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Synthesis of Acetic Anhydride by using Phosphorous Pentoxide, Sodium Acetate and Calcium Chloride as a Catalyst

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***Abstract*: Simple and improved methods have been found to carry out the preparation of acetic anhydride from acetic acid. This preparation was performed by using glacial acetic acid by different catalyst. This method is cheaper and less hazardous. These preparation methods involves following steps refluxing, distillation and finally acetic anhydride was examined and identified by spectroscopic analysis. The advantage of this method is operational simplicity and avoidance of use of organic solvent and eco-friendly preparation.**

***Keywords*: Glacial acetic acid, calcium chloride, phosphorous pentoxide, sodium acetate, sulphuric acid**

I. INTRODUCTION

Acetic anhydride is extensively used in the cellulose acetate industry. It also finds application in the manufacture of aspirin, phenacetin, and other drugs, perfumery chemicals, dye intermediates, flavor bases, explosives, and plastics. The "ketene process," using acetone or acetic acid as the raw material, is widely used for the manufacture of acetic anhydride.[1]The acetyl chloride and sodium acetate readily interact with formation of acetic anhydride.[2,5] The acylation of alcohols is one of the important and routinely utilized transformations in organic synthesis[6] especially in the synthesis of complicated natural products and glycosylation of sugars, acyl groups play a pivotal role as protecting groups of hydroxyls.

Despite a number of precedents, new efficient methodologies for acylation are still in strong demand. Acid anhydrides have been the most commonly used reagents in the presence of an acid or base catalyst.[7] Protection of alcohols and phenols is one of the most common synthetic strategies utilized to mask hydroxyl functionalities during multistep synthetic procedures.[8,9] In addition, O-acetylation procedures are widely employed for the protection and purification of various natural and synthetic products containing carbohydrate substructures.[10,12]

Among various hydroxyl groups protecting moieties, acetyl is perhaps the most frequently used group due to the ease of introduction and its stability.[13,14] In addition, the acetate products can be efficiently converted to their respective original alcohols using various mild procedures.[15,16] Acetylation of alcohols is traditionally carried out in the presence of excessive amounts of acetic anhydride or acetyl chloride and an amine base.[17] Because of its use for the synthesis of heroin by the diacetylation of morphine, acetic anhydride is listed as a U.S. DEA List II precursor, and restricted in many other countries.[18] Although acetic anhydride is banned still it has wide applications in organic synthesis, that's why prepared it.

II. EXPERIMENTAL SECTION

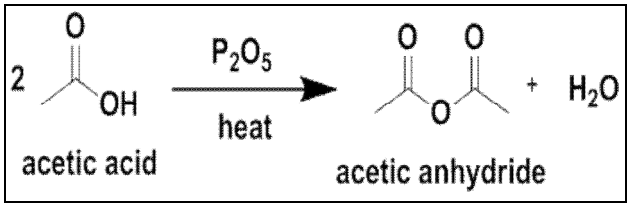
A. Materials

Reactions were monitored by thin layer chromatography on 0.2 mm silica gel F-252 (Merck) plates. Glacial acetic acid and all catalyst were obtained from Aldrich Chemical Co. And used Infrared spectral studies were carried out using shimadzu FTIR/4000 spectrophotometer.[1]HNMR and [13]CNMR were recorded in DMSO-d6 on Bruker Advance II 400 NMR spectrometer. All products were characterized by FT-IR, [1]HNMR, [13]CNMR.

1) *Preparation of Acetic Anhydride by using Phosphorous Pentoxide:* To a round bottom flask different concentrations of phosphorous pentoxide (anhydrous) and glacial acetic acid were mixed thoroughly at 0-5^0 C. Reaction mixture was kept in ice bath for 30 min meanwhile stirring it. Reaction mixture was kept at room temperature then refluxed for 4 hr. The reaction was monitored by TLC. Then the reaction mixture was distilled out to separate unreacted glacial acetic acid. With the help of fractional distillation column product was isolated. Then the Product was confirmed by using spectral technique such as IR, [1]HNMR and [13]CNMR. These products were again confirmed by utilising in different chemical properties.

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a) Scheme 1



(A)

b) Proposed Mechanism

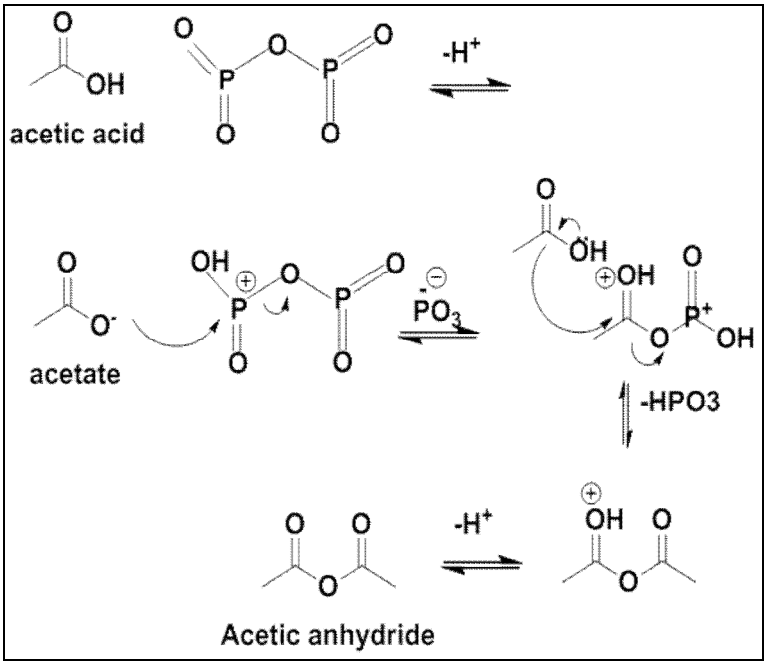


Table 1

Glacial Acetic Acid (moles)	Phosphorus Pentoxide (moles)	(A) (%) yield
0.2	0.2	70.2
0.2	0.1	70.0
0.2	0.05	69.5
0.2	0.03	68.3
0.2	0.025	68.0
0.2	0.015	67.5
0.2	0.017	67.0
0.2	0.005	66.8
0.2	0.0035	65.5
0.2	0.001	65.0

c) Spectral Analysis:

i) IR: Acetic anhydride shows two C=O stretching absorptions, one at very high frequency, 1840 cm–1 (antisymmetric C=O / C=O stetching) the other at 1750 cm–1 (symmetric C=O / C=O stretching)

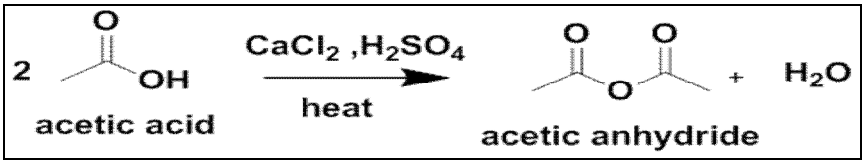
ii) ^{1}HNMR: Acetic anhydride molecule is symmetric therefore two methyl group shows chemical shift 2.24ppm.

iii) ^{13}CNMR: Acetic anhydride molecule is symmetric therefore two carbonyl group shows chemical shift at 167ppm and two methyl group at 20.2ppm.

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2) *Preparation of Acetic Anhydride by using Calcium Chloride:* To a round bottom flask different concentrations of Calcium chloride (anhydrous) and glacial acetic acid were mixed thoroughly at 0-5^0 C. Reaction mixture was kept in ice bath for 30 min meanwhile stirring it and added 5ml concentrated sulphuric acid. Reaction mixture was kept at room temperature then refluxed for 4 hr. The reaction was monitored by TLC. Then the reaction mixture was distilled out to separate unreacted glacial acetic acid. With the help of fractional distillation column product was isolated. Then the Product was confirmed by using spectral technique such as IR, ^{1}HNMR and ^{13}CNMR. These products were again confirmed by utilising in different chemical properties.

a) *Scheme 2*



(B)

b) *Proposed Mechanism*

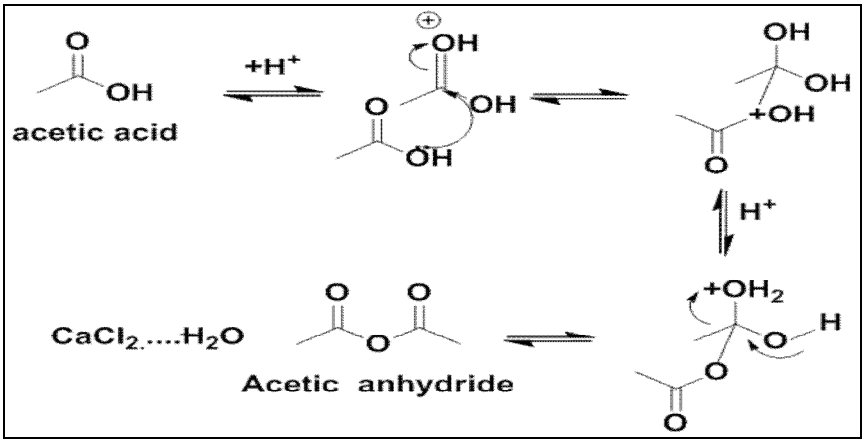


Table 2

Glacial Acetic Acid (moles)	Calcium Chloride (moles)	(B) (%) yield
0.174	0.005	60
0.174	0.009	59.5
0.174	0.01	58.5
0.174	0.025	50
0.174	0.05	45
0.261	0.07	50
0.2	0.1	Nil
0.2	0.181	Nil
0.2	0.20	Nil
0.2	0.454	Nil

c) *Spectral Analysis*

i) *IR:* Acetic anhydride shows two C=O stretching absorptions, one at very high frequency, 1840 cm–1 (antisymmetric C=O / C=O stetching) the other at 1750 cm–1 (symmetric C=O / C=O stretching)

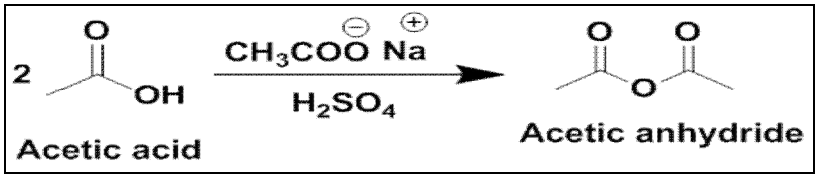
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iii) ^{13}*CNMR:* Acetic anhydride molecule is symmetric therefore two carbonyl group shows chemical shift at 167ppm and two methyl group at 20.2ppm.

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3) *Preparation of Acetic Anhydride By Using Sodium Acetate:* To a round bottom flask different concentrations of sodium acetate (anhydrous) and glacial acetic acid were mixed thoroughly at 0-5^0 C. Reaction mixture was kept in ice bath for 30 min meanwhile stirring it and added 5ml concentrated sulphuric acid. The reaction mixture was kept at room temperature then refluxed for 4 hr. The reaction was monitored by TLC. Then the reaction mixture was distilled out to separate unreacted glacial acetic acid. With the help of fractional distillation column product was isolated. Then the Product was confirmed by using spectral technique such as IR, ^{1}HNMR and ^{13}CNMR. These products were again confirmed by utilising in different chemical properties.

a) Scheme 3



(C)

b) Proposed Mechanism

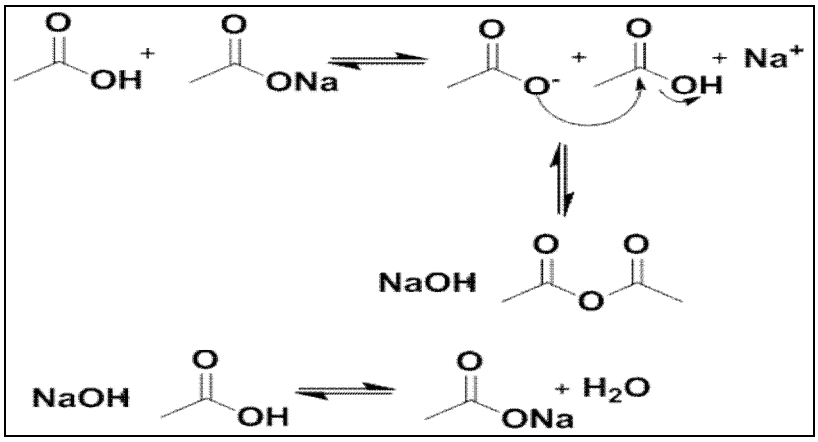


Table 3

Glacial Acetic Acid (moles)	Sodium-Aceated (moles)	(C) (%) yield
0.174	0.012	55
0.174	0.024	53
0.2	0.05	52
0.2	0.07	50
0.2	0.1	48
0.2	0.15	Nil
0.2	0.20	Nil
0.2	0.25	Nil
0.2	0.30	Nil

c) Spectral Analysis:

i) IR: Acetic anhydride shows two C=O stretching absorptions, one at very high frequency, 1840 cm–1 (antisymmetric C=O / C=O stetching) the other at 1750 cm–1 (symmetric C=O / C=O stretching)

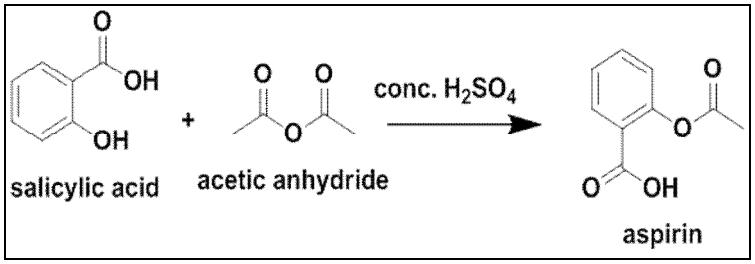
ii) ^{1}HNMR: Acetic anhydride molecule is symmetric therefore two methyl group shows chemical shift 2.24ppm.

iii) ^{13}CNMR: Acetic anhydride molecule is symmetric therefore two carbonyl group shows chemical shift at 167ppm and two methyl group at 20.2ppm.

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III. APPLICATION OF ACETIC ANHYDRIDE

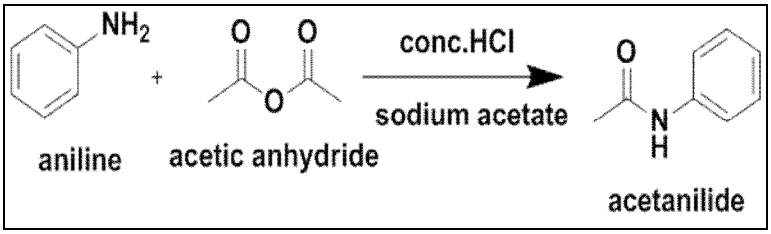
A. Acetic Anhydride Used In Preparation Of Aspirin From Salicylic Acid



Salicylic acid (moles)	Acetic anhydride (moles)	(%) Yield	Physical constant
0.015	A 0.052	60	136^0 C
0.015	B 0.052	55	
0.015	C 0.052	45	

Prepared acetic anhydride was confirmed by using TLC and spectral data of aspirin.

B. Acetic Anhydride Used in Acylation of Amines



Aniline (moles)	Acetic anhydride (moles)	% Yield	Physical constant
0.027	A 0.037	65	116^0 C
0.027	B 0.037	60	
0.027	C 0.037	50	

Prepared acetic anhydride was confirmed by using TLC and spectral data of acetanilide.

IV. RESULT AND DISCUSSION

First, we investigated the catalytic activity of Phosphorous Pentoxide, Sodium Acetate and Calcium Chloride. From table 1 it was observed that 0.2 mole of glacial acetic acid reacted with 0.2 mole of Phosphorous Pentoxide to give maximum yield. From table 2, it was observed that 0.174 mole of glacial acetic acid reacted with 0.005 mole of calcium chloride to give maximum yield. As we increased the concentration of calcium chloride product was not obtained. From table 3, it was observed that 0.174 mole of glacial acetic acid reacted with 0.012mole of sodium acetate gives better yield. In this also as we increased the concentration of catalyst product was not obtained. From the above discussion, it is clear that, among all three catalysts, phosphorous pentoxide gives better yield.

V. CONCLUSION

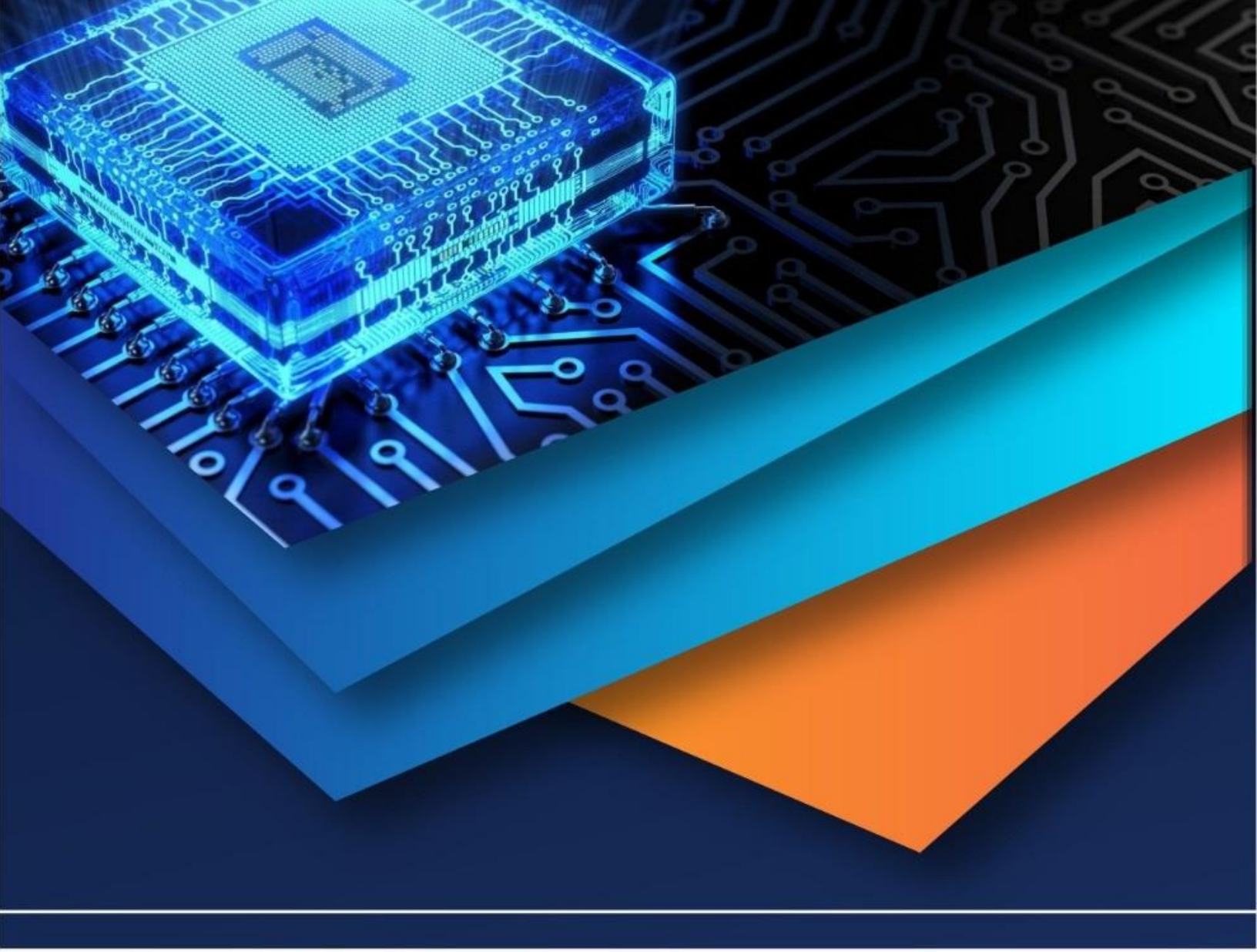
We have mentioned a novel method for the preparation of acetic anhydride from acetic acid by using Phosphorous Pentoxide, Sodium Acetate and Calcium Chloride and from this data we conclude that Phosphorous Pentoxide gives better yield.

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