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, 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. 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.
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-butylacetald in acetonitrile medium are reported in the present work.

MATERIALS
Substrate: The Pyridine aldehyde di-n-butylacetald was 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-butylacetald
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_o = 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-CH),
7.0-8.5 (4H, m, pyridine-H).

2. Action of haloethene compounds on pyridine aldehyde di-n-butylacetald.
a) Reaction of tetrachloroethene with pyridine aldehyde di-n-butylacetald
5 ml of pyridine aldehyde di-n-butylacetald in 10 ml of acetonitrile was taken in a 250ml conical 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-butylacetald
5 ml of pyridine aldehyde di-n-butylacetald in 10 ml of acetonitrile was taken in a 250ml conical 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 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 aldehyde.

RESULTS AND DISCUSSION
The action of haloethene compounds on pyridine aldehyde di-n-butylacetald
The acetal (1) contains the benzal carbon³ 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 nucleophile 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 chlorine atoms of the oxonium 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.

\[ R = \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2^- \]

Mechanism -1

\[ \text{Elimination} \]

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Mechanism -2

R = CH₃·CH₂·CH₂·CH₂⁻

Mechanism -2
The trichloroethene (6) is susceptible for nucleophilic attack like (3) at the acetal (1) resulting in the oxonium ion (7). In this case since 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 cleaved resulting 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°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.

REFERENCES

*Corresponding Author: M. Easuraja*
PG and Research, Department of Chemistry, St. Joseph’s College, Trichy, Tamilnadu, India.