International Journal of Fundamental & Applied Research
Website : www.ijfar.org ,(ISSN- 2320-7973 Volume-4 Issue -12 Month – March 2017 pp. (19 – 23)

Preparation and identification of Tri-4-Chloro,3-methylphenyl phosphate (Ba-salt)

[1] Asha Verma [2] Abdul Rashid Teli
[1] Prof. of Chemistry Govt. Science and commerce college Bhopal
[2] Research Scholar Chemistry Govt. Science and commerce college Bhopal

ABSTRACT
Tri-4-chloro, 3-methylphenyl phosphate has been synthesized by Auger and Dupis method in a ratio of 1:1 phenol and POCl3. The compound has been characterized by IR absorption spectra and elemental detection. The spectra study was conducted on KBr disc. IR spectra of di-4-chloro, 3-methylephenyle phosphate ester clearly reveals different stretching frequency of almost all the bonds present in the compound at their respective wave number.

INTRODUCTION

Organophosphates are widely recognized an important fine chemical in different chemical processes. These are derivatives of orthophosphoric acid and infinite revivifications are possibly by making changes in substituent attached to its phosphorus atom through specific linkage likely C-O-P, C-N-P, and C-S-P. They constitutes a family of large number of encumbers which display a great verity of biological activities in later part of the 1930's a number of neutral phosphate derivatives have been developed into practical insecticides. Owing their owing to their high activity and biodegradability, their application to agriculture, public health and related fields have been growing rapidly moreover , the pesticidal activities of organophosphorus compounds, which are not restricted to phosphate derivatives, also include accaricidal, nematocidal, antihelmentic, insect sterilizing, fungicidal, herbicidal and rodenticidal activities.

In view of their practical application there is obvious need to incur continues investigation on both theory and experimental fronts the hydrolytic reaction of orthophosphate. Hydrolysis is basically double decomposition reaction between water ant the substrate. A vast literature of kinetic investigation of C-O-P linkage is available. Now the attention of scientist is diverted towards other linkage such as C-N-P and C-S-P

Materials and method

It is prepared by Auger and Dupis method in a ratio of 1:1 phenol and $POCl_3$ 6.52 g of 4-chloro-3-methylphenol (A.R.grade sigma –Aldrich) was dissolved in 20 ml of dry benzene, 366 ml of pocl3was taken in a conical flask and kept on a magnetic stirrer. Then a very small amount of the phenol (parent compound) was added slowly to $POCl_3$ and the material was stirred for a period of 6 hours at 60-65 degree after few minute of each addition 3 ml of pyridine was added to the stirred material in installments. Pyridine hydrochloride began to separate at once with the evolution of heat .After the stirring is completed the stirred material was kept open so as to evaporate the solvent then the oily residue left in the flask was treated with water . The milky solution thus obtain was treated with diluted HCl to remove unreacted pyridine as pyridine hydrochloride. The solution was filtered of, first filtrate (very small amount) was rejected .to the clear filtrate barium hydroxide was then added till it become

Corresponding Author : email : abrashid000@gmail.com

International Journal of Fundamental & Applied Research
Website : www.ijfar.org ,(ISSN- 2320-7973 Volume-5 Issue -10+11 Month – January+February 2018 pp. (04 – 06)

alkaline and white ppt. began to separate .the ppt. was then washed several times with distilled water (containing few drops of acetic acid) (to remove inorganic phosphate till dark blue colour of phosphorus was obtained in the filtrate by Allen's test.

Result and Discussion

Tri-4-chloro-3-methylphenyl phosphate has been prepared by using phosphorus penta chloride as phosphorylating agent .the ratio of 3:1 of phenol and PCl_5 was employed for this preparation.

4.889 g of 4-chloro-3-methylphneol (A.R grade sigma-Aldrich) dissolved in 15ml of dry benzene stirred well for minute.1.30 ml of PCl_5 was added .initially the reaction was very rapid and pcl5 dissolved immediately and white insoluble material began to separate .keeping it overnight and then dissolve it an a solvent and thus it was subjected to a steam distillation when aqueous and benzene layer were distilled off separately. The residue left after distilled was treated first with water and then with 10% NaOH solution to remove unreacted phenol. A white residue insoluble in NaOH was obtained. It was washed with distilled water to remove excess of alkali and crystallized from absolute alcohol. Shining crystals of tri--4-chloro 3-methylpheny phosphate were obtained.

ESTIMATION OF ELEMENTS

SNO.	ELEMENTS	PERCENTAGE	
		THEORETICAL	OBSERVEB
1.	Carbon	54.11	53.471
2.	Hydrogen	3.97	3.846
3.	Oxygen	12.98	13.568
4.	Chlorine	23.12	22.547
5	Phosphorus	6.93	6.568

The compound was also identified form its characteristic absorption spectra in KBr pellets IR spectral data of tri-2,5-dichlorophneyl phosphate has been shown in table 4a-3 (the spectral study was conducted on Nicolet protégé model 460 IR spectrophotometer .SIRT Bhopal)

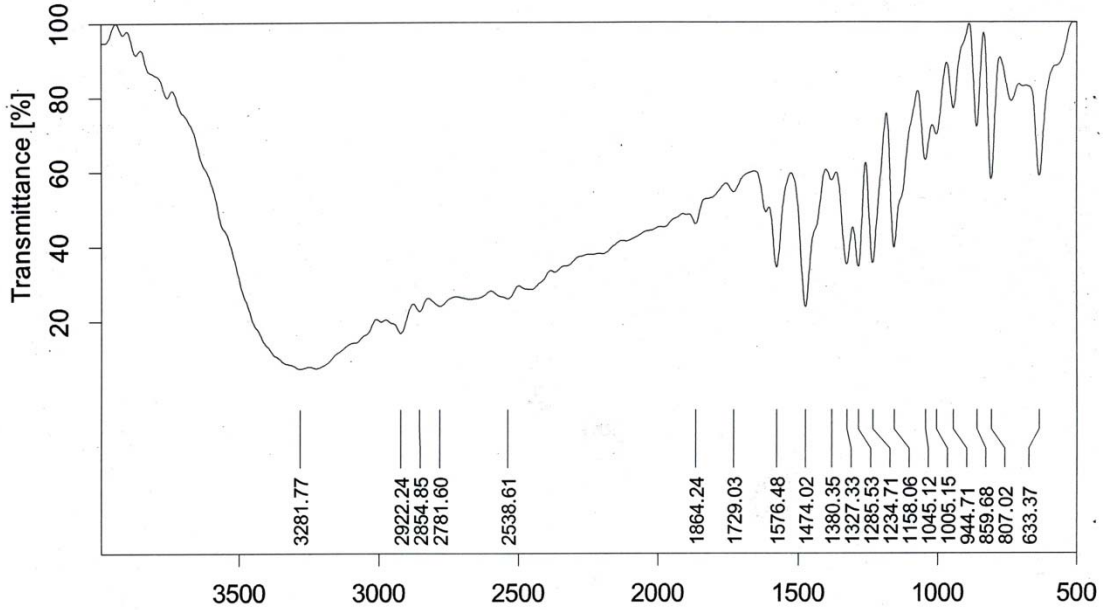
Table 4.A-3

S.NO.	STRETCHING	I.R v Cm^{-1}
1.	(C=O) Stretching	11234.713
2.	(P=O) Stretching	1045.120
3.	(C=H) Adjacent Stretching	807.019
4.	(C=H) Isolated Stretching	859.682
5.	(C=Cl) Stretching	633.369

Corresponding Author : email :

International Journal of Fundamental & Applied Research
Website : www.ijfar.org ,(ISSN- 2320-7973 Volume-5 Issue -10+11 Month – January+February 2018 pp. (04 – 06)

Spectra.4-A.3
IR. spectrum of TRi-25-dichloropheny phosphate



(i) COLOURIMETRIC ESTIMATION OF INORGANIC PHOSPHATE

On hydrolysis phosphate ester produces inorganic phosphate .and its quantitative estimation was made possible by Allen's modified method1.tyhe inorganic phosphate react with the ammonium and forms a phospho molybdate complex $[(NH_4)_3PO_4.12MoO_3]$ Which is reduced to molybdenum blue a soluble complex by addition of 2,5-diaminophenol dihydrogenchloride (amidol) solution. The blue colour so produced took 10 minutes time to fully develop and it remains stable for next thirty minutes. The intensity of the blue colour is directly proportional to the amount of free phosphoric acid. It is independent of tempt over 8-26 degree. The optical density of the blue colour developed followed beer's law was, measured using spectronic 20* spectrophotometer at wavelength (max) 608nm.

The reagents which are needed to carry out the estimation of inorganic phosphate. They are as:

(a) Hydrochloric acid:

Hydrochloric acid of A.R. quality was used .it was standardized by N/10 sodium tetra borate (borax) solution.

(b) Ammoniummolydbate solution:

8.3 g of ammonium molybdate was dissolved in distilled water by thorough shaking and made up to mark in 100 ml standard flask.

(c) Amidol reagent:

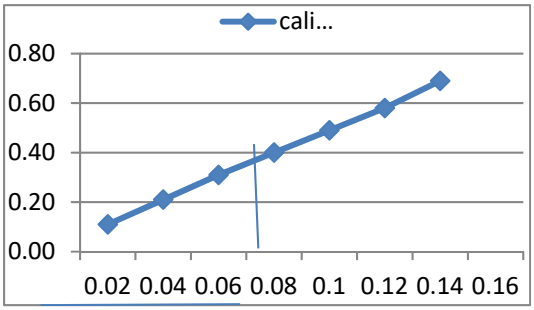
1.4 g of amidol (impure, brownish colour) was taken in a conical flask covered with a carbon paper, 2 g of activated charcoal and 10 ml of distilled water were added into conical flask. Then it is shaken thoroughly for 20 minutes. The colorless amid solution so obtain was filtered into a solution contains 100 ml solution Meta bisulphate (20%). The reagent so prepared was kept in dark and cool place. This solution gradually decomposes and yellow after about six days then it was of no use, and it is discarded.

Corresponding Author : email :

International Journal of Fundamental & Applied Research
Website : www.ijfar.org ,(ISSN- 2320-7973 Volume-5 Issue -10+11 Month – January+February 2018 pp. (04 – 06)

(ii) Buffer solutions:

To maintain different ph values buffer solution (at 20 degree c and 150 degree) which is reported in the table .the interpolated values of these buffer solutions at 98 degree= 100 degree were used. The table illustrates the fact there is so much less variation of the ph values in the lower ph logarithm in higher ph region .this is because at low ph, the buffer solution consists of weak acid, consequently the variation consists of these acid is more likely to



de predominant factor, influencing the variation of ph with tempt..

Similarly in higher ph region the possibility of error will be less. The maximum value of error involved is less then at 98 degree is presumed to be equivalent to ph values at 100 degree.

Table -4.B-1

SNO.	Buffer composition mol dm^{-3}	Measured pH at		calculated pH at 100°
		20°	150°	
1.	0.05 KCl 0.0645 HCl	1.20	1.26	1.24
2.	0.05 KCl 0.0067 HCl	2.20	2.20	2.20
3.	0.05 KCl 0.0147 HCl	3.20	3.41	3.33
4.	0.05 P'	3.97	4.26	4.17
5.	0.05 P' 0.03 NaOH	5.20	5.88	5.60
6.	0.05 P'	6.00	6.70	6.43
	0.0455 NaOH			
7.	0.05 H_3BO_3 0.05 KCl 0.00261 NaOH	7.80	7.26	7.46

P' = potassium hydrogen phthalate

(iii) Calibration of spectronic 20^+ spectrophotometer

Calibration of photoelectric colorimeter:

A standard solution of potassium dihydrogen phosphate was used to calibrate "Systronix" type colorimeter 1.0968g potassium dyhydrogen phosphate was dissolved in 250ml of

1.0967 g of potassium dihydrogen phosphate was dissolved in 10 ml of distilled water in 250 ml standard flask. then it was made upto the mark 5.0 ml of this standard solution (containing 1 mg phosphorus\ml) was distilled water 5.0ml of this solution having 1.0mg of phosphorus per ml was diluted 50 times. The second solution so obtained containing 0.02mg of phosphorus per ml. used to calibrate the instrument. In each run ,a known volume (0.5-7.0ml) of standard solution ,2.0ml of 10M-HCl,2.0ml of amidol reagent and 1.0ml of ammonium molybdate were taken in a 25ml standard flask and the volume was made up to the mark with distilled water. Optical density of blue colour so obtained was plotted against mg of phosphorus present as inorganic phosphate.

Applications

Organophosphates refer to a group of insecticides acting on the enzyme Acetylcholine esterase. Some of their pesticides irreversibly inactivate ACHE which is essential to nerve functioning in insects and many other animals. Due to their versatile application, they are

Corresponding Author : email :

International Journal of Fundamental & Applied Research
Website : www.ijfar.org ,(ISSN- 2320-7973 Volume-5 Issue -10+11 Month – January+February 2018 pp. (04 – 06)

common carriers of organic groups in biosynthesis. They are widely used in a number of ways as fertilizers. In recent years much interest has been shown in the synthesis and mechanism of hydrolytic fragmentation of phosphate esters. Primarily due to their importance in biochemical system. The enzyme acetyl cholinesterase is a target of organophosphate toxicants which itself is biologically significant. Aromatic nitro compounds also posed toxic character, due to the nitro group present in aryl ring. The introduction of phosphate group may enhance or reduce the toxic nature, so that the resultant C-O-P esters may act as a safer (reduction in toxic nature) systems, reflecting the activity of drugs even. The disadvantages of these phenyl phosphate esters are its remarkable stability, although sometimes, hydrolytic condition.

New research in the field of kinetic hydrolysis of phosphate esters can help the academician to design the ortho phosphate pesticides with low toxicity and discovery of novel bioactive molecules.

References

1. Metcalf, R.L. and March R.B J. Econ Entomol, 42 721 (1949).
2. Menzer. R.E. and Dauterma W.C. J. Agric. Food. Chem 18 1031 (1970).
3. Ohkawa, H. Oshita, H. and Miyamoto. J. Biochem Phormatol. 29 2721 (1980a)
4. Smith, T.D. U.S. patent, 3. 539. C.A. 75. 34391 (1971).
5. Dubois K.P. Kinoshita F. and Jackson. P. Arch lnt Pharmacodyn thes. 169 108 (1967)
6. Riser, A. protar 169 (11/12). 132 (1950)
7. Loid. P. 190.204. 248.
8. Kosolapoff, G.M. and Maies. L. Eds. “Organic Phosphorus Compounds” Vol. 1-7 Interscience, New York (1972-1976)
9. Kosolappoff G.M. “Organopnosphorus Compounds” John Wiley New York (1950)
10. Fest C. and Schmidt, K.J. Insecticide phosphorsaure ester in chemise der pflanzenschatc und Schadling-Sbekenp fungsmittel. Vol 1 Wegler R. Ed. Springer Verlag. Berlin. 1970.
11. Allen, R.J.L., Biochem., J., 34,858 (1940).
12. Kosower, E.M., An introduction to physical organic chemistry. John Wiley and Sons , INC, New York and London, 51 & 68 (1968).
13. Schaleger, L.L and Long. F.A. Advances in Physical Organic Chemistry. Academic press London, P.I. Vol. 1 (1963).
14. Auger, V., and Dupis, P., C.R. Lebd. Seanc. Acad. Sci., Poris, 146,1152 (1904).
15. John, A.D., St, U.S. Pat. Z., 462, 306 (1923).
16. Shuman, R.L., U.S. Pat. Z., 2, 133 (1938).
17. Willamson, Ann., 92,316 (1854).

Corresponding Author : email :