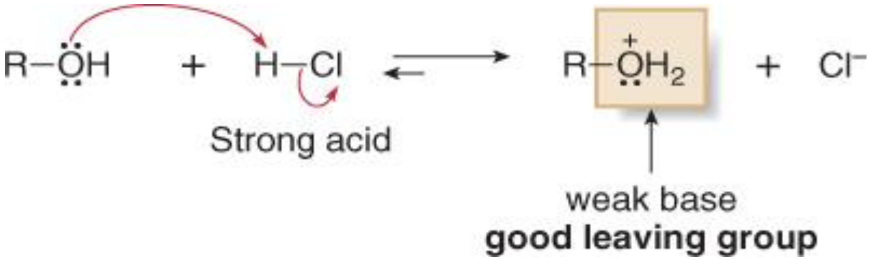
- **NaH is an especially good base for forming alkoxide because the by-product of the reaction, H_2, is a gas that just bubbles out of the reaction mixture.**

Reactions of Alcohols

- **Recall that, unlike alkyl halides in which the halogen atom serves as a good leaving group, the OH group in alcohols is a very poor leaving group.**

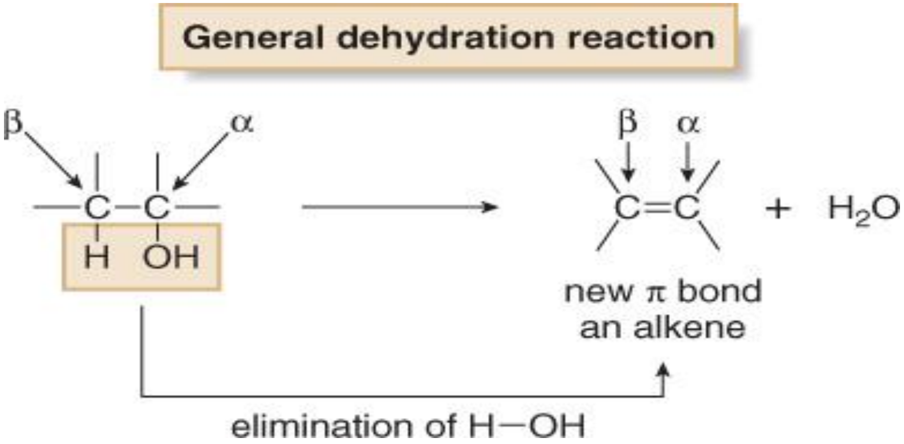


- **For an alcohol to undergo *nucleophilic substitution*, OH must be converted into a better leaving group. By using acid, $^{-}$OH can be converted into H_2O, a good leaving group.**



Reactions of Alcohols—Dehydration

- **Dehydration,** like dehydrohalogenation, is a *β elimination reaction* in which the elements of OH and H are removed from the α and β carbon atoms **respectively**.

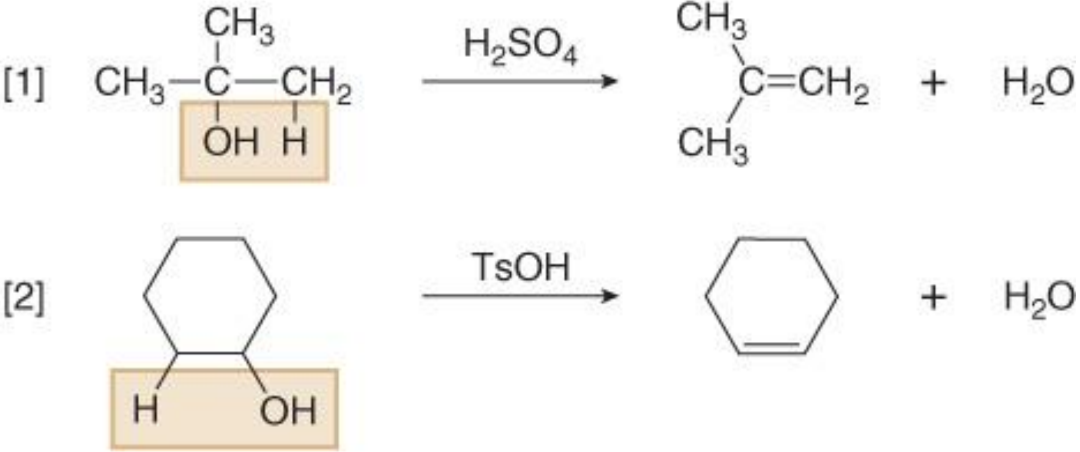


- Dehydration is typically carried out using *H_2SO_4* and other strong acids, or *phosphorus oxychloride ($POCl_3$)* in the *presence of an amine base*.

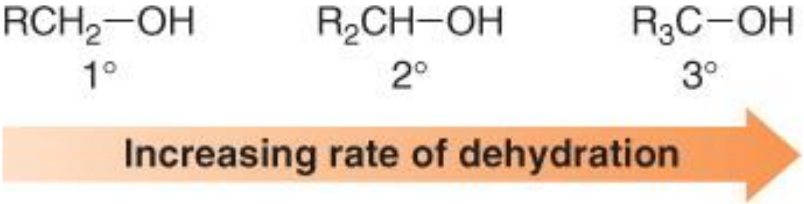
Reactions of Alcohols—Dehydration

- **Typical acids used for alcohol dehydration are *H_2SO_4 or p-toluenesulfonic acid (TsOH).***

Examples

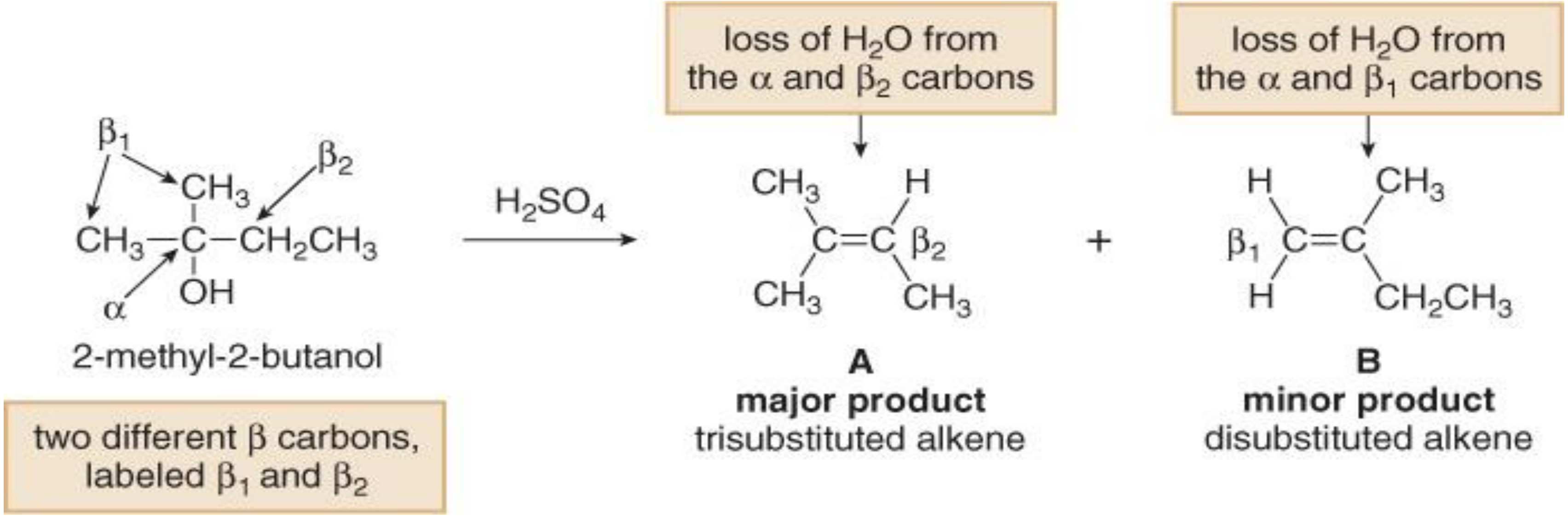


- **More substituted alcohols dehydrate more easily, giving rise to the following order of reactivity.**



Reactions of Alcohols—Dehydration

- **When** an alcohol has two or three **β carbons**, dehydration is ***regioselective*** and follows the ***Zaitsev rule***.
- **The *more substituted alkene* is the *major product* when a mixture of constitutional isomers is possible.**



2-methyl-2-butanol

two different β carbons, labeled β_1 and β_2

loss of H_2O from the α and β_2 carbons

A
major product
trisubstituted alkene

loss of H_2O from the α and β_1 carbons

B
minor product
disubstituted alkene

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Reactions of Alcohols—Dehydration

- The *E1 dehydration of 2^0 and 3^0 alcohols* with acid gives **clean elimination products** without any by-products formed from an *S_N1 reaction*.
- Clean elimination takes place because the reaction mixture contains *no good nucleophile* to react with the intermediate carbocation, so *no competing S_N1 reaction occurs.*
- This makes the *E1 dehydration of alcohols* much more synthetically useful than the *E1 dehydrohalogenation of alkyl halides.*

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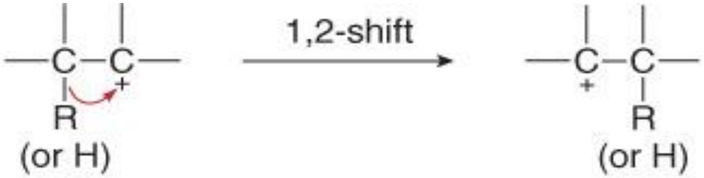
Carbocation Rearrangements

- Often, when carbocations are intermediates, a less stable carbocation can rearrange to a more stable carbocation by a shift of a hydrogen or an alkyl group. This is called a rearrangement.
- Because the migrating group in a 1,2-shift moves with two bonding electrons, the carbon it leaves behind now has only three bonds (six electrons), giving it a net positive (+) charge.

Carbocation rearrangement



- Movement of a hydrogen atom is called a 1,2-hydride shift.
- Movement of an alkyl group is called a 1,2-alkyl shift.

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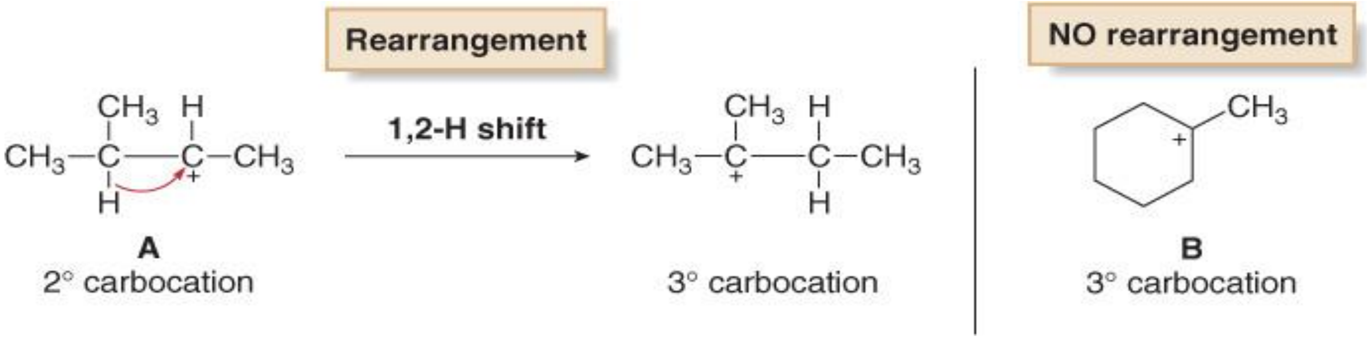
Carbocation Rearrangements

- A 1,2-shift converts a *less stable carbocation* to a *more stable carbocation.*
- Rearrangements are not unique to dehydration reactions. Rearrangements occur whenever a carbocation is formed as a reactive intermediate.

Consider the example below. 2^0 Carbocation A rearranges to the more stable 3^0 carbocation by a 1,2-hydride shift, whereas carbocation B does not rearrange because it is 3^0 to begin with.



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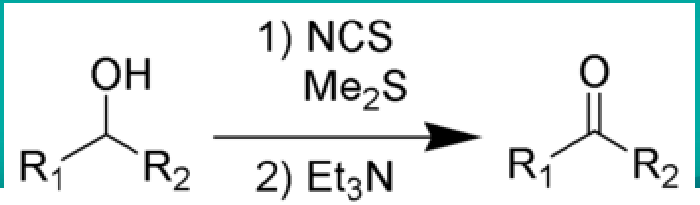
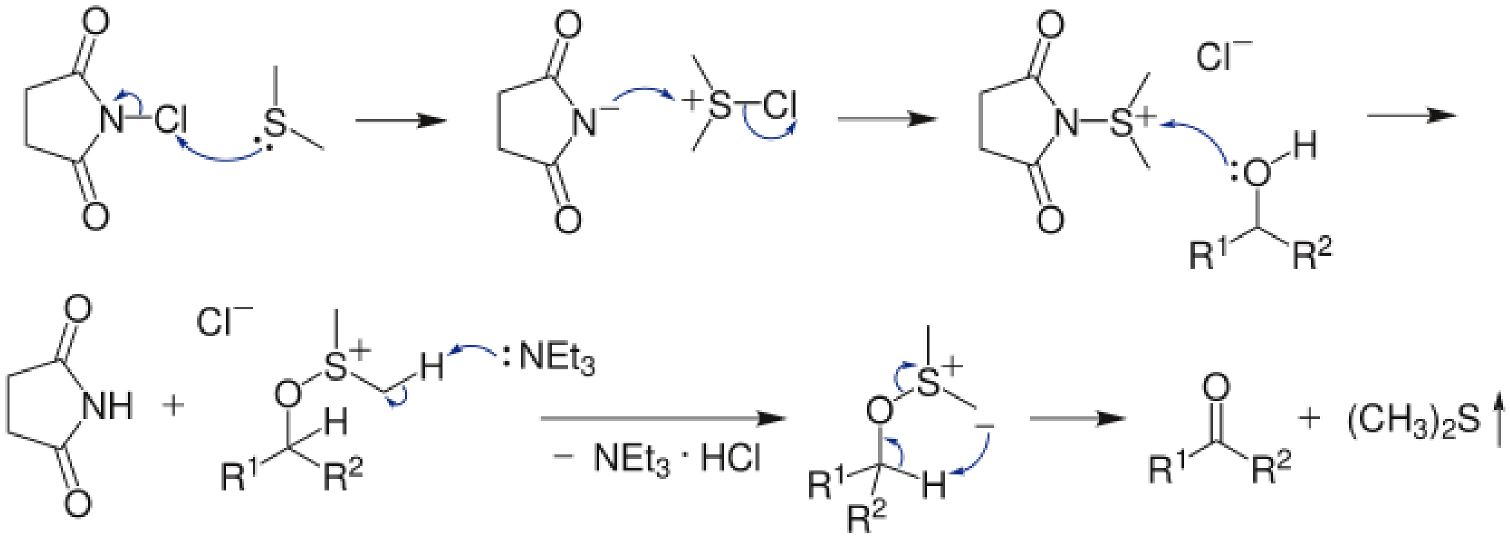
Corey-Kim Oxidation

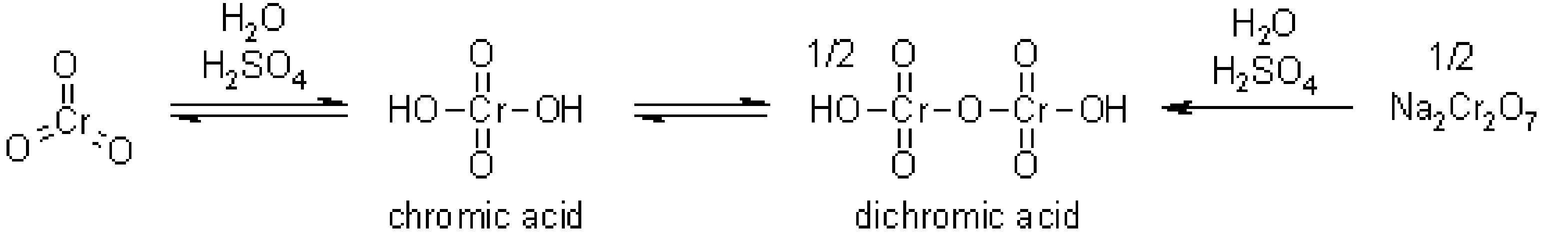




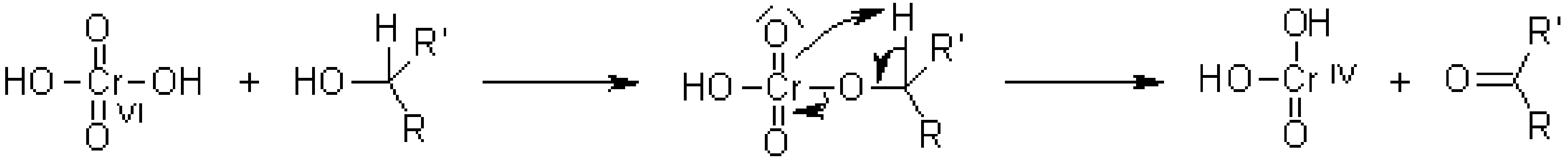
Dimethyl sulfide (Me_2S) is treated with N-chlorosuccinimide (NCS), resulting in formation of an "active DMSO" species that is used for the activation of the alcohol. Addition of triethylamine to the activated alcohol leads to its oxidation to aldehyde or ketone and generation of dimethyl sulfide. In variance with other alcohol oxidation using "activated DMSO," the reactive oxidizing species is not generated by reaction of DMSO with an electrophile. Rather, it is formed by oxidation of dimethyl sulfide with an oxidant (NCS).

Jones Oxidation

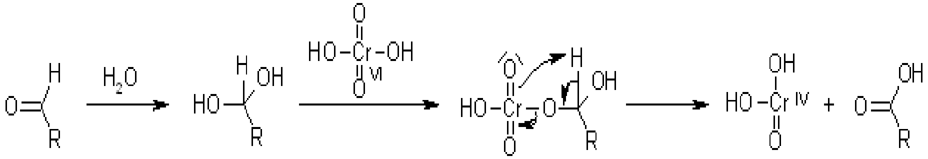
The Jones Reagent is a mixture of chromic trioxide or sodium dichromate in diluted sulfuric acid, which forms chromic acid in situ.



The alcohol and chromic acid form a chromate ester that either reacts intramolecularly or intermolecularly in the presence of a base (water) to yield the corresponding carbonyl compound:



Aldehydes that can form hydrates in the presence of water are further oxidized to carboxylic acids:



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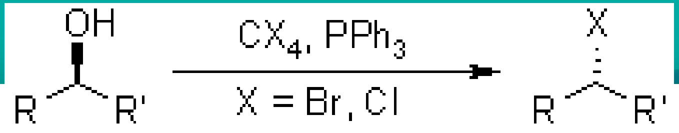
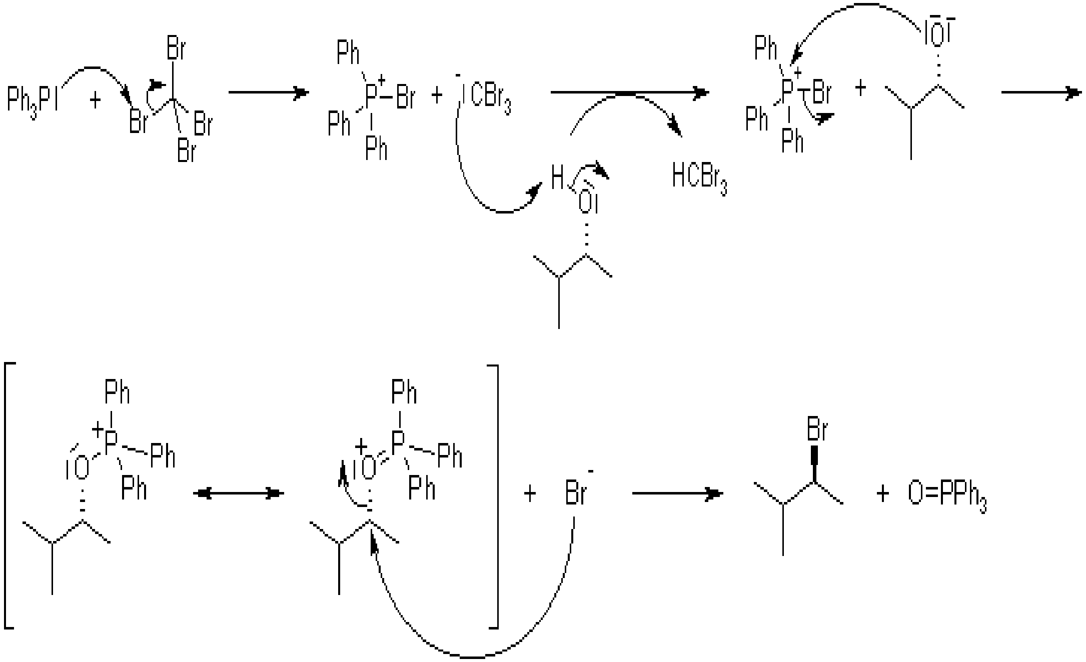
Appel Reaction



The reaction proceeds by activation of the triphenylphosphine by reaction with the tetrahalomethane, followed by attack of the alcohol oxygen at phosphorus to generate an oxyphosphonium intermediate. The oxygen is then transformed into a leaving group, and an S_N2 displacement by halide takes place, proceeding with inversion of configuration if the carbon is asymmetric.



Interesting Alcohols – Industrial applications

CH_3OH

- **Methanol (CH_3OH)** is also called wood alcohol, because it can be obtained by heating wood at high temperatures in the absence of air. Methanol is extremely toxic because of the oxidation products formed when it is metabolized in the liver (Section 12.13). Ingestion of as little as 15 mL causes blindness, and 100 mL causes death.

$(CH_3)_2CHOH$

- **2-Propanol [$(CH_3)_2CHOH$]** is the major component of rubbing alcohol. When rubbed on the skin it evaporates readily, producing a pleasant cooling sensation. Because it has weak antibacterial properties, 2-propanol is used to clean skin before minor surgery and to sterilize medical instruments.

$HOCH_2CH_2OH$

- **Ethylene glycol ($HOCH_2CH_2OH$)** is the major component of antifreeze. It is readily prepared from ethylene oxide by reactions discussed in Section 9.15. It is sweet tasting but toxic.

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Conclusion of The Chapter

- Conclusion #1
  - The fundamental of alcohols and ethers with its nomenclature were understandable.

- Conclusion #2
  - The fundamental of alcohols and ethers included its reactions involves were practically explained.

- Conclusion #3

  - The fundamental of alcohols and ethers were practically shown in industrial application especially in wine production and sterilization.

Co-author Information

Nurlin Abu Samah is an analytical chemistry lecturer since 2010 and currently she further her PhD study in Universitat Autonoma de Barcelona, Spain. She was graduated from Universiti Kebangsaan Malaysia for her Master of Science in Chemistry. During her undergraduate, she was studied in Universiti Sains Malaysia, Penang.

nurlin@ump.edu.my