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Spectral Studies of Some Prepared Phosphorus-Nitrogen Compounds

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ABSTRACT

The study reveals the preparation and spectral studies of some aminophosphine and diaminophosphine halides namely N- ethyl-isopropylamino dichlorophosphine (I), N-propyl-s-butyl amino dichlorophosphine (II), N- isobutyls-butyl amino dichlorophosphine (III), N-morpholino dichlorophosphine (IV), chloro bis (N--methyl-isobutyl mino) phosphine (V), chloro bis (diethly amino) phosphine (VI) and chloro bis (diphenyl amino) phosphine (VII), through the reaction of phosphorus trichloride and the secondary amine under anhydrous condition. The molecular structure of the compounds were investigated by infrared, ^1H nmr and mass spectra. The spectral studies were utilised in some qualitative and quantitative calculations. Some relations concerning the effect of various substituents on band positions and excitation energies (E) were constructed.

INTRODUCTION

Phosphorus-nitrogen compounds have recently received attention since their derivatives have a wide applications in industry as detergents, flame retardants, pepticides and plastics. These compounds are phosphazanes which contain formal phosphorus–nitrogen single bonds[1]. It can be classified into four types depending on the coordination of phosphorus nitrogen single bond. A cyclic equatorial P–N bond has been reported[2]. The bond length of P–N inphosphazanes is greater for P (III) compared to P (Vi) [3]. The lone pair of electrons on the nitrogen atom is partially or wholly delocalised towards the phosphorus atom. In recent years more studies were done on phosphazane compounds[4]. Burg[5]

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had reported a new types of amino-phosphine by Grignard reaction on $(CH_3)_2 NPCl_2$, where P–N bond was susceptible to further Grignard reaction. Noth [6] had synthesised the tertakis (dimethyl amino) phosphine and pentakis (dimethyl amino) triphosphine by the reaction of chloro bis (dimethyl amino) phosphine and sodium metal. The action of $.PCl_3$ on aromatic amine hydrochloride was studied [7,8] and gave the corresponding ph–NPCI compounds. Electron diffraction studies on the amino halo phosphines R_2NPX_2 had provided evidence for a planar arrangement of ligands around the nitrogen atom [9,10]. Tetravalent phosphorus compounds are highly reactive towards nucleophiles[11], The reactivity is due to polarizability of P (III) atom, where it can be deformed by both +ve and —ve charges. The nucleophilic action can be attirbuted to a factors as the I.P., the energy of sp^3 bond with a large coloumbic contribution and the low repulsion energy between the nucleophile and the electronically saturated center[12]. The first two parameteres determine the high nucleophilic reactivity of the amines, but owing to factor three, phosphine reacts more readily at negative centres i.e. halogen, oxygen and sulphur. The nucleophilic attack on P III is particularly facile owing to the reduced repulsion on approaching the nucleophilic and the greater polarizability of phosphorus atom[13].

The IR absorption spectra of phosphorus-nitrogen compounds is highly characterised and can be used as a molecular finger print for identification purposes and is quantitatively related to the number of absorbing molecules present [14, 15].

The ν_{P-N} have been determined by several workers[16–18] with a value of 743 cm^{-1}, where the ν_{P-N-c} group with the two bands in the region 702–736 and 489–1006 cm^{-1} were assigned to ν_{P-N} and ν_{N-c} respectively. The ν_{P-c2} in most organo phosphorus compounds lies within 420–587 cm^{-1} region and are sensitive to the number and nature of groups bonded to phosphorus atom [20–26].

The nmr studies are of considerable interest in phosphorus chemistry. The chemistry shifted peaks in p^{31} nmr show a fine structure arising from p^{31} nucleus interacting with other magnetically active nuclei in the same molecule. The large chemical shift may attribute to the change in bond angles for some tetravalent phosphorus compounds [27–29]. The mass spectrum of some alkyl amino phosphine have been studied by

Holmann ([30]) and Clasen ([30]), while those of phosphorus-nitrogen compounds were studied by Gregor et al. ([31–33]).

EXPERIMENT

i – All chemicals used were BDH and Merck grade. The dry diethyl ether was used as solvents and purified by recommended method(35).

ii– Preparation of phosphorus–nitrogen compounds from phosphorus trichloride reacts with the secondary alkyl amine under anhydrous conditions and gives either the alkyl amino dichloro phosphine or the chloro bis (alkyl amino) phosphine.

The reaction product depends upon the amount of reactant, temperature, nature of radical and time of reflux.

The molar ratio of PCl_3: alkyl amine is 1:2 gives the alkyl amino dichloro phosphine and the formed by product of the amine hydrochloride can be further reacted with PCl_3 to give the same product, but with molar ratio of 1:4, the chloro bis (alkyl amino) phosphine is formed. The different phosphozane compounds were prepared in the present study by stirring a cold solution (–3 °C) of PCl_3 (20 gm) in three necked flask with a condenser for 15 minutes using a magnetic stirrer, then the calculated amount of the secondary amine was dissolved in 400 ml of dry ether and add dropwise under cooling and stirring conditions for 2 hrs. The mixture was further stirred for 1.5 hrs to mentain the room temperature, then stirred vigoursly for 5 hours where it becomes yellow. The product was filtered under vacuum to separate the solid amine hydrochloride and washed several times with dry ether. The solvent was then evaporated and the product was distilled under vacuum and a pure colourless liquid was collected and its b.p at the applied pressure was recorded.

The purity of the product was checked by thin layer chromatography using a mixture of butanol, acetic acid and water with a ratio of 4 : 1 : 1 (v / v) as an eluent.

The following compounds were obtained and b.p, refractive index and chemical analysis were determined:

I– N–Ethyl-isopropyl amino dichloro phosphine

b.p 40–41 °C at 100 mm $\quad n_D^{20} = 1.4801$

Analysis found: % C ,30.2; H, 6.4; N, 8.2; Cl, 370; P, 15.9.
For $C_5H_{12}NPCl_2$

Calcd.: % C, 31.9; H, 6.38; N, 7.4; Cl, 37.7; P, 16.48.

II– N–Propyl-s-butyl amino dichloro phosphine

b.p 65°C / 200 mm $n_D^{20} = 1.4890$

Analysis found: % C, 38.5; H, 77; N, 6.1; Cl, 33.2; P, 14.9
For $C_7H_{16}NPCl_2$

Calcd.: % C, 38.8; H, 7.4; N, 6.48; Cl, 32.87; P, 14.35

III–N–Isobutyl-s-butyl amino dichloro phosphine

b.p 68°C / 200 mm $n_D^{20} = 1.4905$

Analysis found: % C, 39.9; H, 8.4; N, 6.2; Cl, 30.5; P, 12.9
For $C_8H_{18}NPCl_2$

Calcd.: % C, 41.73; H, 7.8; N, 6.08; Cl, 30.86; P, 13.47

IV–N–Morpholino dichloro phosphine

b.p. 28°C / 200 mm

Analysis found: % C, 24.2; H, 4.7; N, 6.5; Cl, 36.9 ; P. 15.4
For $C_4H_8NOPCl_2$

Calcd.: % C, 25.5; H, 4.25; N, 7.4; Cl, 37.7; P, 16.4

V–Chloro bis (N–Methyl–isobutyl amino) phosphine

b.p. 58°C / 200 mm $n_D^{20} = 1.4830$

Analysis found: % C, 48.5; H, 8.7; N, 10.5; Cl, 11.5; P.12.3
For $C_{16}H_{24}N_2PCl$

Calcd.: % C, 50.3; H, 10.6; N, 11.74; Cl, 14.8; P, 12.99

VI– Chloro bis (diethyl amino) phosphine

b.p. 48°C / 100 mm $n_D^{20} = 1.4901$

Analysis found: % C, 41.9; H, 9.0; N, 12.9; Cl, 15.0; P, 13.8
For $C_8H_{20}N_2PCl$

Calcd.: % C, 45.6; H, 9.5; N, 13.3; Cl, 16.8; P, 14.7

VII– Chloro bis (diphenyl amino) phosphine b.p. 38°C

b.p. 38°C / 300

Analysis found: % C, 70.1; H, 4.2; N, 6.1; Cl, 9.5; P, 8.1

For $C_{24}H_{20}N_2PCl$

Calcd.: C, 715; H, 4.9; N, 6.95; Cl, 8.81; P, 7.7

iii- Equipments:

a- The IR spectra were recorded using SP 1200 spectrophotometer. The solids were prepared by grinding the solid compounds with KBr in in discs. The liguids were prepared in liquid cell or as a thin films where a calibration using a polystyrene strip was performed.

b- ^1H nmr spectra were obtained from a varian associates Model A-60 spectrometer equipped with a 60 MC. / sec. radio frequency source.

c- The MS polarograms were recorded using MAT 112 Mass Spectrometer. The operation was performed under elecctron energy of 70 ev with electron impact ionization.

d- The microanalyses were carried out by the microanalytical laboratory Cairo University.

e- The refractive index was measured using a CARL ZEISS type refractometer at 20°C.

RESULTS AND DISCUSSION

The study reveals the preparation of some alkyl amino dichloro phosphine compounds namely. N-Ethyl-isopropyl dichloro phosphine I, N-propyl-s-butyl-dichloro phosphine II, N-isobutyl-s-butyl dichloro phosphine III, N-morpholino dichloro phosphine IV, as well as some chloro bis (dialkyl amino) phosphine as chrolo bis (N-methyl-isobutyl amino) phosphine V, chloro bis (diethyl amino) phosphine VI and chloro bis (diphenyl aminlo) phosphine VII.

The structure of these compounds have been determined by means of chemical analysis, refractive index and spectral methods as IR, ^1H nmr and mass spectrometry (MS).

A- IR studies:

The infrared absorption spectrophotometry was helpful in elucidating the structure of these compounds and illustrated the effect of different substituent" frequencies as follows: The characteristic bands for com-

pound I as representative for these compounds is given in table (1) and the cumulative data for all the compounds are given in table (2). The bands within 2995–2950 and 2870–2775 cm^{-1} region can be assigned to asymmetric and symmetric stretch of CH_3 group, while these bands located at 2942–2920 and 2850–2720 cm^{-1} may attribute to the inplane and out of plane vibration of CH_2 group. The bands with inflection located at 1478–1450 and 1450–1350 cm^{-1} may be due to asymmetric and symmetric deformation of methine group (γCH). The frequencies of the γ_{CH} have been correlated and a linear relationship was obtained from the representation of γ_{CH} asymmetric versus the γ_{CH} symmetric for the prepared phosphorus-nitrogen compounds. The relation gave a straight line from which the following relation have been concluded:

Table (1)

Vibrational Spectrum of (C_2H_5) (iso–C_3H_7) $NPCl_2$
(N–Ethyl–isopropyl amino dichloro phosphine).

em^{+1}	I	Proposed Assignment
2950	V.S.	CH_3 Stretch
2920	Sh.S	CH_3 i. PStretch.
2840	W.M.	CH_3 Stretch
2800	V.W.	CH_3 Stretch
1590	M	CH_3 Deformation
1452	V.S.	CH_3 Deformation
1385	Sh.	CH_3 Defor + CH_1 0.0.PO Scisoors
1375	V.S.	CH_3 i. P. Scissors.
1295	M	CH_3 Yock
1176	S	CH_2 O.O.P. Wag.
1165	S	CH_2 i.P. Wag.
1118	S	CH_3 Yock
1080	M	CH_3 Yock
1070	V.W.	CH_2 i.P. Twist.
1045	S	P–N asym, PNC Stretch.
973	S	NC_2 Stretch
942	M	NC_2 Stretch
922	W	NC_2 Stretch
894	M	NC_2 Stretch
805	M	CH_2 Yock
778	V.S.	P–N Stretch Symm.
645	M	PNC (PN) Sym. Stretch.
482	M	P–Cl Sym. Stretch.
410	W	PNC Deformation
312	M	PNC Deformation.

V.S. = Very Strong
M = Medium
W = Weak
Sh = Shoulder

i.p = in plane
0.0.P = out of plane

Table (2) Cumulative Table

Compound		ν P – N					ν N<C C					ν P – Cl					γ C – H				
	Q	ν	A	log To/T	Δν 1/2	E	ν	A	log To/T	Δν1/2	E	ν	E	log To/T	Δν 1/2	E	ν	A	log To/Y	Δν 1/2	E
I $C_5H_{12}NPCl_2$	2.5	778	1.348	0.2697	0.25	0.096	973	1.9	0.273	0.3	0.12	482	8.15	1.0188	0.4	0.059	1590	1.414	0.1767	0.4	0.197
II $C_7H_{16}NPCl_2$	3.5	736	2.778	0.3474	0.4	0.091	968	2.418	0.39	0.31	0.1199	463	6.634	0.8092	0.41	0.057	1478	1.500	0.1895	0.39	0.183
III $C_8H_{18}NPCl_2$	4.5	714	3.564	0.2969	0.6	0.088	960	2.534	0.422	0.3	0.1189	461	5.068	0.3620	0.7	0.0577	1470	2.588	0.1176	1.1	0.182
IV. $C_4H_8NPCl_2$		800	9.844	0.7572	0.65	0.0992	898	3.446	0.383	0.45	0.1113	531	8.388	1.3979	0.3	0.0658	1446				0.1792
V. $C_{10}H_{24}NPCl$	2.5	743	2.464	0.1122	1.1	0.092	962	1.64	0.273	0.31	0.1191	538	12.848	0.9179	0.7	0.066	1468	1.396	0.0436	1.6	0.1818
VI. $C_6H_{20}N_2PCl$	2.14	676	2.655	0.3319	0.8	0.082	915	3.204	0.533	0.6	0.113	485	8.504	0.6541	0.65	0.60	1465	1.897	0.1581	1.2	0.1815
VII. $C_{12}H_{16}N_2PCl$		805	5.184	0.5761	0.45	0.0997	1018	1.104	0.368	0.15	0.1262										

$Q = \frac{\text{M.wt Of Side Chain}}{\text{no of N atoms}}$ – A = absorbance $\Delta\nu_{1/2}$ half hand width

ν = Frequencey (Cm^{+1}) E = Excitation Energy

$$\gamma CH_{sym} = 705 + 0.47\ \gamma CH_{asym}.$$

It was found that the relation accomodated the results for the studied compounds very well and can be utilised for the determination of that band frequency for any similar compounds. The excitation energy (E) in ev was calculated from IR spectra of γ-$_{CH}$ in table (2). The energy values were found to be inversely related to Q values to certain limits ($Q \cong 110$) then stabilises, where:

$$Q = \frac{\text{Mol. wt. of the side chain attached to nitrogen atom Adjacent to phosphorus}}{\text{Number of nitrogen atoms}}$$

The results indicated that there is apparent connection between the absorption frequency of methine group and the degree of substitution in energy values occur with increasing the length of the side chain above the calculated limits and any inductive effect is over–shadowed by the N–alkyl group. The band frequencies at 778, 736, 714, 800, 743, 676 and 805 cm^{-1} may attributed to ν_{P-N} for compounds I, II, III, IV, V, VI and VII respectively, while the bands located at 973, 968, 966, 898, 962, 915 and 1018 cm^{-1} corresponds to ν_{C-N} in the combination $P\text{–}N\lessdot^{C}_{C}$.

The inflection at 482, 463, 461, 531, 538 and 485 cm^{-1}can be assigned as ν_{P-C}l for compound (I-VI). Some of these characteristic bands have been studied quantitatively [(ν_{c-N}, ν_{P-N} and ν_{P-c}l)] and the absorbarnce values (A) were determined from the relation

$A = \frac{1}{CL} \log \frac{To}{T} \cdot \Delta\gamma \frac{1}{2}$, where $\Delta\gamma \frac{1}{2}$ is the calculated half

L = path length and C is concentration (C = 1).

In order to trace the different parameters affecting the substituting effect in the N-alkayl group, the values of A, E and Q were correlated for the different group frequencies as follows:

i— The values of A, E and Q for ν_{P-N} were found to be inversely related indicating that the frequency of P-N group is highly affected by substitutoin.

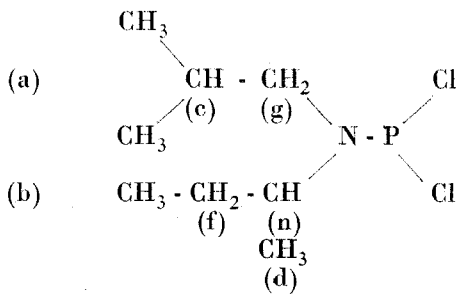
ii— For ν_{P-Cl}, the energy (E) values decrease with increasing the molecular weight of the chain attached to the nitrogen atom and a noticable bathocromic shift occurred in band position if the chloride is replaced by iodide in some compounds [36]. The shift in band frequencies may due to decreasing the polarizing effect of phosphorus atom in these compounds.

iii— E values were found to be proportionaly related to Q for $N^{\nu}<^{C}_{C}$, but the slope of that line was small indicating that the $N<^{C}_{C}$ group was slightly affected by substitution and the energy increases according to the following sequence:

$$\text{Et, isopropyl} > N > \text{propyl, butyl} > N > \text{iso-butyl, s-butyl} > N > \text{Et, Et} > N$$

^{1}H nmr studies:

The ^{1}H nmr spectra of the phosphorus-nitrogen compounds illustrate the overlap of signals assigned to different types of proton enviroments. Some of these signals show a multiplet hyperfine structure according to the first order splitting rule. A resultant downfield shift in δ values occur. If compared with these of the reactant secondary amines due to the shielding effect of the phosphorus atoms formed in the reaction product. The chemical shifts relative to TMS signals were recorded here for compound (III) as an example. but a detailed ^{1}H studies for the series were summarised elsewhere [36]. The structure of compound III can be represented as follows:



The spectrum illustrates that the protons of CH_3 groups designed by the letter (a) appeared at 0.8 ppm as a doublet of triplet, while (b) appears at $\delta = 0.9$ ppm as triplet and (d) at $\delta = 1.2$ ppm as a doublet

in the intensity ratio (1:1). The methine proton (e) appears at $\delta = 1.55$ ppm in the form 1:5:10:10:10:51 and (c) at 1.9 ppm as septet, while the methylene proton (g) appears at $\delta = 2.9$ ppm as a doublet of doublet with $J_{H-H} = 7.5$ Hz and $J_{P-H} = 15$ Hz, whilst the proton (f) appears at $\delta = 3.5$ ppm as a doublet of quartet due to vertual coupling with the methyl proton (b) with the methine proton (e).

Mass Spectrometry (MS):

The molecular ion of the type $Cl_2PNR_2^+$ or $ClP(NR_2)_2^+$ have been examined to prove the structure of the prepared compounds. Such compounds have several possible decomposition routes:

1— Loss of successive neutral chlorine

$$Cl_2PNR^+ \xrightarrow{-2Cl} PNR^+$$

2— Loss of neutral nitren $Cl_2.PNR^+ \longrightarrow Cl_2P^+$

3— Fragmentation of group NR while still attached to chlorine $Cl_2PNR^+ \longrightarrow Cl_2PN^+$

The MS fragmentation patterns were studied and the spectrum of compound VI as representative for this series in table (3) shows positive ions M^+, $(M-Cl)^+$, $(M-NC_4H_5)^+$ and $(C_2H_5)^+$ at m/e = 210.5, 175,

Table (3)

Mass Spectrum Of $C_8H_{20}N_2PCl$

Ion	RI m/e	RI at room temp	RI 60°C	RI 100°C
M^+	210.5	6.38	4	2.2
$(M-Cl)^+$	175.	6.3	5	–
$(M-C_2H_5)^+$	181.5	10.6	–	2
$(M-NC-_4H_5)^+$	138.5	52.1	20	4.2
PCl^+	66.5	2.3	4	–
$(NC_4H_{10})^+$	72	23.4	30.5	22.0
$(C_2H_5)^+$	29	100	100	100
$C_2H_5)^+$	28	15	24	22
$(C_2H_3)^+$	27	4.2	6	6
$(CH_3)^+$	15	5.3	8.2	7
$(CH_2)^+$	14	3.2	4.2	7.2
(Cl)	35.5	2.3	8	6
$(M-NC_4H_{10})-C_2H_5$ C_2H_5NPCl	109.5	6.38	4.2	–
$(M-NC_4H_{10})-Cl$ C_2H_5NP	103	5.3	10	10
$(M-Cl)-2NC_4H_{10})$	31	11.7	80	16
$(M-Cl)-C_4H_{10})$	59	2.3	86	66

138.5 and 29 where RI = 6.38, 6.3, 52.1 and 29. The study illustrates that the decomposition of these compounds occurs via route 1, 2 and 3 but the majority of the ions produced via rote 1 and the fragmentation of compound II gives $(M—21C)^+$ ion possible having the quasi amonium structure. $(R — N = P)^+$ The sequence of fragmentation in the MS study is in complete confirmity with the E values calculated for the different groups from infrared and energy values of N—C>P—N> PCl.

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