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Synthesis and characterisation of some phosphate esters

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ABSTRACT

Organic phosphates are very important due to their wide range of applications in various branches of chemistry. Organic phosphates are attached to human and plants very closely in their biochemical functions. They are tribasic acid due to the presence of three hydroxyl group and are formed by the replacement of acidic hydrogen by an alkyl or aryl or their substituted derivative. These compounds consist of likages like C-O-P, C-N-P, C-S-P etc.

Key words : Synthesis, Estimation of Elements, IR Specra, Phosphate Esters.

INTRODUCTION

Phosphate esters and anhydrides dominate the living world. Organophosphorus compounds are the essential constituents of protoplasm and play important role for maintenance of life, e.g. nucleotide, genetic informations, metabolic intermediate phosphates, photosynthesis, saccharide synthesis, nucleic acid helices and involvement in co-enzyme systems. Organophosphorus compounds play a central role in life processes[1], in living organism for growth, development and maintenance of all plants[2] and animals[3]. They are also used as defoliants[4], cancer chemotherapeutic agents[5], anti-tumor agents[6] as well as in the treatment of glaucoma[7,8]. Recently phosphonoformate trianion (PFA) was found to be effective anti-viral agent against AIDS chemotherapy under the names of Foscarnet and Foscavir[9]. Foscarnet is also active against herpes simplex virus (HSV) and AIDS related human cytomegalovirus[10].

Organic phosphate having C-N-P linkages are of great importance. They are used for antiviral activity[11], insecticidal activity[12], smoke generation[13], for biological investigations and textile commodities[14]. With such a broad spectrum biological activity of azophosphates, the knowledge regarding their bond cleavages and their stabilities are important.

EXPERIMENTAL

Synthesis of phosphate Esters

The method of synthesis of phosphate esters (mono, di and tri), have been illustrated as :

Mono-2-chloro-5-nitro aniline phosphate (Ba-Salt)

It is prepared by Auger and Dupis[15] method. 3.4514 g of pure 2-chloro-5-nitro aniline (A.R. Grade Sigma-Aldrich) were dissolved in 15.0 ml of dry benzene and 10.0 ml of pyridine in a round bottom flask of 250 ml capacity and stirred well for half an hour. Then 1.866 ml of $POCl_3$ is added drop by drop so that 2-chloro-5-nitro aniline and $POCl_3$ had molar ratio of 1:1. The whole reaction mixture was refluxed for 18 hours at 80°C. After this, the reaction mixture was kept at room temperature over-night. Now, 100

ml of distilled water was introduced into the flask and shaken well. Two layers were separated. Aqueous layer contained mono-2-chloro-5-nitro aniline phosphate and benzene layer was rejected.

In the aqueous layer, few drops of phenolphthalein were added. Then saturated solution of barium hydroxide was added drop by drop till pink colour appeared. A white precipitate was obtained which was filtered and washed several times with distilled water (containing few drops of acetic acid) to remove inorganic phosphate if present. It was then dried to obtain Ba-salt of mono-2-chloro-5-nitro aniline phosphate.

Di-2-chloro-5-nitro aniline phosphate

It was also prepared by Auger and Dupis method. 2-chloro-5-nitro aniline (A.R. grade Sigma-Aldrich) and $POCl_3$ were taken in 2:1 ratio. 7.0 ml of pyridine was added slowly to a stirred solution of 2-chloro-5-nitro aniline (3.45g) and $POCl_3$ (0.933 ml) in dry benzene (25.0 ml). Pyridine hydrochloride were began to separate immediately with the evolution of heat. The mixture was stirred on a magnetic stirrer at 60 to 65°C for a period of 10 hrs. The yellowish oily residue left after stirring was treated with H_2O and then with 5% NaOH. The filtrate thus obtained was acidified with dilute HCl to precipitate the chloride which on washing with distilled water was converted into free diester. This free diester was finally dissolved in CCl_4 and filtered off to remove impurities.

Tri-2,5 dichloro aniline phosphate

It was prepared by Rudert P method[16]. 4.86 grams of 2,5-dichloro aniline was taken in a round bottom flask. 25.0 ml of dry benzene and 15.0 ml of pyridine were used as solvent. Then 0.6 ml of H_3PO_4 was added dropwise with continuous stirring. The whole reaction mixture was refluxed for 68 hours. The refluxed solution was kept overnight, and then 100 ml of distilled water was added into the flask. Now this solution was transferred to separating funnel and was shaken well. Two layers were separated-the lower aqueous layer was rejected as it contained monoester, while the light benzene layer was transferred to a beaker. It was then treated with 10% NaOH solution. Two layers were formed, lower layer was rejected as it contained diester while light benzene layer was transferred to a petty disc and evaporated. Small brownish-white needle shaped crystals of triester were formed which is then recrystallised by chloroform. All the chemicals used belonged to BDH (AR) and Riedel quality.

RESULTS AND DISCUSSION

Mono-2-chloro-5-nitro aniline phosphate (Ba-Salt)

Molecular Formula : $C_6H_4N_2O_5PClBa$

Estimation of elements*

S. no	Element	Percentage	
		Theoretical	Observed
1	Carbon	18.58	19.66
2	Hydrogen	1.04	2.17
3	Nitrogen	7.22	6.44

courtesy: IISc Bangalore

I.R. absorption spectra

The spectral study of mono-2-chloro-5-nitro aniline phosphate was conducted on Nicolet Protege Model 460 IR Spectrophotometer from IIT Roorkee.

ν (KBr) cm^{-1} : 3357, 3126, 1250, 1216, 1072 (P-N).

Di-2-chloro-5-nitro aniline phosphate

Molecular Formula : $C_{12}H_9N_4O_6PCl_2$

Melting point of diester was observed 116°C while that of parent compound 2-chloro-5-nitro aniline phosphate was observed 108°C.

Estimation of elements*

S. no	Element	Percentage	
		Theoretical	Observed
1	Carbon	35.40	36.55
2	Hydrogen	2.23	2.40
3	Nitrogen	13.76	14.53

*Courtesy : IISc Bangalore

I.R. absorption spectra

The spectral study of Di-2-chloro-5-nitro aniline phosphate was conducted on Nicolet Protege Model 460 IR Spectrophotometer from IIT Roorkee.

ν (KBr) cm^{-1} : 3366, 3050, 1346, 1217, 1081 (P-N)

Tri-2,5 dichloro aniline phosphate

Molecular formula : $C_{18}H_{12}N_3OPCl_6$

Estimation of elements*

S. no	Element	Percentage	
		Theoretical	Observed
1	Carbon	40.79	43.97
2	Hydrogen	2.28	4.13
3	Nitrogen	7.92	8.70

*Courtesy : IISc Bangalore

Melting point of triester was observed 56°C while that of the parent compound 2,5-dichloro aniline was observed 46-47°C.

I.R. absorption spectra

The spectral study of Tri-2,5-dichloro aniline phosphate was conducted on Nicolet Protege Model 460 IR Spectrophotometer from IIT Roorkee.

ν (KBr) cm^{-1} : 3350, 2926, 1264, 1075, 909 (P-N).

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