COMPARATIVE STUDY OF SODIUM BOROHYDRIDE CATALYSED REDUCTION REATIONS: SYNTHESIS AND CHARACTERIZATION OF BENZYL ALCOHOL AND ANTIBACTERIAL ACTIVITY

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Abstract

The project of this thesis is the comparative study of sodium borohydride catalyzed reactions and to synthesize benzyl alcohol via the reduction reaction of Benzaldehyde. Then it will be check for antibacterial property using Disc Diffusion Method. The scope of the work is highly effective in medical field because of its Antibacterial property. In my work I have compared the sodium borohydride catalyzed reaction by taking ethyl acetoacetate for one reaction and Benzaldehyde for another reaction with sodium borohydride. Spectral (FT-IR) Method was used to establish the bond shifting of carbonyl group into hydroxyl group. The main objectives of the thesis Comparison sodium borohydride catalyzed reaction, Synthesis of benzyl alcohol, Detection of the compound by TLC, Characterization by FT-IR, Evaluation of anti-bacterial property.

INTRODUCTION

Sodium Borohydride Catalysed Reactions

The utilization of sodium borohydride as a reducer in chemistry has been known for over 40 years [1]. Its mild reducing properties leave considerable selectivity within the reduction of organic compounds. Aldehydes and ketones are, generally , readily converted into their corresponding alcohols within the presence of a spread of functional groups including nitro, acid , ester, amide, carbonate, carbamate, lactone, epoxide, nitrile, halide, alkene, and alkyne. The ready availability, high stability, mild reaction conditions, simple "work- up", and high yields contribute to the widespread use of sodium borohydride for the reduction of aldehydes and ketones[1]. The development of methods for the chemoselective reduction of the group (e.g., aldehydes vs. ketones) continues to be of interest in chemistry [2-7]. during this paper we report the complete results2 of our studies on the chemoselective reduction of varied sorts of aldehydes and ketones with sodium borohydride. The order of reactivity among carbonyl groups is conjugated enones< ketones < conjugated enals< aldehydes. generally , a group of 1 type are often selectively reduced within the presence of a group of a less reactive type. Sodium borohydride (as well as other complex metal hydrides) may be a "nucleophilic" reagent therein the speed of reduction is said to the electrophilicity of the group [1]. The difference in reactivity between aldehydes and ketones towards sodium borohydride can vary by quite three orders of magnitude [8].This suggests the likelihood of selective reduction. In recent years, an outsized number of reagents which will selectively reduce aldehydes within the presence of ketones are reported [2]. Generally, aldehydes are more vulnerable to reduction than ketones, for both electronic and steric reasons. The reagents "normally" employed for group reduction, like sodium borohydride, lithium aluminum hydride, and diborane, are too reactive under the standard conditions to usefully cash in of the inherent difference in reactivity between aldehydes and ketones. the bulk of the reported methods achieve chemoselectivity through the modification ofthe ligands on the hydride donor so as to attenuate reactivity. This approach has resulted within the development of an outsized number of latest reagents for reduction. A conceptually different strategy would involve the modification of the reaction conditions to attenuate reactivity. Using this strategy, we've found that sodium borohydride alone provides chemoselectivity like the simplest of the reported methods. Advantages of UsingSodiumborohydrideAs a Catalyst,We find that the reduction of aldehydes and ketones by sodium borohydride follows an equivalent pattern like lithium aluminum hydride. The reactions occur rapidly at temperature in most cases, although occasionally heating is required and therefore the corresponding alcohols are formed in comparable yields. Unsaturated aldehydes and ketones, in three examples studied, furnish the unsaturated alcohols. The experimental techniques are quite different, for whereas lithium aluminum hydride must be utilized in non- hydroxylic solvents and must be rigorously shielded from moisture, the reductions with sodium borohydride could also be administered in water or methanol solution. This represents a gain in convenience and economy, and suggests a possible further advantage within the reduction of ether-insoluble compounds, like the sugars, that lithium aluminum hydride is unsuitable.

However, a limitation is imposed by the problem hydrolyzable nature of the intermediate alkyl borates in certain cases. The n-alkyl borates are very rapidly hydrolyzed and thus, where the reduction of an aliphatic aldehyde is administered in an solution of sodium borohydride, hydrolysis of the intermediate boron ester takes place concurrently. Other types undergo hydrolysis less readily [9] and within the reduction of aromatic aldehydes and a few of the ketones studied subsequent heating with alkali were necessary so as to liberate the alcohols. Stable complexes with boric acid are formed by anhydroxyl acids [10] and by many polyhydroxy compounds' [11] and therefore the isolation of such products present a drag which has not been satisfactorily solved. Thus acid and glucose, although evidently reduced by sodium borohydride, form complexes from which boron-free reduction products couldn't be isolated.

The reduction of the carboxylate group of acids by sodium borohydride doesn't occur to any appreciable extent under the conditions described above for the reduction of carbonyl groups. Moreover, these conditions aren't appropriate, due to the alkaline medium, for the reduction of easily hydrolysable derivatives of carboxylic acids. Acid chlorides could also be successfully reduced however by employing a suspension of sodium borohydride in dioxane or other inert solvent. The reaction is vigorous with aliphatic acid chlorides but aromatic acid chlorides require heating. Simple acid chlorides are converted to the alcohols in good yields but the results for unsaturated and other polyfunctional acid chlorides are less clean- cut.the reaction mechanism of reduction of carbonyl compound is given below:

Under conditions favorable for the reduction of acid chlorides, sodium borohydride is without action on the esters and nitriles tested. Acids and acyl anhydrides show only slight reduction on pro- longed heating of the mixtures. it's with reference to these types that the milder reducing of sodium borohydride, as compared with lithium aluminum hydride, is most clearly evident. The lower reactivity of the borohydride is advantageous in permitting the selective reduction of acid chloride or carbonyl groups within the presence of other functional groups which, with lithium aluminium hydride, would even be reduced. The lower reactivity of the disadvantageous in permitting the selective reduction of acid chloride or carbonyl groups within the presence of other Functional groups which, with lithium aluminium hydride, would also reduced functional groups which, with lithium aluminium hydride, would even be reduced.

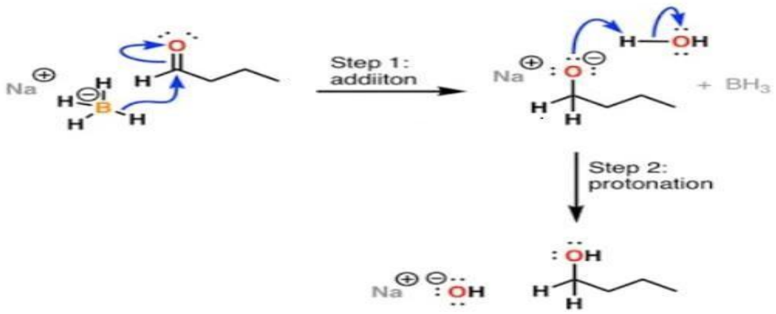


Fig.1.1 Reaction Mechanism for Reduction of Carbonyl Compound.

Reduction Of Aldehydes With Sodium borohydride

Reduction of aldehydes into corresponding alcohols is a crucial transformation in organic synthesis. Conventionally, aldehyde reduction is typically through with flammable solvents like ethanol, 2-propanol, and methanol, albeit it's unstable in either methanol or ethanol due to solvolysis[12].To only mention few examples, several reducing agents like borohydride derivatives [13-16],organohydride[17],and Ni- nanoparticles [18] are recently reported.Reaction mechanism for reduction of Benzaldehyde is shown in figure 1.2. Sodium borohydride is usually employed since this reagent is low priced, easy to handle, and environmentally benign reducer that quickly reduce ketones, acid chlorides, and aldehydes [12]. However, this traditional procedure has disadvantage for practical utility i.e. employing a great deal of solvent, for a particular condition consuming tons of energy for reflux, and requiring long reaction times [13].

From ecological point of view, demonstrating reactions without the utilization of solvent aren't only interest for minimizing waste and energy usage, but in various cases, also offer significant synthetic advantages in term of simplicity, selectivity and yield [19].Solvent-free organic reaction are often administered at temperature . additionally , it are often accelerated by grinding with mortar and pestle, heating, shaking, irradiating with microwaves or ultrasounds.

An example for aldehydes reduction with sodium borohydride under solvent free condition was reported [14]. The reduction of aldehydes with NaBH4 activated by solid acids was performed by grinding employing a mortar and pestle. A limitation in grinding with mortar and pestle is that tiny amount of samples could be essentially lost when ground into the surface of the mortar. This results in poor yields since sample recovery is difficult. additionally , the energy couldn't be quantified since it's conducted by hand. Thus, strong and weak grinding could affect the response time and therefore the obtained product. As there's an increasing need for fine chemicals synthesis utilizing ‘‘green’’ methods, ultrasound has gained significance attention as a clean and valuable tool in accelerating chemical reactions in comparison to standard methods and thus, within the past three decades an incredible number of organic reactions are reported using this technology [19].Ultrasound irradiation have some important advantages not only accelerating a reaction but also providing beneficial in other ways like substantial decreases of response time , improved yield, increased selectivity, avoided forcing conditions like hightemperature and high , lower costs and ease in handling and processing, and reduced the amount of steps during a reaction [20-21].Thus, during this work, we present simple, efficient, and rapid reduction of aldehydes with sodium borohydride into alcohols under ultrasonic condition.

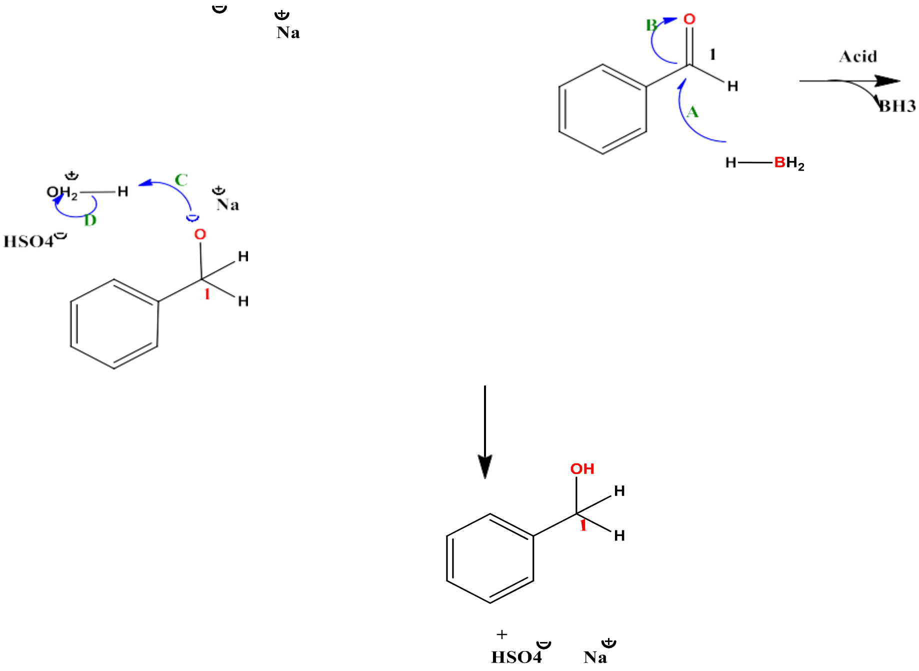


Fig.1.2 Reaction mechanism for reduction of Benzaldehyde.

Different Type Of Modification To Control The Reducing power Of $NaBH_4$

Controllingthe reducingpower of NaBH4 has been achieved by differing types of modifications, such as the use of hydrides with bulky substituent, i.e. electron-withdrawing or electron-releasing groups, the change of the sodium cation to transition metal cations in the preparationofmodifiedreducingreagents, the use of quaternary ammonium and phosphoniumtetrahydroborates, theuseofLewis acids andmixedsolvent systems, utilization of polymeric supports and anion exchange resin, performing the reduction reactions with sodium borohydride under unconventional energy sources like microwave and ultrasound irradiations.

Propertiesof Benzyl Alcohol

- Benzyl alcohol is an compound with the formula C6H5OH.The IUPAC name of this compound is phenyl methanol. At temperature Benzyl alcohol exists as a colourless liquid that features a mildly aromatic smell.
- This compound is extremely soluble in water.it forms miscible mixtures with ether and other alcohols.
- Many plants are known to naturally produce benzyl alcohol.the essential oils are extracted from jasmine ,ylang-ylang ,and hycinth contain some amount of benzyl alcohol
- The reaction between carboxlylic acids and benzyl alcohol results in the formation of esters
- This compound undergoes a ritter reaction with acrylonitrile to yield N-benzyl acrylamide.
- When deprtonated it yields a benzylate anion
- It may be a precursor to many esters
- In addition to Antiseptic properties, benzyl alcohol with a degree of 10% possess weak local anesthetic and antipruritic activity.

- Benzyl alcohol may be a anti microbial agent.It is utilized in the manufacture of soaps, shampoos, and skin lotions due to its antifungal and anti microbial properties .The role of protein and RNA synthesis within the bacterial action was also determined. The mechanism of action these compounds is said to their lipophilia.lethel effect of Benzyl alcohol and phenethyl alcohol stops when protein synthesis inhibited.

- Benzyl alcohol is employed as an antimicrobial preservative. it's bacteriostatic mainly against Gram positive organisms and a few fungi. it's utilized in a variety of pharmaceutical preparations in concentrations of up to twenty .conentrations of fifty or more are employed when it's used as a solubiliser.
- Benzyl alcohol is employed as a preservative in foods and cosmetics.
- It is employed as a disinfectant at a degree of 10%.

EXPERIMENTAL METHODS

The 1H & 13C NMR spectra were recorded on a BRUKER 400 MHz NMR spectrometer using DMSO as solvent. the space temperature Fourier transform infrared spectra of sodium borohydride sodium were recorded within the range 400-4000 cm-1 at a resolution of ±5 cm-1 employing a BRUKER spectrophotometer equipped with a LiTaO3 detector, a KBr beam splitter, a He-Ne laser source and a boxcar atomization used for 250 averaged interferograms collected for both the sample and thus the background. High performance liquid chromatography. an appropriate HPLC instrument equipped with UV detector. Column using Themoquest Hypersil ODS 150 X 4.6mm, 5µm (or) equivalent. The quantum chemical computations of this heterodimer were employed with density functional theory (DFT) method by using Gaussian 09 [11] program package with basis set of 6-311++G (d,p). The SCXRD crystallographic information file (CIF) file of sodium borohydride was used as an input.

SPECTRAL METHODS

Infrared Spectroscopy

Most of the spectra give sufficient information about the structure of the compound. The Infra- Red spectrum is one among the spectra. Unlike UV spectrum which comprises of relatively few peaks, IR technique provides a spectrum containing an outsized number of absorption bands from which a wealth of data are often derived about the structure of an compound . The absorption of Infra-Red radiations causes the varied bands during a molecule to stretch and bend with reference to each other . The IR spectroscopy is widely used as a characterization technique for metal complexes. the essential theory involved is that the stretching modes of the ligands changes upon complexation thanks to weakening or strengthening of the bonds involved within the bond formation leading to subsequent change within the position of the bands appearing within the IR Spectrum. The changes within the structural features of the ligands are observed as changes in bands observed, mainly within the fingerprint region (4000-400 cm-1). The bands thanks to the metal ligand bonds are mainly observed within the far IR region (600-100 cm-1).

FT –IR Analysis (Fourier-Transform Infrared spectrometers)

Shimadzu IR tracer -100 Fourier transform infrared spectrophotometer, was used for the present study. For FT-IR measurements, the Ag nanoparticles solution was centrifuged at 10,000 rpm for 30 min. The pellet was washed 3 times with 20 ml of de-ionized water to urge obviate the free proteins / enzymes that aren't capping the silver nanoparticles. The samples were dried and grinded with KBr pellets and analyzed on a Shimadzu FT-IR Affinity model within the diffuse reflectance mode operating at a resolution of 4 cm-1.

- Sample preparation

Instructions vary counting on the sort of sample .Liquid samples observe contact with the Germanium crystal and don't require any special treatment. Solid samples, on the opposite hand, don't observe contact. A Pressure Tower on the ATR accessory is employed to squeeze solid samples against the crystal surface liquid samples. Apply 1-2 drops of liquid to the middle of the Germanium crystal with a disposable pipette (avoid the contact between the pipette and crystal).Allow the liquid to opened up to form a skinny film (it is ok if the liquid spreads across the whole crystal).Leave the pressure tower tilted back. Solid samples: Place solids on the middle of the Germanium crystal with a micro spatula (avoid contact between the spatula and crystal).Carefully bring the pressure tower upright by coitus interruptus the silver release knob and tilting the Tower forward (do not let the tip fall on the crystal).Use spatula to position the sample underneath the Tower's pressure tip. Rotate the knob on top of the Tower clockwise in order that the pressure tip presses your sample on to the Germanium crystal. Stop rotating the knob once you hear a "click". These "clicks" are created by an error –clutch safety mechanism that forestalls the tip from applying an excessive amount of pressure to crystal.

- Working principles of Fourier-transform Spectrometers

Turn on the spectrometer by pressing the facility switch (remember the instrument should be connected to an influence source).Turn on the pc and monitor attached and log into your GT account. Once Windows has completed the PC start-up process, double click on the [IR solution] icon on the desktop to start out the FT –IR software. When available, the instrument stores the background spectrum obtained from the newest use. Since it's best to get a background spectrum just before obtaining your sample spectrum, it's advisable to click [No] on the above message window. The instrument has been preconfigured to initialize as soon because the IR solution software starts. Initialization could also be verified on the status window displayed on rock bottom left corner of the IR solution. However, should this not occur, you'll manually initialize the instrument by clicking the measurement menu then choosing Reinitialize.

Again, the status window should display the INIT success message upon a successful initialization. If a sampling accessory is in situ , the spectrometer may have to perform an automatic adjustment, which restscertain parameters to accommodate the change within the optical path. The instrument will take a couple of minutes to perform the auto-adjustment, and a progress bar are going to be displayed Check to form sure that each one messages shown for a successful initialization are present. Normally, the scan parameters needn't be changed, but if necessary, it are often found while on the measure tab, on rock bottom right corner of the screen. It consists of 5 tabs, namely: Data, More, Files and Advanced

Typical operation involves the subsequent steps:

- Setup spectrometer configuration
- Collect background spectrum

- Apply sample to ATR accessory
- Collect sample spectrum
- Find major peaks
- Print spectrum
- Clear sample spectrum and report
- Clean ATR accessory

REDUCTION REACTION OF CARBONYL COMPOUNDS WITH SODIUM BOROHYDRIDE

Reduction of Benzaldehyde with Sodium borohydride Chemicals required:
Benzaldehyde = 500mg Sodium borohydride = 187.148mg
Ethanol = 5ml

Proedure:

500mg of benzaldehydewas accurately weighed during a weighing machine then transferred into a 50ml round bottom flask containing 5mL ethanol. Then 187.148mg of sodium borohydride was added into it. This mixture was stirred for quarter-hour employing a stirrer at temperature until TLC showed complete disappearance of the starting material. The reaction was stopped by adding solution of acid drop wise, while stirring, to quench the reaction (The addition of HCL will cause frothing and release H2 gas). The organic layer and aqueous layer were separated with ester then the organic layer was combined with sodium sulfate crystal and kept to calm down . After few minutessodium sulphate was filtered off. Then the solvent was evaporated employing a rotary evaporator with a water bath at temperature .

Fig. 4.2 Synthesis of Benzyl Alcohol.

Reduction of Ethyl acetoacetate With Sodium borohydride

Chemicals Required:

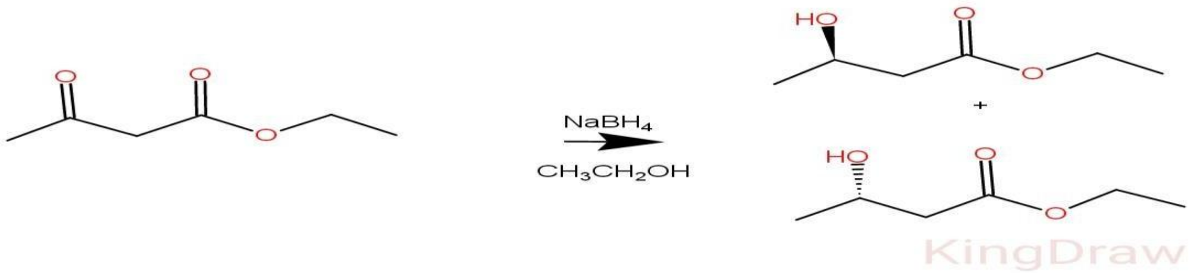
Ethyl acetoacetate = 500mg

Sodium borohydride = 152.610mg

Ethanol = 5 ml

Proccedure:

500mg of ethyl acetoacetate was accurately weighed in a weighing balance and then transferred into a 50ml round bottom flask. 5ml of ethanol is added into it. Then 152.610mg of sodium borohydride was added into it. This mixture was stirrered for 15 minutes using a stirrer at room temperature until TLC showed complete disappearance of the starting material. The reaction was stopped by adding aqueous solution of Hydrochloric acid drop wise, while stirring, to quench the reaction (The addition of HCL will cause frothing and release H_2gas). The organic layer and aqueous layer were separated with Ethyl acetate and then the organic layer was combined with sodium sulphate crystal and kept to settle down. After few minutessodium sulphate was filtered off. Then the solvent was evaporated using a rotary evaporator with a water bath at room temperature.



Ethyl acetoacetate Racemic mixture

Fig.4.3 Synthesis of Racemic Mixture of Ethyl S-3-Hydroxy Butanoate and Ethyl R-3-HydroxyButanoate

Antibacterial activity

Disc diffusion method was used for testing antibacterial activity. Esherihiacoil (E coil) was used in this study. A stock solution of the extract was prepared by dissolving 10mg/mlof Dimethyl sulfoxide(DMSO) to produce a final concentration of1 mg/ml .The stock solution was then loaded to sterile disc at desired concentration. Cephalosporinwas used as the positive control and DMSO serve as the negative control.The disc was allowed to air dry and place over the agar plate previously swabbed with test pathogen and incubated at 37^0c and zone of inhibition was measuredthe schematic representation is given below:

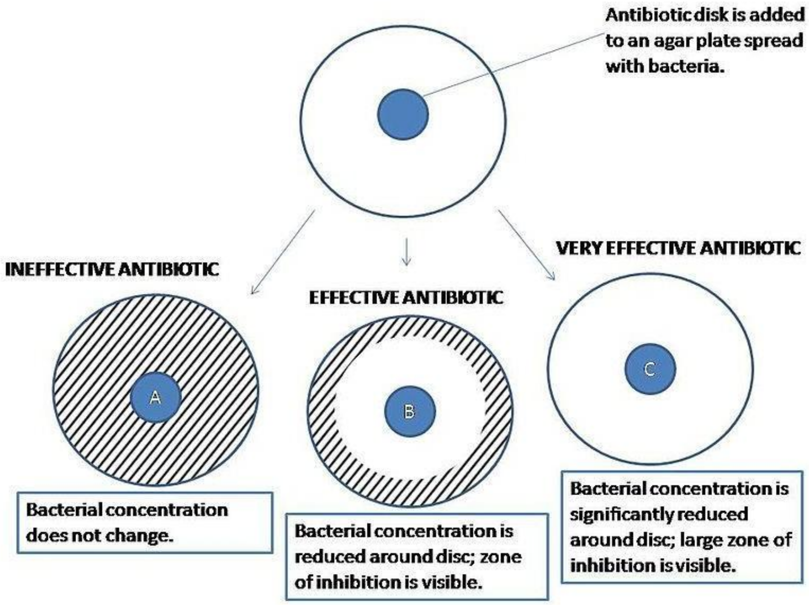


Fig.4.4 Schematic RepresentationofDisc Diffusion

RESULTS AND DISCUSSION

5.1 ANALYTICAL AND SPECTRAL (FT-IR) CHARACTERISATION

5. 1.1 Reduction of Benzaldehyde with $NaBH_4$

Thin Layer Chromatography (TLC)

Analytical TLC was performed on pre-coated aluminium sheets of silica (60F254), and visualized using $KMnO_4$. The reaction was checked by TLC until completion using Hexane-Ethyl acetate mixture in 4:1 ratio. A single spot on the TLC sheet confirm the formation of the product.R_f value was calculated. It was obtained about 0.66 c m^{-1}.

$$\mathbf{R_f} = \frac{\text{Distance traveled by sample}}{\text{Distance traveled by solvent}}$$

$$\mathbf{R_f} = 2.6 / 3.9$$

$$= 0.66 cm^{-1}$$

Fig.5.1TLC plate for Benzyl Alcohol before Column Chromatography.

COLUMN CHROMATIOGRAPHY

Column chromatography was carried out for the purification of the product.After performing column chromatography, the total number of fractions was about ‘15’.TLC was carried out for each fraction. While checking TLC, Fraction number 10-13 shows single spot of the product. After that these fractions were combined together and checked for TLC. A single spot on the TLC sheet was obtained and confirmed the purity of the synthesized sample. TLC sheet of the compound is shown in the figure.

Fig.5.2 TLCplate of Benzyl Alcohol after Column Chromatography.

Reduction of Ethyl acetoacetate with $NaBH_4$

Both the Analytical techniques Column and Thin layer chromatography was carried out. Many spots were obtained on the TLC sheet, which indicated the decomposition of the product and also the components in the fractions of the column chromatography were too numerous, it was very hard to isolate them.

Fig.5.3 TLC plate for racemic mixture of ethyl S-3-hydroxy butanoate and ethyl R-3-hydroxy butanoate before column chromatography.

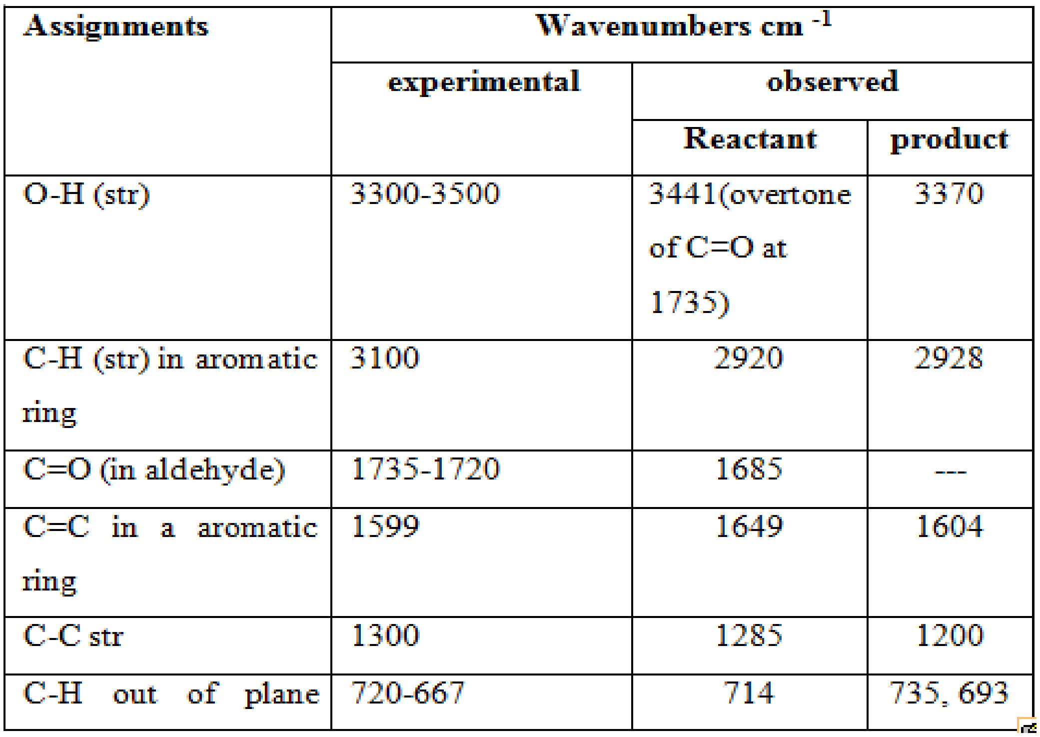
Fig .5.4TLC plate for racemic mixture of ethyl S-3-hydroxy butanoate and ethyl R-3-hydroxy butanoate after column chromatography

COMPARATIVE STUDY OF THE REACTIONS

The comparative study of sodium borohydride catalysed reactions by considering the reduction of Ethyl acetoacetate and Benzaldehyde. After the experimental study of those two reactions, it had been clearly evident that reduction of Ethyl acetoacetate with sodium borohydride may be a temperature sensitive reaction. So its product was unstable and decomposed thanks to the temperature effects. But the reduction of benzaldehyde with sodium borohydride gave a stable product with good yield. The conclusion of the study is that thermal stability of sodium borohydride catalyzed reduction reaction of Ethyl acetoacetate is extremely much less than that of Benzaldehyde.SpectralCharacterization:

FT-IR Spectral Studies

In order to review the bond shifting of group into hydroxyl , FT-IR Spectrum for both Benzaldehyde reactant and Benzyl alcohol product was separately taken. The IR spectrum of the compound showed characteristic band at 3441 &3370 cm-1, Aromatic ring appeared at 2928 cm-1, group appeared at 1685 cm-1, C=C showed band at 1649 &1604 cm-1,C-C stretching at 1200 cm-1 and C-H at 735 & 693 cm-1.Figure 5.4. represents the tabular column of bond shifting for the reactants and merchandise .



Assignments	**Wavenumbers cm $^{-1}$**		
	experimental	**observed**	
		Reactant	**product**
O-H (str)	3300-3500	3441(overtone of C=O at 1735)	3370
C-H (str) in aromatic ring	3100	2920	2928
C=O (in aldehyde)	1735-1720	1685	---
C=C in a aromatic ring	1599	1649	1604
C-C str	1300	1285	1200
C-H out of plane	720-667	714	735, 693

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Table No.5.1 Tabular column of bond shifting for the product and reactant

The FT-IR spectrum of Benzyl Alcohol and benzaldehyde is shown below

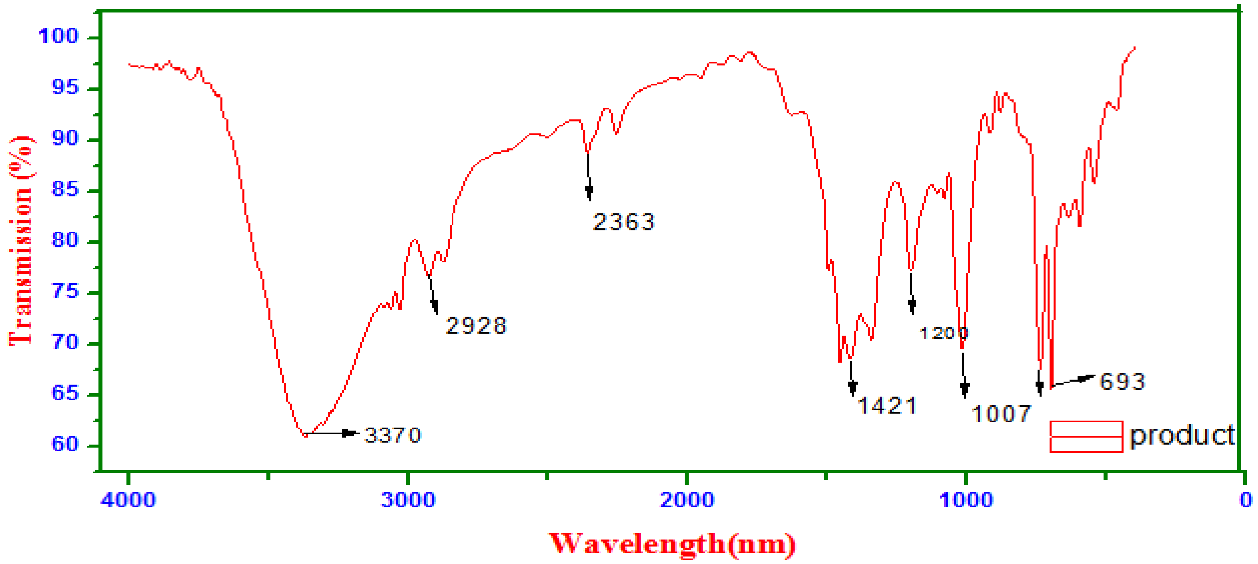

Fig.5.5 FT-IR Spectrum of Benzyl Alcohol.

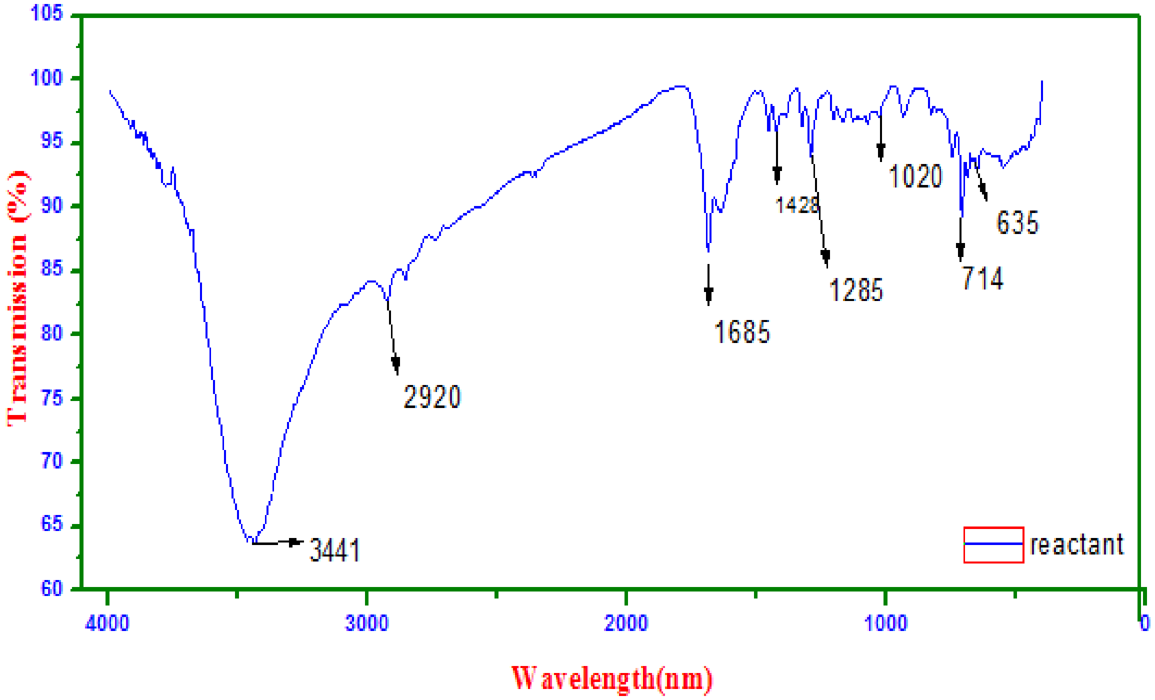

Fig.5.6 FT-IR Spectrum for Benzaldehyde.

ANTIBACTERIAL ACTIVITY

According to the results of Disc diffusion assay, this sample has active compounds that are effective for the prevention of infections caused by E.coli. the utmost zone was produced by the compound against the E. coli was 20mm. The inhibition showed by positive controlwas 30mmdiameters. It shows that benzyl alcohol has antibacterial activity against gram negative bacteria like E. coli.

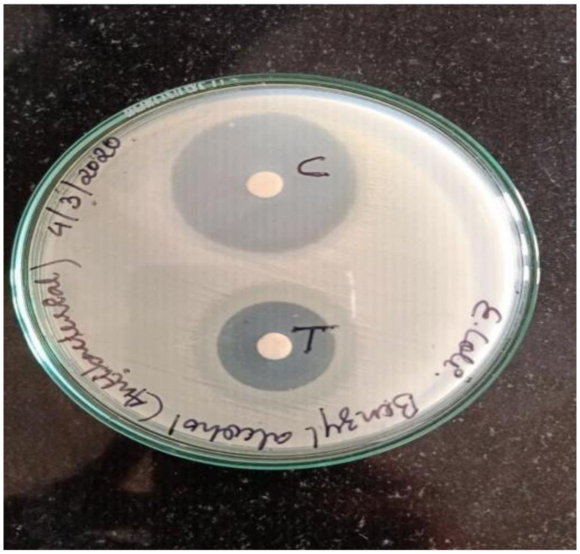

Fig.5.7 Antibacterial Activity of Benzyl Alcohol.

CONLUSION

The Thesis deals with the comparative study of catalyzed reduction of sodium borohydride with Ethyl acetoacetate and Benzaldehyde,characterisation and antibacterial reactivity of the merchandise obtained.

The reduction of sodium borohydride with Ethyl acetoacetate is a temperature dependent reaction. the merchandise obtained was purified by chromatography and TLC was conducted. there have been many spots on TLC plate which indicated the decomposition of the merchandise , the components within the fractions of chromatography were too numerous to isolate.This indicated that product is unstable.However, the merchandise i.e. benzyl alcohol obtained by reduction of sodium borohydride and Benzaldehydegave one spot on TLC plate which indicates the purity of product. The FT-IR Spectroscopic study of thiscompound establishes the bond shifting of group into hydroxyl.

According to the result of Disc diffusion assay, benzyl alcohol has active compounds that are effective for the prevention of infections caused by E.coli.

After the experimental study of these two reactions, it was clearly evident that reduction of Ethyl acetoacetate with sodium borohydride is a temperature sensitive reaction and the reduction of benzaldehyde with sodium borohydride gavemore stable product with good yield. Thus we can conclude that the thermal stability of sodium borohydride catalyzed reduction reaction is very much lower than that of Benzaldehyde.

Futher advanced studies on biological aspects such as Antibacterial activities of benzyl alcohol can be conducted in future.

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