Pinacol Pinacolone Rearrangement Chemistry Questions with Solutions

Q1. What is the name of the first molecular rearrangement identified by chemists?

(a) Beckmann rearrangement
(b) Curtius rearrangement
(c) Claisen rearrangement
(d) Pinacole pinacolone rearrangement

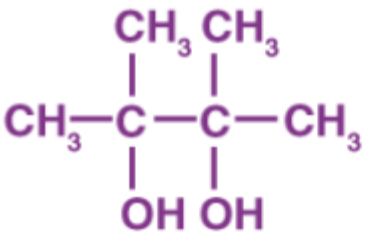
Answer: (d), Pinacol pinacolone rearrangement is the first molecular rearrangement identified by chemists.

Q2. What is a rearrangement reaction?

Answer: A rearrangement reaction is a comprehensive class of organic reactions where an organic substituent migrates from one atom to another in the same or different species, resulting in a structural isomer of the original molecule.
For example, alkene on heating with a strong acid yields isomeric alkene.

Q3. What is a pinacol?

Answer: Pinacol is a white solid organic diol compound. It consists of two hydroxy groups (-OH) on vicinal carbon atoms. The simplest member of this group is 2,3- dimethyl- 2,3- butanediol.

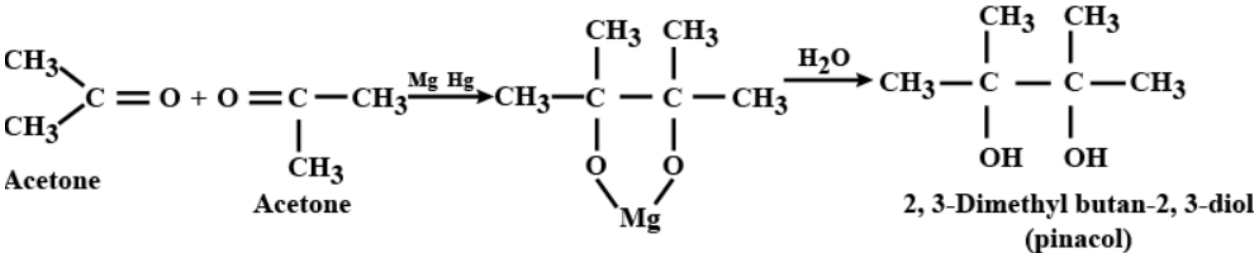


Pinacol

Structure of Pinacol:

Q4. How can you synthesise a pinacol?

Answer: Pinacol can be synthesised by a pinacol coupling reaction of acetone. Foremost we heat a ketone with the magnesium amalgam, which is then reduced with water.



Q5. Which intermediate carbocation is more stable in pinacol pinacolone rearrangement?

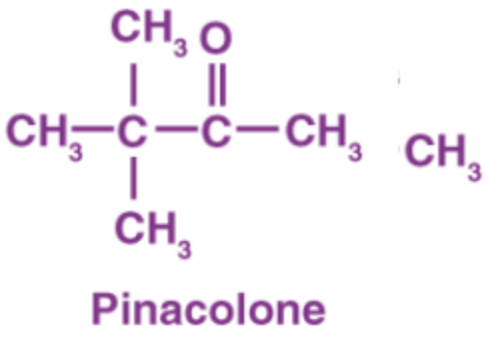
(a) 1° carbocation
(b) 2° carbocation
(c) 3° carbocation
(d) 4° carbocation

Answer: ©, 3° carbocation is more stable in pinacol pinacolone rearrangement.

Q6. What is a pinacolone?

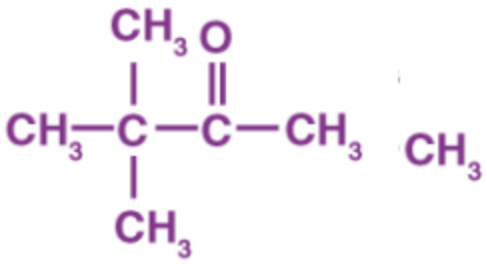
Answer: Pinacolone is a colourless liquid ketone with a molecular formula of $C_6H_{12}O$. It has a peppermint or camphor-like odour.

Structure of pinacolone:



Q7. What is the IUPAC name of the simplest pinacolone?

Answer: The IUPAC name of simplest pinacolone is 3,3-dimethyl-2-butanone.

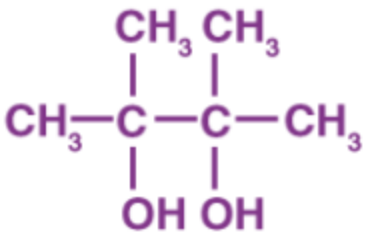


Pinacolone

Q8. What is pinacol pinacolone rearrangement?
Answer: The pinacol pinacolone rearrangement is an approach to convert a 1,2-diol to a carbonyl compound. It takes place under acidic conditions. The name of the reaction derives from the rearrangement of pinacol to pinacolone.

Q9. Who discovered the pinacol pinacolone rearrangement?
(a) Wilhelm Rudolph Fittig
(b) Louis Pasteur
(c) Alfred Nobel
(d) Marie Curie
Answer: (a), The pinacol pinacolone rearrangement was discovered by Wilhelm Rudolph Fittig.

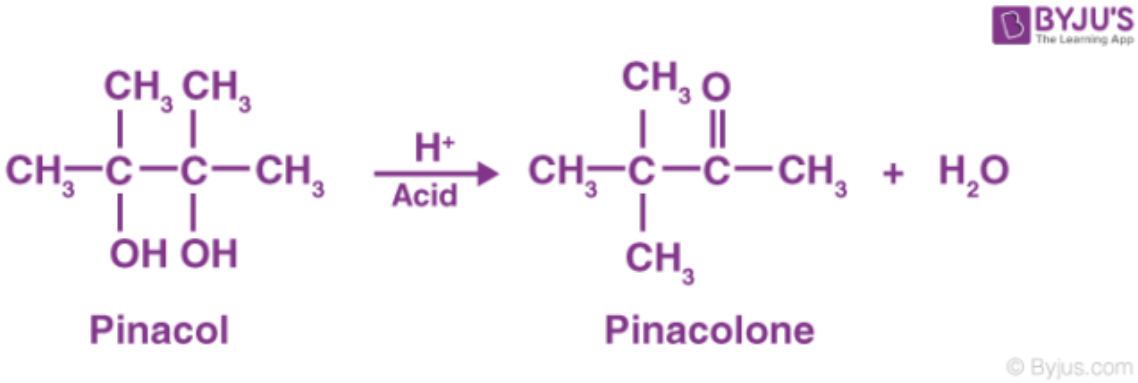
Q10. What is the IUPAC name of the simplest pinacol?
Answer: The IUPAC name of the simplest pinacol is 2,3- dimethyl- 2,3- butanediol.



Pinacol

Q11. How can you synthesise a pinacolone?

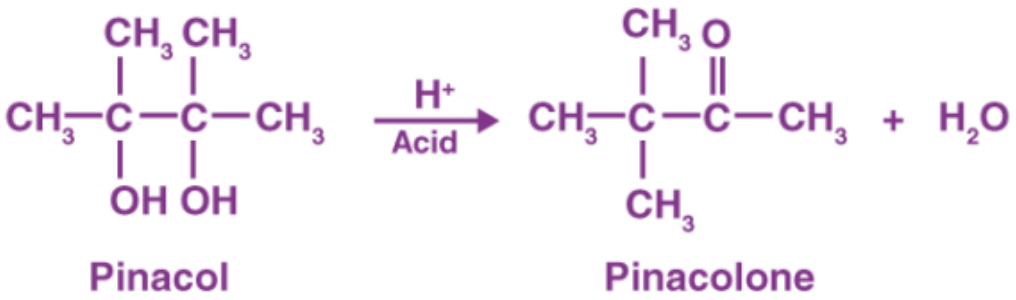
Answer: When pinacol is treated with dilute or moderately concentrated sulphuric acid, a rearrangement reaction occurs, leading to the formation of ketone called pinacolone. The rearrangement is known as pinacol-pinacolone or pinacolic rearrangement.



Q12. What are the applications of pinacolone?
Answer: Pinacolone plays an essential role in pharmaceutical industries.

- Pinacolone is useful in manufacturing pesticides, herbicides, fungicides and fertilisers.
- Pinacolone is useful in manufacturing stiripentol drugs.
- Pinacolone is useful in manufacturing cyanoguanidine drugs.
- Pinacolone is useful in the retrosynthetic analysis of vibunazole.

Q13. Explain pinacol pinacolone rearrangement in detail.
Answer: Pinacol is a white solid organic diol compound. It consists of two hydroxy groups (-OH) on vicinal carbon atoms. In contrast, Pinacolone is a colourless liquid ketone with a molecular formula of $C_6H_{12}O$. It has a peppermint or camphor-like odour.
The pinacol pinacolone rearrangement is an approach to convert a 1,2-diol (pinacol) to a carbonyl compound (pinacolone). It takes place under acidic conditions. The name of the reaction derives from the rearrangement of pinacol to pinacolone.
The reaction proceeds via the formation of a positively charged intermediate, and then the methyl group migrates from one carbon centre to another leading to the formation of pinacolone.

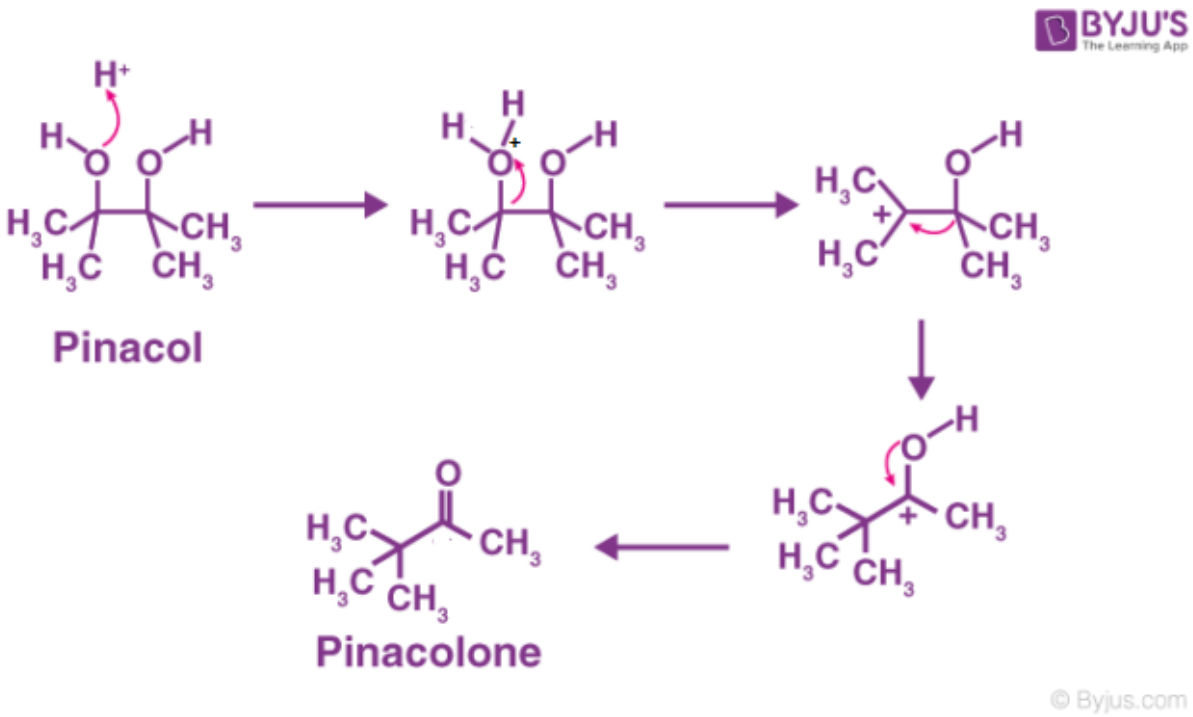


Q14. What is migratory aptitude?
Answer: The ease with which any group undergoes nucleophilic 1,2 shift is known as its migratory aptitude. All the groups do not migrate with equal ease in 1,2 nucleophilic rearrangement.

Q15. What is the order of migratory aptitude of different groups?
Answer: The ease with which any group undergoes nucleophilic 1,2 shift is known as its migratory aptitude. All the groups do not migrate with equal ease in 1,2 nucleophilic rearrangement.
The migratory aptitude of the phenyl group is more than hydrogen, which is more than the alkyl group. However, we can not apply it to unsymmetrical pinacol substrates. The most stable cation controls the reaction pathway in an unsymmetrical pinacol.

Practise Questions on Pinacol Pinacolone Rearrangement

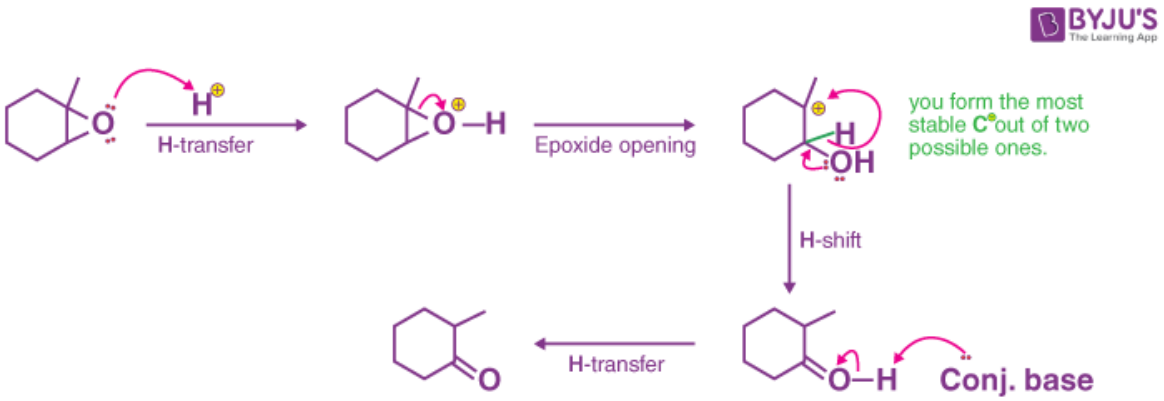
Q1. Explain the mechanism of pinacol pinacolone rearrangement?
Answer: The Pinacol Pinacolone rearrangement mechanism proceeds through four steps. Each of these steps is explained below.
Step 1: Protonation: Foremost, the oxygen atom being electron-rich, shares its pair of electrons with an electron-deficient proton.
Step 2: Loss of Water: Oxygen would try to retain its stability since the positive charge on oxygen is highly unstable. Thus leading to the elimination of water.
Step 3: Rearrangement of Carbocation: Rearrangement will occur since tertiary carbocation is more stable than secondary carbocation.
Step 4: Deprotonation: Oxygen, being electron-rich, will donate its electron pairs to an electron-deficient carbon atom and lose a proton.



Q2. Enlist the factors that affect the formation of pinacolone.
Answer: The factors that affect pinacolone formation are enlisted below.

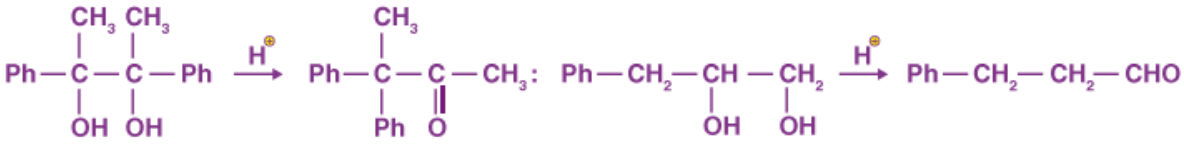
- Stability of carbocation
- Migratory Aptitude of the group
- Steric Hindrance

Q3. Explain pinacol-like rearrangement of the epoxide.
Answer: Some epoxides open their ring in an acidic medium forming carbocations. As these carbocations look exactly the same as carbocation in the pinacol rearrangement, they can undergo a similar mechanistic pattern leading to the formation of a carbonyl compound which is known as pinacol-like rearrangement of the epoxide.



Q4. What is semi-pinacol rearrangement?
Answer: Semi-pinacol rearrangement is just like pinacol pinacolone rearrangement. In it, the reactant specie is alcohols which have a very good leaving group at the carbon centre. The leaving groups may be an iodo group, diazo group or tosyl group. However, the best result is obtained with the tosyl group.

Q5. Predict the products of the pinacol rearrangement of 2,3- dipheny| - 2,3- butanediol and 3-phenyl -1.2- propanediol. Give the name of a simple chemical test that would show whether your prediction was correct or not.
Answer: The products of the pinacol rearrangement of 2,3- dipheny| - 2,3- butanediol and 3-phenyl -1.2- propanediol are shown below.



Iodoform test can show whether the prediction of the product is correct or not.