

IMPORTANT REARRANGEMENTS IN ORGANIC SYNTHESIS

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Abstract

Rearrangements occur to acquire stability in organic reactions. Wagner Meerwein Rearrangement, Pinacol Rearrangement, dienone phenol rearrangement, ring expansion, these all are the important rearrangement reaction. Wagner-Meerwein Rearrangement and Pinacol-Pinacolone Rearrangement reactions are described in simplified way here. Generally there occur a carbonium ion rearrangement to acquire stability in the reaction. Wagner-Meerwein and Pinacol-Pinacolone Rearrangements is the important rearrangement reactions in this kind.

Introduction

Organic reactions usually give normal products but in some cases products other than normal products are obtained. Those products are known as abnormal products or we can say it as 'rearranged products'. Sometimes rearranged products are the major product or exclusive. This is due to their extra stability than normal product. Rearrangement reactions occur to acquire stability. Rearrangement reaction generally includes migration of an alkyl group to electron deficient center like in Wagner Meerwein rearrangement, pinacol rearrangement, dienone phenol rearrangement. In these types of rearrangements migration of alkyl or any other substituent take place to electron deficient carbon center. Rearrangement reactions are those in which an atom or group migrate to another center within the molecule.

Wagner-Meerwein Rearrangement:

When alcohol (β carbon should have more than two aryl or alkyl group) is treated with acids, a rearranged product will be formed to acquire stability. This type of rearrangement is known as Wagner-Meerwein Rearrangement. The rearrangement which occur with elimination of water in the dehydration of an alcohol or removal of hydrogen halides in dehydrohalogenation of alkyl halide are known as "Wagner-Meerwein Rearrangement [1].

For example [2]- *Camphenilol* which is a natural product gives *Santene* which is a key component of sandal-wood oil in the presence of acid.

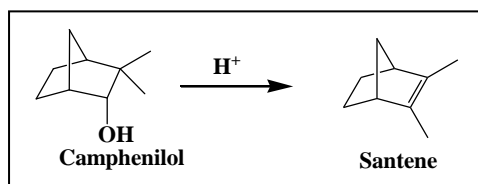


Figure 1

Here *Camphenilol* converted into *Santene*. In the reactant two methyl group are present on β carbon. But in the product those methyl group are present on different carbon. So it can be predicted here that, there is a rearrangement of methyl group take place. It can goes through a stepwise mechanism i.e. by a classical ion or by concerted mechanism i.e. by a non-classical ion [3].

Mechanism:

Here In this *Wagner-Meerwein rearrangement* (figure 2), alcoholic group of *Camphenilol* attacks on the acidic proton (step 1). By attacking the species will converted into an oxonium ion (step 2). Oxonium ion is an unstable species. So there is removal of water molecule and it will form secondary carbocation. As secondary carbocation is less stable than tertiary carbocation. So there is a migration of alkyl group take place from adjacent position of carbocation (Step 3). To stabilize this tertiary carbocation, there is an E1 elimination take place(Step 4). It will converted into the main product Santene. The firstly formed cation (In Step 2) cannot eliminate hydrogen ion because it will form the strained alkene i.e. bridgehead alkene which is not stable according to Bredt's rule(Step 5).

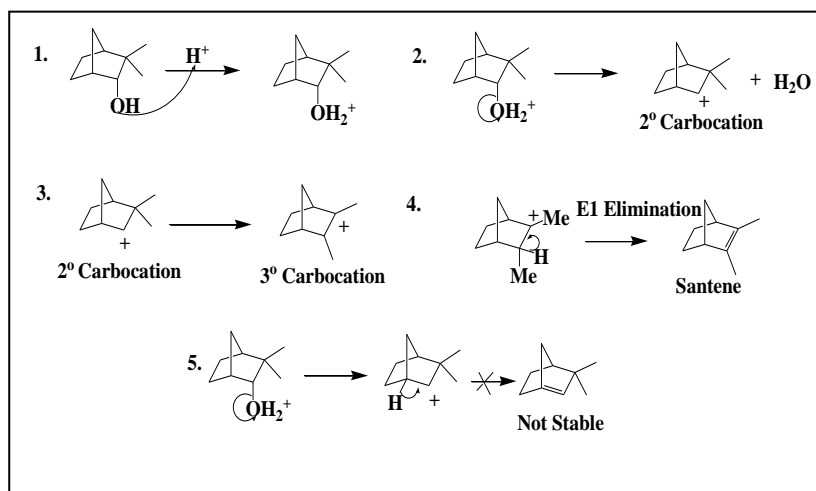


Figure 2

Wagner Meerwein rearrangement is a migration of alkyl group to a positive centre. Acid catalysed dehydration of *Isoborneol* will give *Camphene*(figure 3).

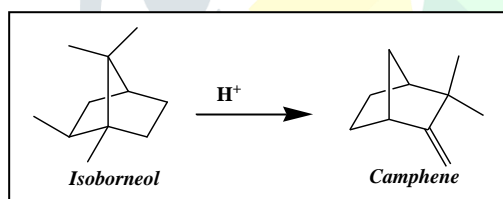


Figure 3

Mechanism:

Wagner-Meerwein rearrangement was first discovered in bicyclic terpenes. Here in the presence of acid Isoborneol converted into Camphene(figure 4). Alcoholic group in Isoborneol will abstract proton from acid and after that there is formation of carbocation. There is a migration of alkyl group take place to stabilize the Carbocation. By the loss of hydrogen ion from the adjacent carbon, it will converted into Camphene.

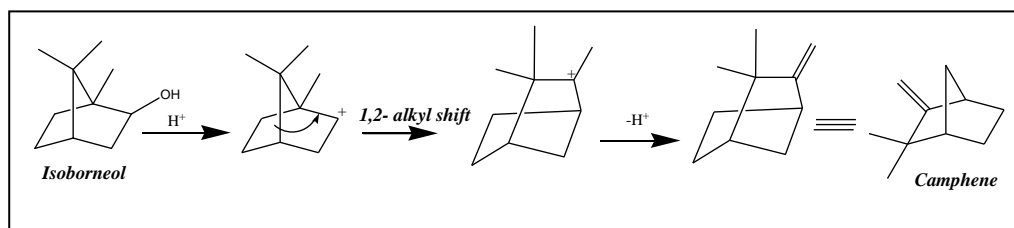
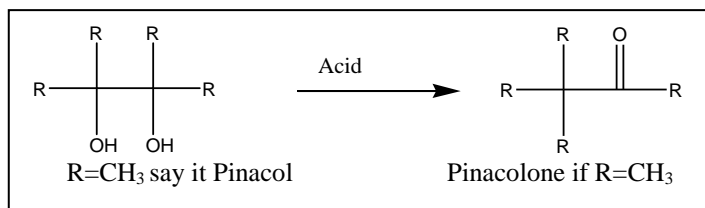


Figure 4

Pinacol Rearrangement:

Pinacol on treatment with acids rearranges to Pinacolone [6]. It is one of the earliest rearrangement reported by Rudolph Fittig in 1860 [7]. The driving force for this rearrangement is carbonyl formation and acquires stability. The treatment of 1,2-Diol with acids leads to this kind of rearrangement.



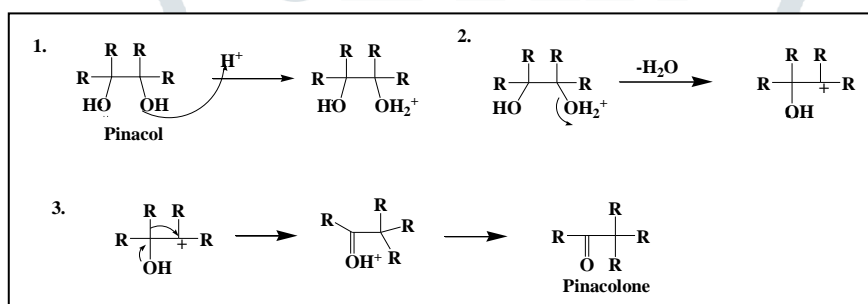
Mechanism:

It contains the following steps to form the carbonyl compound [8].

Pinacol rearrangement involves the two process:

- Loss of water molecule to form the carbonium ion.
- 1, 2- alkyl shift to form the Pinacolone.

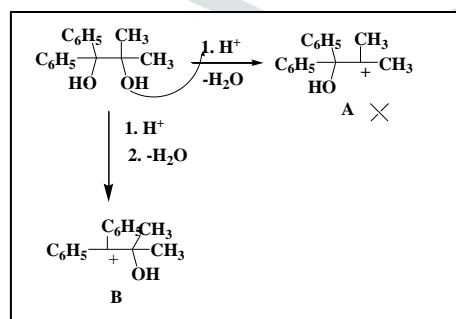
Pinacol in the presence of acid form oxonium ion which is very unstable (Step 1). It will lead to removal of water molecule from the species and formation of carbocation (Step 2). Further 1, 2- alkyl shift take place to acquire stability and there will be formation of *Pinacolone* (Step 3).



General observation:

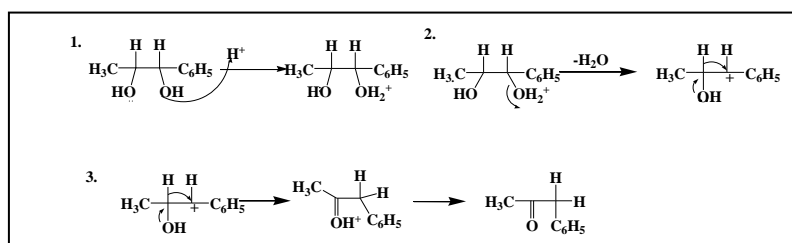
1. Relative Stability:

If the groups attach to Pinacol are different then the pathway of reaction depends on the stability of carbocation. The reaction will go through that pathway in which carbocation formation acquires stability.

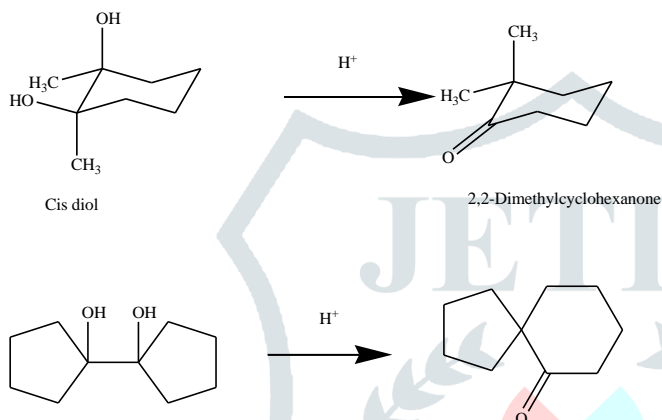


2. Migratory Aptitude:

It is not so easy to predict the migratory aptitude of the group. Generally phenyl group migrates over alkyl group and hydrogen group migrates over alkyl and phenyl.



Another examples of Pinacol Rearrangements are as [9][10]:



Conclusion

Rearrangement reactions governs thermodynamic stability in an organic reaction. The reactions in which migration takes place are generally referred as 'rearrangements'. Generally rearrangements reactions involves the carbocation rearrangement leads to thermodynamic stability in the reaction. Wagner-Meerwein rearrangement and Pinacol-Pinacolone rearrangement take place in the presence of acids. Generally Wagner-Meerwein rearrangement take place in alcohols leads to the formation of alkene. Pinacol rearrangement take place in diol leads to the formation of carbonyl compounds.

References

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