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ACTION OF TRICHLOROETHENE AND TETRACHLOROETHENE ON PYRIDINE ALDEHYDE DI-n-BUTYLACETAL AT LOW TEMPERATURE

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ABSTRACT

The reaction of pyridine aldehyde di-n-butyl acetal catalyzed by haloethenes in contrast to those catalyzed by Lewis acids, N-halocompounds etc., has received only little attention. Aliphatic acetals give ether and alcohols as the major products, while aromatic homocyclic acetals yield esters and ethers as the main products[7]. This feature induced the authors to take up the title investigation.Haloethenes are synthetically very useful reagents and vary widely in their acceptor synthon character and reactivity, hence their application in the present work.

KEYWORDS

Pyridine aldehyde di-n-butylacetal, trichloroethene, tetrachloroethene and acetonitrile.

INTRODUCTION

Acetals play a vital role in bioorganic research in exploring, antimalarial, antiviral, antibacterial, anti-inflammatory, antitumor and anticancer activities. The action of heterocyclic aromatic acetals by Lewis acids[3], the rearrangements of aromatic acetals over solid acids[7], action of aromatic and heteroaromatic acetals by halo compounds[1, 11] are reported in literature.

Acetal derivatives of aldehyde are valuable in synthesis either as intermediates or as protecting groups. It is known that acetals are susceptible to addition[8], oxidation[6], reduction[2], rearrangement, condensation and hydrolysis in presence of catalysts.

The use of titanium chloride and stannic chloride in organic reactions is of relatively recent origin. Titanium tetrachloride and its alkoxy derivatives have been used in many reactions[17].

Antony[10] investigated the effect of ring substituent on the mechanism of rearrangement of aromatic acetals by the action of acid chloride. The reaction conducted in 1, 2-dichloroethane has been postulated to pass through carbocation intermediate which on subsequent alkoxide coordination yields esters. Apart from the metal halides and alkoxides, non-metallic compounds such as boron trifluoride, iodine and its interhalogen compounds have also been used extensively by various researchers.

Alphonse[15] has investigated the action of various Lewis acids on aromatic acetals and proposed mechanism based on carbocation intermediate.

The reactions of aliphatic acetals catalyzed by solid acids[16] have been extensively studied by various researchers and in most cases synthetically important α, β-unsaturated ethers have been obtained as the major products. The unsaturated ether was shown to be formed by the elimination of alkoxy group and the removal of a proton from the β-carbon of acetal. The elimination may occur either in a concerted or stepwise manner depending on the nature of the catalyst. The results of the action of haloethenes on Pyridine aldehyde di-n-butylacetal in acetonitrile medium are reported in the present work.

MATERIALS

Substrate: ThePyridine aldehyde di-n-butylacetalwas prepared and its purity was checked spectroscopically.

Solvent: The acetonitrile was purified by standard method and used as the solvent.

Reagents: BDH samples of trichloroethene and tetrachloroethene were bought and used for the reactions.

EXPERIMENTAL SECTION

1. Acetal preparation.

Pyridine aldehyde di-n-butylacetal

53.5gm (0.5mol) of freshly vacuum distilled Pyridine aldehyde and 89gm (1.2mol) 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. 0.05g of *p*-toluenesulphonic acid and 80ml of pure dry benzene were added to the solution and the mixture was refluxed for 6 hours.

The flask was cooled to room temperature and the contents were washed with 1M sodium bicarbonate solution and then with water. The solution was dried over potassium carbonate. After evaporation of the solvent, the crude acetal was distilled under reduced pressure. Pure acetal was collected at 186°C (10mm of Hg) and the yield was 60%.

n_D = *1.464 at 34°C*

IR : ν *1020-1140* cm^{-1} *(C-O-C)*

PMR : δ *0.9, 1.3-1.7, 3.5 (n-butyl), 5.45(1H, s, pyridyl-C<u>H</u>),*

7.0-8.5 (4H, m, pyridine-H).

2. Action of haloethene compounds on pyridine aldehyde di-n-butylacetal.

a) Reaction of tetrachloroethene with pyridine aldehyde di-n-butylacetal

5 ml of pyridine aldehyde di-n-butylacetal in 10 ml of acetonitrilewas takenin a 250mlconical flask, 3.5 g of tetrachloroethene was dissolved in 10 ml of acetonitrile and was added drop wise to the same flask, fitted with a magnetic stirrer. The temperature was kept at -20°C.The reaction mixture was stirred and the stirring was continued for 1 hour. The reaction mixture was washed with water and the product was extracted with diethyl ether. The resulting reaction mixture was spotted at the TLC. The product was separated by column chromatography and was identified by IR and PMR spectrum to be the ester

b) Reaction of trichloroethene with pyridine aldehyde di-n-butylacetal

5 ml of pyridine aldehyde di-n-butylacetal in 10 ml of acetonitrilewas takenin a 250mlconical flask, 2.7 g of trichloroethene was dissolved in 10 ml of acetonitrile and was added drop wise to the same flask, fitted with a magnetic stirrer. The temperature was kept at -20°C.The reaction mixture was stirred and the stirring was continued for 1 hour. The reaction mixture was washed with water and the product was extracted with diethylether. The resulting reaction mixture was spotted at the TLC. The product was separated by column chromatography and was identified by IR and PMR spectrum to be the aldehyde.

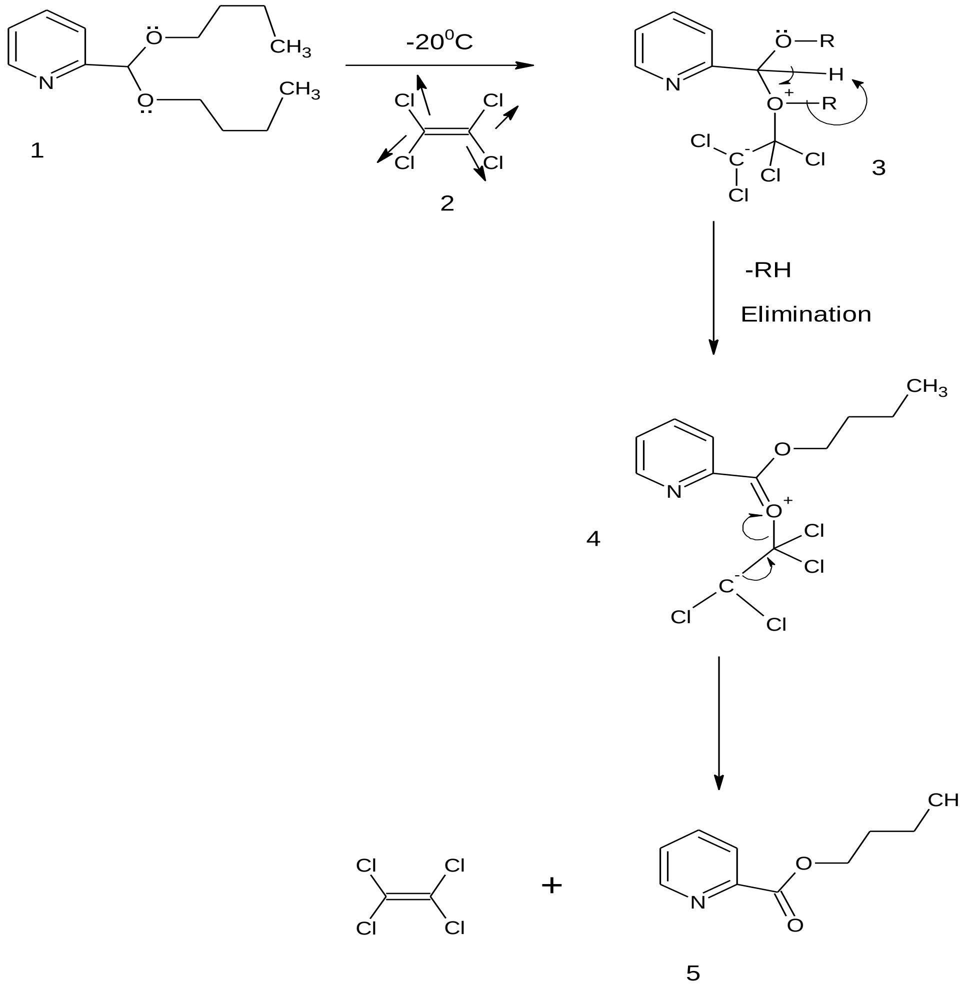
RESULTS AND DISCUSSION

The action of haloethene compounds on pyridine aldehyde di-n-butylacetal

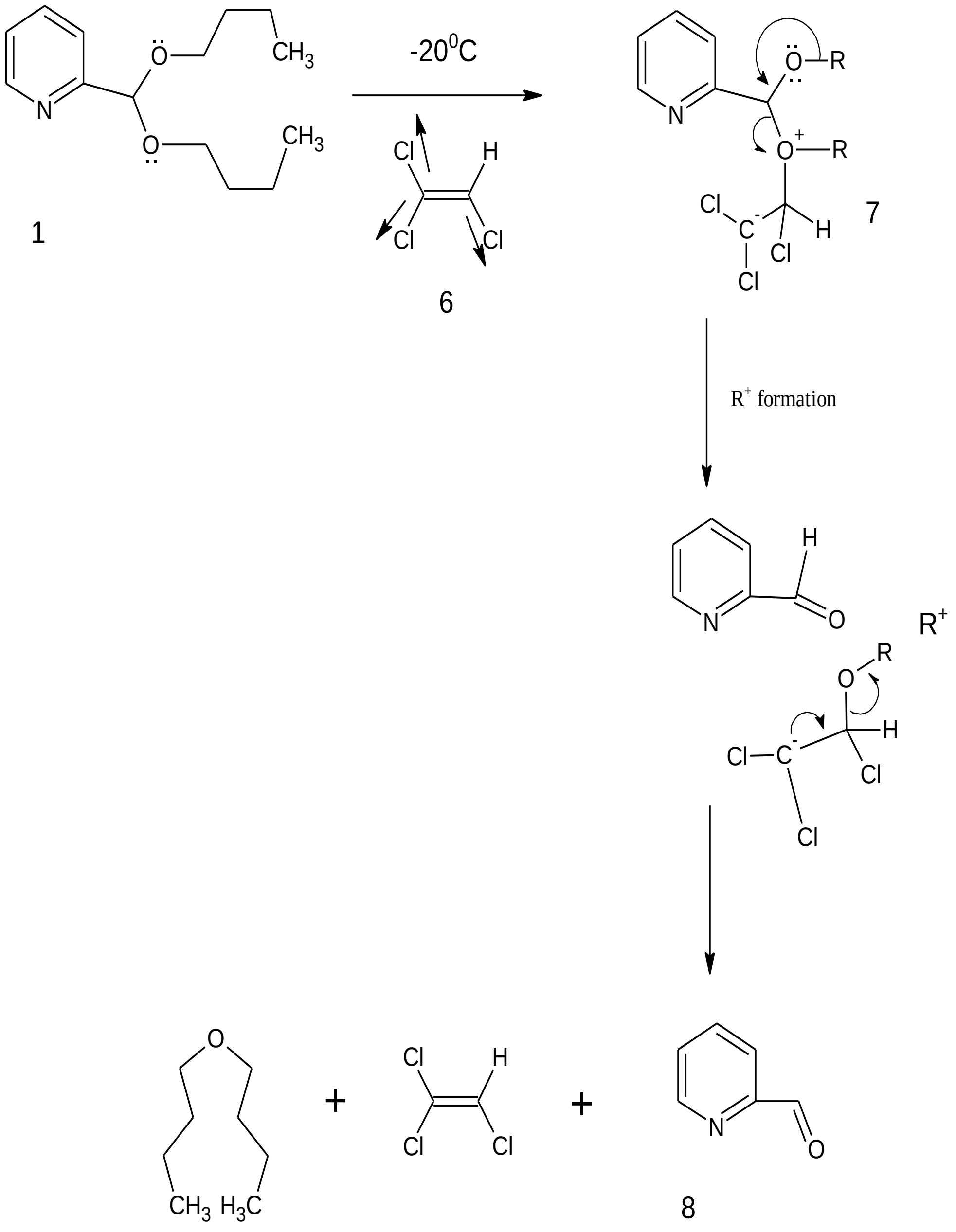
The acetal (1) contains the benzal carbon[3] atom which is surrounded by one H atom and the other three bulky groups namely benzene ring and the two butoxy groups.Thus the acetal requires steric relief. Thus the butoxy oxygen atom with two lone pairs is longing to attack any acceptor synthon. This is the driving force for the attack of the alkoxy oxygen on the acceptor synthon.

The action of tetrachloroethene and trichloroethene on the pyridine aldehyde di-n-butylacetal gave the corresponding ester and aldehyde respectively. The formation of ester indicates that this reaction may pass through the mechanism as shown in **scheme–1**.

Tetrachloroethene (2) is an alkene which is ready to draw neucleophile towards it, since the four chlorine atoms are having electron withdrawing inductive effect (-I effect) thus the acetal (1) makes use of its lone pair on the alkoxy oxygen and forms oxonium ion (3). Each of the chlorineatoms of the oxoniumion intermediate (3) is posing the steric hindrance to the R group of the alkoxy oxygen atom of the oxonium ion. The steric hindrance experienced by the R group is the driving force for the R to get cleaved as RH abstracting the methine H atom. Thus the intermediate (4) is resulted. The reagent tetrachloroethene which has acted as the catalyst is relieved when the ester (5) is formed as the product.



R= CH_3-CH_2-CH_2-CH_2- Mechanism -1



R= CH_3-CH_2-CH_2-CH_2-

Mechanism -2

The trichloroethene (6) is susceptible for nucleophilic attack like (3) at the acetal (1) resulting in the oxonium ion (7). In this casesince the acceptor synthon is only trichloroethene, the R group attached to the oxonium oxygen is not so much sterically hindered as in the case of (3). Hence the R group found in the other alkoxy group is cleavedresulting in aldehyde (8) as shown in **scheme-2**.

CONCLUSION

The reactions of the pyridine aldehyde di-n-butylacetal with tetrachloroethene and trichloroethene were studied at -20^{o}c. The products formed and the proposed mechanisms followed are given. The reagents tetrachloroethene and trichloroethene were found to yield the products ester and aldehyde respectively.

The formation of ester is explained by the mechanism in scheme-1 while the formation of aldehyde is explained by the mechanism in scheme-2. Just as the tetrachloroethene and the trichloroethene, 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.

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