

Reaction of Inorganic Salts on Benzaldehyde Di N-Butylacetal

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Abstract

The reaction of benzaldehyde di n-butylacetal catalyzed by halomethanes in contrast to those catalyzed by Lewis acids, n-halocompounds, etc., has received only a little attention. Aliphatic acetal gives butyl 3-chlorobenzoate and 2-chlorobenzaldehyde as the main products. This reaction features induced the authors to take up the title investigations. Halomethanes are synthetically very useful reagents and vary widely in their acceptor synthon character and reactivity, hence their applications in the present work.

Keywords: Benzaldehyde di n-butylacetal, Barium Chloride, Hydroxyl Ammonium Chloride, and Acetonitrile

Introduction

Acetal derivatives of aldehyde are valuable in synthesis either as intermediates groups, and it is susceptible to addition, oxidation, reduction rearrangement is condensation in the presence of catalysts.

Antony investigated the effect of ring substituent on the mechanism of rearrangement of aromatic acetals by the action of acid chloride¹. An action conducted in 1, 2-dichloroethane has been postulated to pass via carbocation intermediate which on subsequent alkoxide coordination yields esters formation.

Apart from the metal halides and alkoxides, nonmetallic compounds such as boron trifluoride, iodine, and its interhalogen compounds have also been used extensively by various researchers

The use of titanium chloride and stannic chloride in organic reactions is of relatively recent origin. Titanium tetrachloride and its alkoxyderivatives have been using in many reactions.

The literature contains a few references on the preparations and reactions of aromatic and heteroaromatic acetals resulting in synthetically important compounds as the major products^{7, 8}. But the literature lacks detail study on the action of acid amides and alkali metal halide on aromatic acetals.

Acetals play a vital role in bio-organic research in exploring anti-malarial, anti-bacterial, anti-inflammatory, anti-tumor and anti-cancer activities. The studies of enzymes thrombin inhibitor, ADP-ribose linkages to proteins bioprosthetic devices and knee replacement has been made through the investigation of acetals. The acetal research has contributed much towards the synthesis of catalytic antibodies oligonucleotide and hypolipidemic agents.

Acetals are also used to analyze plasmalogens riboacetal internucleotide linkage; lipase-catalyzed selective deacetylation, bio-mechanical aspects of bone and interface reactions and stereo chemical structure of synthesized and natural plasmalogalactosylceramides from an equine brain. Bruck who studied the action of BTE on aromatic acetals in $CDCl_3$. An acetal is a functional group with the following connectivity $R_2C(OR')_2$, where both R' groups are organic aroma smell. The central carbon atom has four bonds, and it is saturated, and the geometry is tetrahedral.

Therefore two $R'O$ groups may be equivalent to same or not. The two R groups can be the equivalence to each other (a "symmetric acetal") or not (a "mixed acetal"), and one or both can even be hydrogen atoms rather than organic aroma smell (fragments).

Materials

Substrate: The benzaldehyde di n-butylacetal was prepared and its purity was checked by TLC (Thin Layer Chromatography)

Solvent: Acetonitrile was purified by standard distillation and used as the solvent.

Reagents: Merck samples of Barium Chloride and Hydroxyl Ammonium Chloride were bought and used for the reactions.

Experimental Section

Acetal Preparation

Benzaldehyde di n-butylacetal: 100ml of freshly vacuum distilled benzaldehyde, and 200ml of distilled n-butyl alcohol were taken in a 500ml round-bottomed flask fitted with a Dean-Stark apparatus carrying a reflux condenser attached to a calcium chloride guard tube. 8g of calcium chloride and 100 ml of pure dry benzene were added and the mixture was reflux for 8 hours. The flask was cooled to room temperature, and the contents were poured into a separating funnel. The solution was washed with water. The solution was dry over anhydrous sodium sulfate.

The unreacted alcohol and benzene removed by atmospheric distillation. The remaining mixture was distilled under reduced pressure. Pure acetal was collected at 196°C-200°C.

An Action of Barium Chloride on Benzaldehyde Di n-Butylacetal

A reaction of barium chloride with benzaldehyde di n-butylacetal: 5 ml of benzaldehyde di n-butylacetal dissolved in 10 ml of acetonitrile is taken in a 250 ml conical flask, 5.28 g of barium chloride was dissolved in 10 ml of water and is added drop wise to the same flask, fitted with a magnetic stirrer. The reaction mixture is stirred well, and the stirring is continued for half an hour, and the mixture is washed with water and the product is extracted with diethyl ether. The resulting reaction mixture is spotted at the TLC. The product is separated by column chromatography.

An action of Hydroxyl Ammonium Chloride on benzaldehyde di n-butylacetal

An action of Hydroxyl Ammonium Chloride with benzaldehyde di n-butylacetal

5 ml of benzaldehyde di n-butylacetal dissolved in 10 ml of acetonitrile is taken in a 250 ml conical flask, 1.76 g of Hydroxyl Ammonium Chloride was dissolved in 10 ml of water and is added dropwise to the same flask, fitted with a magnetic stirrer. The reaction mixture is stirred and the stirring is continued for half an hour. The reaction mixture is washed with water, and the product is extracted with diethyl ether. The resulting reaction mixture is spotted at the TLC, and then the product is separated by column chromatography.

Results and Discussion

An action of inorganic salts on benzaldehyde di n-butylacetal

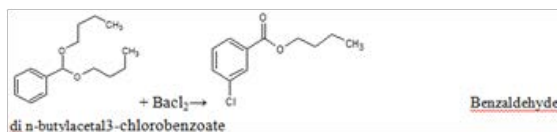
The acetal contains the benzal carbon atom which is surrounded by one H atom and the other three bulky groups namely benzene ring and the two butoxy groups. Thus the acetal requires steric relief. Thus the butoxy oxygen atom with two lone pairs is longing to attack any acceptor synthon. This is the driving force for the attack of the alkoxy oxygen on the acceptor synthon.

The action of Barium Chloride, Hydroxyl Ammonium Chloride, Sodium on the benzaldehyde di n-butylacetal gave the corresponding butyl 3-chlorobenzoate, 2-chlorobenzaldehyde respectively.

Barium Chloride, Hydroxyl Ammonium Chloride, Sodium are inorganic salts which are ready to draw nucleophile towards it since the chosen inorganic salts are having electron withdrawing inductive effect thus the acetal makes use of its lone pair on the alkoxy oxygen and forms oxonium ion.

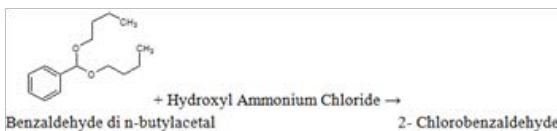
An R group is undergoing steric hindrance and, the R group is the driving force for the R to get cleaved as RH abstracting the methine H atom. Thus the intermediate is results. The reagent Barium Chloride, Hydroxyl Ammonium Chloride which has acted as the catalyst are relieved when the butyl 3-chlorobenzoate, 2-chlorobenzaldehyde is formed as the products.

Mechanism: 1



di n-butylacetal3-chlorobenzoate

Mechanism: 2



Conclusion

The reactions of the benzaldehyde di n-butylacetal with Barium Chloride, Hydroxyl Ammonium Chloride were studied at room temperature.

The reagents Barium Chloride, Hydroxyl Ammonium Chloride, were found to yield the products butyl 3-chlorobenzoate, 2-chlorobenzaldehyde respectively.

The formation of butyl 3-chlorobenzoate, 2-chlorobenzaldehyde are explained by the ¹H NMR, IR spectra.

The Presence of Cl is confirmed by the confirmatory element test. Just as the Barium Chloride, Hydroxyl Ammonium Chloride many more acceptor synthons can be used to react with the acetals and such reactions can be run.

Many more aromatic nuclei like furan, pyrrole, thiophene, pyridine, etc. other than the benzene nucleus can be used in the synthesis of the acetals. The

same reagents used in the present study can also be treated with aliphatic acetals, heteroaromatic acetals with different hetero atoms such as N, S, and O.

The same reactions can be carried out even at a high temperature (or) at low temperature. Variety of alcohols can be used to synthesize the different acetals excluding what has reported in the present study. Many more solvents can try out other than acetonitrile.

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