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CHEMISTRY (CH-608) : PAPER-VIII

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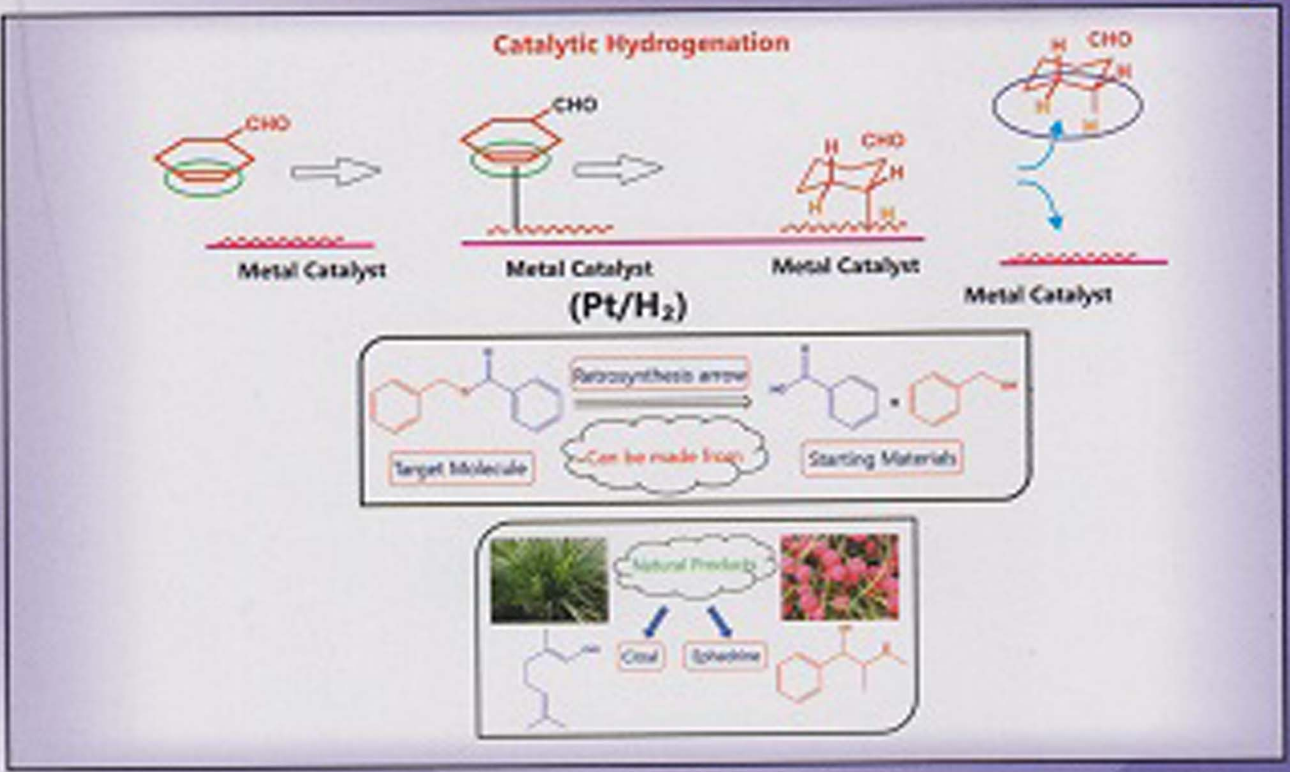

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T.Y.B.Sc. ORGANIC CHEMISTRY-III (S-VI) **ISBN 978-93-5451-379-4**
First Edition : February 2022

Published By :
NIRALI PRAKASHAN
Abhyudaya Pragati, 1312, Shivaji Nagar,
Off J.M. Road, Pune – 411005
Tel - (020) 25512336/37/39
Email : niralipune@pragationline.com

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Printed By :
YOGIRAJ PRINTERS AND BINDERS
Survey No. 10/1A, Ghule Industrial Estate
Nanded Gaon Road
Nanded, Pune - 411041

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Preface ...

The present book entitled **"Organic Chemistry-III** is written as per new revised syllabus prescribed for the Sixth Semester of T.Y.B.Sc. (Chemistry) with effect from June 2021-2022. This book is targeted mainly to the undergraduate students of Savitribai Phule Pune University, but will be found useful for the graduate students and Teachers of other universities also. The book is divided into four chapters. Each chapter begins with basic concepts containing theory, set of formulae and explanatory notes followed by a number of solved problems. Multiple choice questions, short, long answer type questions and unsolved problems are also given at the end of each topic.

The problems are judiciously selected and are given topic and section-wise. The approach is straight forward and step-by step solutions are elaborately provided. More importantly the relevant formulas used for solving the problems can be located in the beginning of each chapter. There are number of diagrams for illustration.

Chapter 1 in the book is devoted to Retrosynthetic Analysis and Applications. Chapter 2 is concerned with Organic Reaction Mechanism and Synthetic Applications. Chapter 3 is related to Reagents in Organic Synthesis. Chapter 4 is concerned with Natural Products. Multiple choice questions per topic are added in every topic to prepare for online examination in any pandemic situation and helpful for competitive exam. Short and long answer type questions are given which will give better idea of the question paper format and better understanding of concepts.

All precautions have been taken to avoid mistakes and misprint in the book. However, it is possible that some mistakes and misprints might have passed unnoticed. Such mistakes and misprint, if brought to our notice will be thankfully acknowledged.

We are thankful to Shri Jignesh Furia and staff of Nirali publication for publishing the book in attractive look. We have a pleasure to thank Mr. Akbar Shaikh for the bulk of typing, Mrs. Anjali Muley for figures drawing and Mr. Kiran Velankar for proof reading.

Suggestions to improve the quality of the book will be gladly accepted.

Authors

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Syllabus ...

1. RETROSYNTHETIC ANALYSIS AND APPLICATIONS (06 L)

Introduction. Different Terms used - Disconnection, Synthons, Synthetic Equivalence, FGI, TM, One Group Disconnection. Retrosynthesis and Synthesis of Target Molecules : Acetophenone, Crotonaldehyde, Cyclohexene, Benzylbenzoate, and Benzyl Diethyl Malonate.

2. ORGANIC REACTION MECHANISM AND SYNTHETIC APPLICATIONS (12 L)

1. Chemistry of Reactive Intermediates (Carbocations, Carbanions, Free Radicals, Carbenes, Nitrenes, Benzynes etc.).
2. Wolff Rearrangement (Step Up).
3. Hoffmann Rearrangement (Step Down).
4. Simmons-Smith Reaction.
5. Michael Reaction.
6. Wittig Reaction and McMurry Reaction.
7. Diels-Alder Reaction.
8. Functional Group Interconversions and Structural Problems using Chemical Reactions.

3. REAGENTS IN ORGANIC SYNTHESIS (10 L)

Reagents : Preparation and applications of following reagents :

Reducing Reagents : Lithium Aluminium Hydride ($LiAlH_4$), $NaBH_4$, DIBAL-H, $Li(tBuO)_3AlH$ and Raney Nickel.

Oxidizing Reagents : DMSO either with DCC or Ac_2O, Dess-Martin Reagent, Osmium Tetroxide, Selenium Dioxide (SeO_2), DDQ.

4. NATURAL PRODUCTS (08 L)

Terpenoids : Introduction. Isolation. Classification. Citral - Structure Determination using Chemical and Spectral Methods. Synthesis of Citral by Barbier and Bouveault synthesis.

Alkaloids : Introduction. Extraction. Purification. Some examples of Alkaloids and their Natural Resources. Ephedrine - Structure Determination using Chemical Methods. Synthesis of Ephedrine by Nagai.

■■■

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[A] TERPENOIDS

[B] ALKALOIDS

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Chapter **1**…

Retrosynthetic Analysis and Applications

Contents …

1.1 INTRODUCTION

The concept of retrosynthetic analysis was outlined and developed by American chemist Elias James Corey, for which he won the Nobel Prize in Chemistry in 1990. Prior to this method becoming the standard practice, there was no formalized approach to organic chemical synthesis, and many methods involved significant trial and error with available simple molecules. By starting with the target molecule, retrosynthesis allows chemists to work "in reverse", by breaking up the complex target structure to arrive at the simple precursors.

Retrosynthesis helps in understanding the complex nature of natural products and provides multiple possibilities of synthetic routes, from which the most cost-effective and environmentally friendly path can be selected. This technique is especially useful for planning the synthesis of organic compounds, which have much more complex structures.

Retrosynthetic analysis is a problem-solving technique for converting the structure of a target molecule to a sequence of gradually simpler structures along a pathway which ultimately leads to simple or commercially available starting materials for a chemical synthesis. So, the ultimate goal of Organic Synthesis is to assemble an organic compound/target molecule from readily available starting materials and reagents in the most efficient way.

1.2 DESIGN OF ORGANIC SYNTHESIS AND RETROSYNTHESIS

Any given organic compound can be synthesized by many different routes. A synthetic route is a sequence of reactions designed to convert commercially available starting materials into the desired substance.

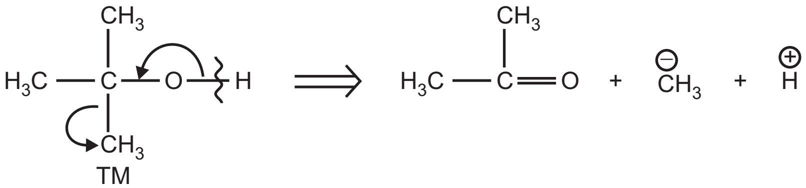
In practice, number of different routes for synthesis of given organic molecule are devised and compared to select the best one. In general, the best synthesis of a substance involves conversion of the cheapest and readily available starting materials into the desired product by the least number of steps and in the highest possible overall yield.

Formulation of synthesis of organic molecules usually involves a stepwise procedure of working backward from the structure of the final product to the structures of available starting materials. This is **retrosynthesis** ('retro' in Latin means "backward" or reverse). Possible reactions that might lead to the desired final product are considered first. Compounds needed for these final reactions are next examined and subjected to retrosynthesis. This procedure is repeated until simpler and easily available starting compounds are encountered. This process of converting an organic molecule into simpler precursor structures is **Retrosynthetic analysis.**

1.3 TERMS USED IN RETROSYNTHESIS

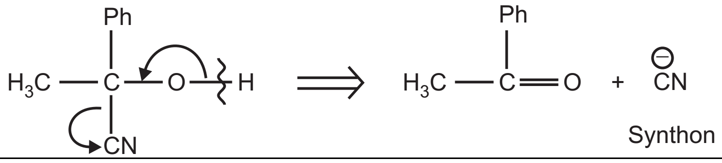
(i) Target Molecule (TM) : The molecule whose synthesis is being planned is termed as the target molecule and is usually written as (TM). e.g. If we want to synthesize tert-butyl alcohol $(CH_3)_3C–OH$ then tert-butyl alcohol is the target molecule.

(ii) Disconnection : It is an imaginary analytical operation, which breaks a bond and converts a molecule into a possible starting material or materials. Thus, it is the reverse of a chemical reaction. It is denoted by a symbol ⇒ and a curved line is drawn through the bond being broken. Thus,

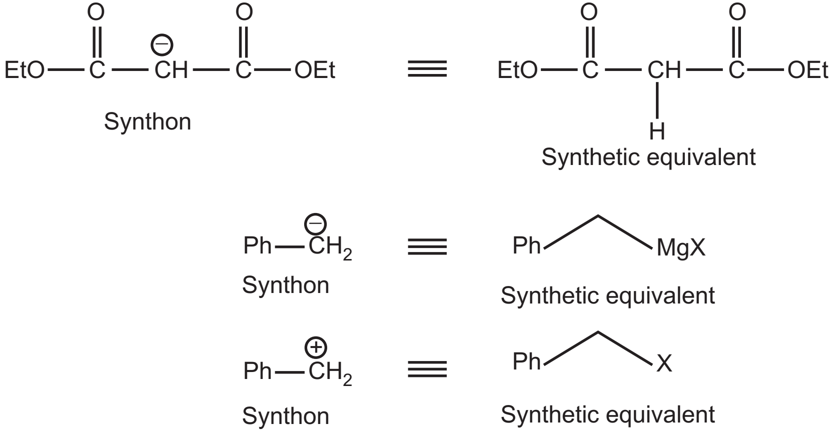


Sometimes it is also called as dislocation.

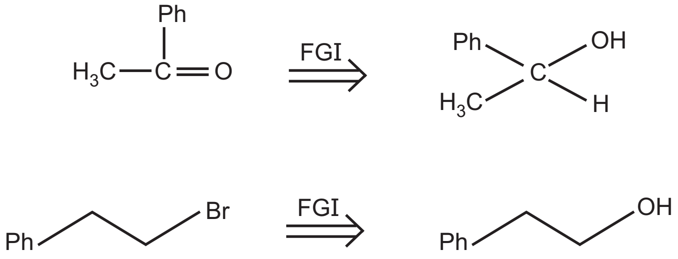
(iii) Synthon : It is an imaginary fragment, usually an ion which is produced by a disconnection. Synthon cannot itself be used because many times it is too unstable.



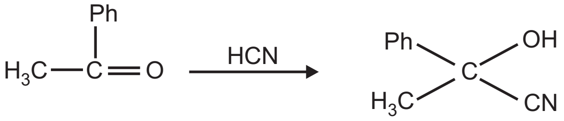
(iv) Synthetic equivalent : It is a reagent which can provide required synthons and carrying out the function of a synthon is called as synthetic equivalent.



(v) Functional Group Interconversion (FGI) : It is the operation of writing one functional group for another so that disconnection becomes possible. Again, it is the reverse of a chemical reaction. Here, FGI is denoted by the symbol ⇒ with FGI written over it. Thus,



(vi) Reagent : A compound which reacts to give an intermediate or target molecule in planned synthesis is known as reagent. For example, carbonyl compounds react with HCN or NaCN to give cyanohydrins.



1.4 ONE GROUP DISCONNECTIONS

The disconnection approach is mainly applicable to a carbon chain attached to any of the heteroatoms like O, N, or S. Here, a bond between carbon and heteroatom is good point to initiate a disconnection. This is called a 'One-group' C-X disconnection as we need to identify only one functional group in the target molecule like alcohol, ester, ether, amide etc. to make the disconnection.

A good disconnection should have

(i) A good reasonable mechanism which will give the required product.
(ii) Greatest possible simplification.
(iii) Recognizable and readily available starting materials.

On the basis of retrosynthetic analysis, actual synthetic scheme is designed. This involves following steps :

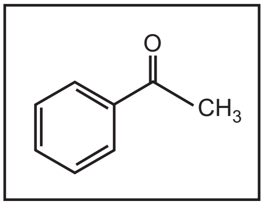
(i) Writing the actual synthetic plan with reagents and reaction conditions.
(ii) Steps in the synthetic sequence should be in a rational order.
(iii) Aspect of chemo selectivity should be considered so that unwanted reactions will not occur elsewhere in the molecule.
(iv) Protecting groups are used if necessary.
(v) The synthetic plan has to be modified in case of failure.

1.5 RETROSYNTHESIS AND SYNTHESIS OF TARGET MOLECULES

When a target molecule is given for retrosynthesis, the first step is to find out the functional group in the TM and then start the retrosynthetic analysis. Observe the synthons obtained and consider possible synthetic equivalents. If necessary, FGI is also considered.

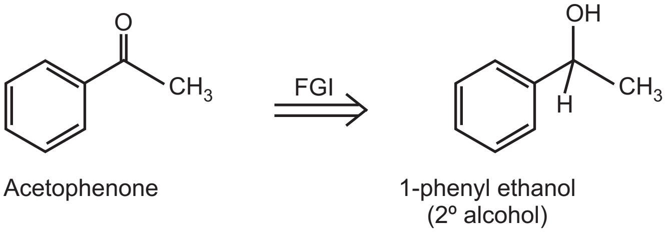
Consider the retrosynthesis and synthesis of the following target molecules.

1.5.1 Acetophenone

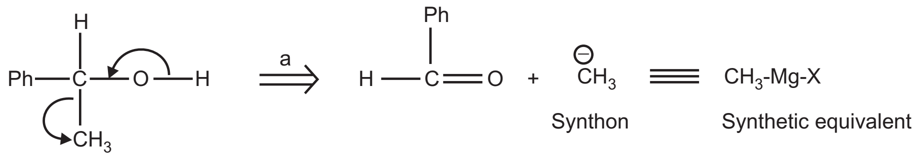


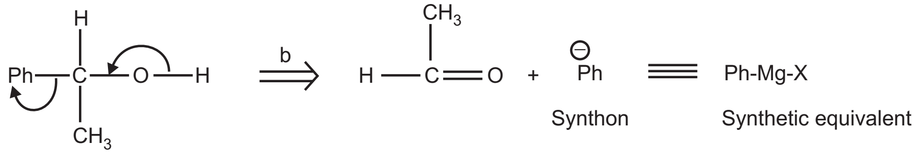
TM-1 Acetophenone

Retrosynthetic Analysis : The TM-1 is an aryl ketone and its retrosynthetic analysis suggests that it can be easily obtained by oxidation of secondary alcohol.



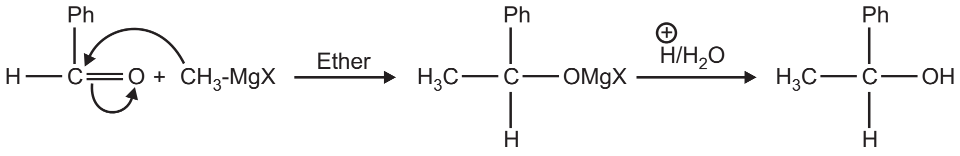
This secondary alcohol has one functional group and contains one alkyl and one aryl group. We know alcohols can be prepared by using Grignard's reagent and carbonyl compounds (aldehydes/ketones). Thus, we can have two different types of disconnection approach for retrosynthesis of TM-1.

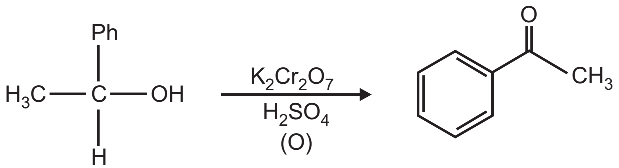




Synthesis :

(a)

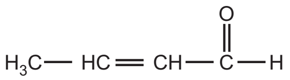




TM-1

Similarly, it can be synthesized by using route (b) also.

1.5.2 Crotonaldehyde

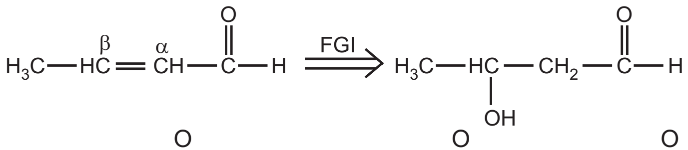


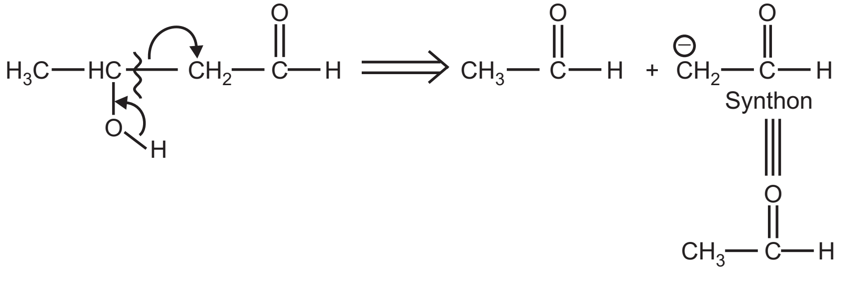
$$H_3C-HC=CH-\overset{O}{\overset{\|}{C}}-H$$

TM-2

The TM-2 is an α, β-unsaturated aldehyde. It is the dehydration product of aldol. Hence, the disconnection will need FGI.

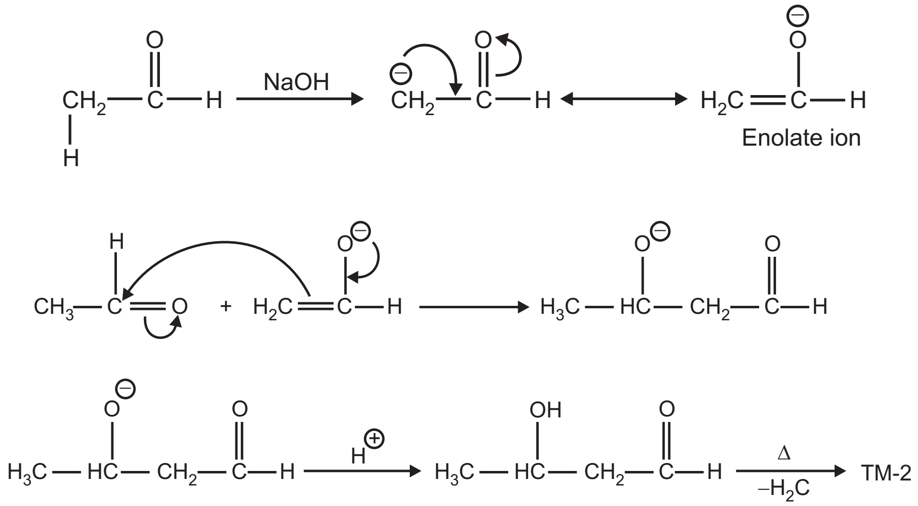
Retrosynthesis :



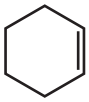


Thus, the TM-2 can be obtained by aldol condensation of acetaldehyde.

Synthesis :

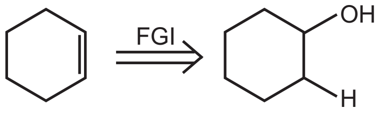


1.5.3 Cyclohexene

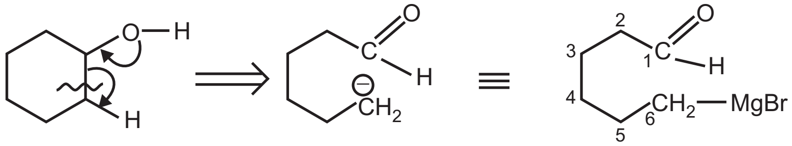


TM-3

Retrosynthesis : Cyclohexene is an unsaturated cyclic compound which is obtained by dehydration of corresponding secondary alcohol. The disconnection needs FGI.

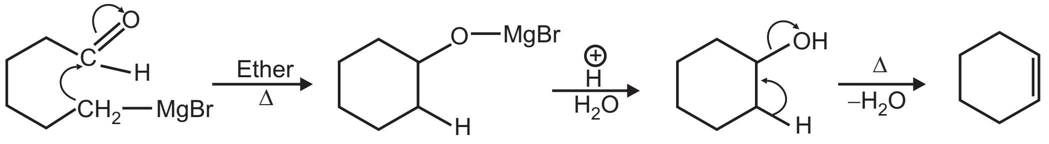


Cyclohexene Cyclohexanol (2° alc.)



Synthon Synthetic equivalent

Synthesis :



TM-3

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Publisher : Nirali Prakashan

ISBN : 9789354513794

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