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Fourier Transform ^{1}H NMR and IR Spectra of Novel O-Aryl-O-ethyl-2-chloroethyl Phosphonates

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Fifteen novel O-aryl-O-ethyl-2-chloroethyl phosphonates with their FT-^{1}H NMR and IR spectral data are reported.

Key Words: O-Aryl-O-ethyl-2-chloroethyl phosphonates, ^{1}H NMR, IR Spectra.

INTRODUCTION

Organophosphorus compounds have added attractions because of their widespread use as pesticides, insecticides and nerve gases[1,2]. The proton magnetic resonance spectra of organophosphorus compounds exhibit a characteristic feature of splitting the signals of the protons proximate to phosphorus atom. This is because phosphorus present[3] in nature in 100 % abundance as ^{31}P with the spin quantum number ½. Infrared spectroscopy also gives characteristic peaks[4] for the identification of organophosphorus compounds. Recently, we have synthesized a series of novel O-ethyl-O-aryl-2-chloroethyl phosphonates which showed good fungitoxicity[5] and nematotoxicity[6]. Herein, the detailed ^{1}H NMR and IR spectra of these compounds are reported.

EXPERIMENTAL

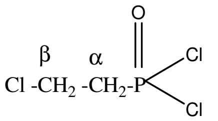
The phosphonates (**1-15**) were synthesized by condensing 2-chloroethyl phosphonyl chloride first with ethanol followed by substituted phenols in the presence of triethyl amine[5]. The ^{1}H NMR spectra were recorded on a Varian EM-360L,60 MHz instrument using CCl_4 as solvent with TMS as internal standard (chemical shifts in δ ppm and *J* values in Hz). The IR spectra were obtained by a Perkin-Elmer 457 spectrophotometer (liquid samples as liquid film or in CCl_4 and solid samples in KBr discs).

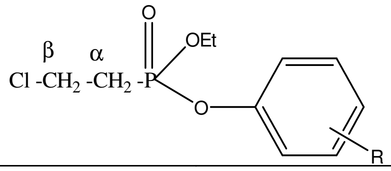
RESULTS AND DISCUSSION

The ^{1}H NMR spectra of 2-chloroethyl phosphonyl chloride (precursor of the prepared phosphonates **1-15**) showed two doublets of triplets at 3.2 and 3.95 δ accounting for O=P-$\mathbf{CH_2}$ and Cl-$\mathbf{CH_2}$, respectively. Both these doublets have coupling constants 16 Hz and 8 Hz for H-P coupling and H-H coupling, respectively. When the two chlorine atoms of 2-chloroethyl phosphonyl chloride were replaced by

O-ethyl and O-phenyl groups, as in case of phosphonate **1**, the coupling constant ${}^{2}J_{H-P}$ increases by 2 units and ${}^{3}J_{H-P}$ by 4 units. ${}^{3}J_{H-P}$ is further increased by 6-10 units in case of more -I groups introduced in the phenolic moieties as in other phosphonates **2**-**15**. Table-1 shows the comparison between the coupling constants of the phosphonates and their precursor.

TABLE-1





α-CH_2	β-CH_2	α-CH_2	β-CH_2
${}^{2}J_{H-P}$ =16 Hz	${}^{3}J_{H-P}$ =16 Hz	${}^{2}J_{H-P}$ = 18 Hz	${}^{3}J_{H-P}$ = 20 Hz
${}^{3}J_{H-H}$ =8 Hz	${}^{3}J_{H-H}$ =8 Hz	${}^{3}J_{H-H}$ = 8 Hz	${}^{3}J_{H-H}$ = 8 Hz

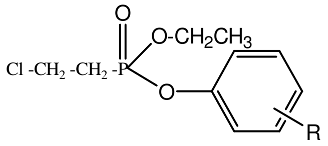
The ${}^{1}H$ NMR chemical shifts and coupling constants of various protons are presented in Table-2. The coupling constants ${}^{2}J_{H-P}$ and ${}^{3}J_{H-H}$ are found to be 18-19 Hz and 8 Hz, respectively for all the phosphonates, but ${}^{3}J_{H-P}$ for compound 11 (R=2-Cl,4-NO_2) and 13 (R=2,4,5-Cl_3) is found to be 22 Hz and that for **14** (R=2,4,6-Cl_3) is 24 Hz (Table-2). This is further increased in case of **15** (R=Cl_5) where the coupling constant is 26 Hz. In earlier report[7], in case of O,O-*bis*-aryl isopropyl phosphonates, ${}^{3}J_{H-P}$ was in the range of 19.5-21.5, whereas in present case it increases up to 24 Hz which is a new observation. These enhanced coupling constants with electron withdrawing substituents in the phosphonates can be explained by the theory proposed by Hendrickson *et al*[3].

The FT IR spectra of the synthesized phosphonates are given in Table-3, which shows the presence of all the peaks corresponding to P-O-alkyl, PO-alkyl, P-O-aryl, PO-aryl, P=O and P-CH_2 stretching frequencies apart from other expected peaks.

The P-O alkyl stretching showed absorbance at 818-887 cm^{-1}. In most of the cases, there are strong peaks, but a few of them have medium intensities. The compound **7** (R=2-Cl) and **11** (R=2-Cl,4-NO_2) showed weak peaks at 825 cm^{-1}. All the compounds showed strong peaks for PO-alkyl stretching at 1024-1051 cm^{-1}. In case of compounds **9** (R=3,4-Me_2), **10** (R=3-Me, 4-Cl) and **11** (R=2-Cl,4-NO_2), strangely there are two peaks at 1038 and 1051 cm^{-1}. Because of the intensities of both the peaks were found to be strong, it was undetermined to assign which peak is for PO-alkyl stretching. Same case was also observed in case of **14** (R = 2,4,6-Cl_3) where it came at 1025 and 1064 cm^{-1} both having strong intensities.

The P-O-aryl stretching was observed at 985-923 as mostly strong peaks. In earlier report[8], P-O, O-*bis*-aryl stretching was observed at 950-910 cm^{-1}. Hence it was concluded that P-O-aryl bond was stronger in case of present series as compared to the previous one.

TABLE-2
^{1}H NMR SPECTRAL DATA OF



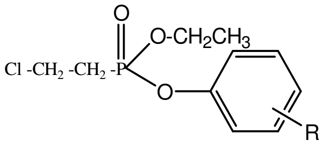
(**1-15**)

Com. No.	R	δ Values					
		$-OCH_2C\mathbf{H}_3$ (3H, t, *J*=8 Hz)	Cl-$CH_2C\mathbf{H}_2$-P=O- (2H,d, t)(J values are in Parentheses)	$-OC\mathbf{H}_2-CH_3$ (2H, q, *J*=8 Hz)	Cl-$CH_2C\mathbf{H}_2$-P=O- (2H,d, t)(*J* values are in parentheses)	-O-**Ar**	Others
1	H	1.28	2.40 (18Hz, 8Hz)	3.82	4.05 (20Hz, 8Hz)	7.38 (5H,s)	–
2	4-Me	1.29	2.40 (18Hz, 8Hz)	3.78	4.02 (20Hz, 8Hz)	7.22 (4H,s)	2.32(3H,s, Ar-**Me**)
3	4 –C (Me)$_3$	1.28	2.40 (18Hz, 8Hz)	3.78	4.05 (20Hz, 8Hz)	7.34 (4H,dd,*J*=9Hz)	1.32(9H,s, Ph-C$\mathbf{Me}_3$)
4	4-OMe	1.28	2.38 (18Hz, 8Hz)	3.74	4.00 (20Hz, 8Hz)	7.02 (4H,dd,*J*=9Hz)	3.80(3H,s, Ph-O-**Me**)
5	2-NO_2	1.36	2.56 (19Hz, 8Hz)	3.88	4.12 (20Hz, 8Hz)	7.8 (4H,m)	–
6	4-NO_2	1.34	2.52 (19Hz, 8Hz)	3.86	4.10 (20Hz, 8Hz)	7.6 (4H,m)	–
7	2-Cl	1.32	2.50 (18Hz, 8Hz)	3.82	4.02 (20Hz, 8Hz)	7.45 (4H,m)	–
8	4-Cl	1.28	2.40 (18Hz, 8Hz)	3.70	4.02 (20Hz, 8Hz)	7.32 (4H,dd,*J*=9Hz)	–
9	3,4-Me_2	1.28	2.30 (18Hz, 8Hz)	3.78	4.02 (20Hz, 8Hz)	7.08 (3H,m)	2.28(6H,s, Ar-$\mathbf{Me}_2$)
10	3-Me,4-Cl	1.30	2.36 (18Hz, 8Hz)	3.78	4.02 (20Hz, 8Hz)	7.2 (3H,m)	2.38(3H,s, Ar-**Me**)
11	2-Cl,4-NO_2	1.42	2.62 (19Hz, 8Hz)	3.82	4.20 (22Hz, 8Hz)	8.15 (3H,m)	–
12	2,4-Cl_2	1.34	2.52 (19Hz, 8Hz)	3.86	4.10 (20Hz, 8Hz)	7.45 (3H,m)	–
13	2,4,5-Cl_3	1.36	2.52 (19Hz, 8Hz)	3.76	4.10 (22Hz, 8Hz)	7.68(1H,s) & 7.74(1H,s)	–
14	2,4,6-Cl_3	1.36	2.66 (19Hz, 8Hz)	3.88	4.18 (24Hz, 8Hz)	7.50 (2H,s)	–
15	Cl_5	1.42	2.72 (19Hz, 8Hz)	3.88	4.18 (26Hz, 8Hz)	–	–

The PO-aryl stretching was observed at 1235-1202 cm^{-1} as strong peaks which is comparable with 1240-1200 cm^{-1} in case of previous series[8]. The most common P=O stretching was observed at 1268-1249 cm^{-1} all as strong peaks.

Another important vibration namely P-CH_2 stretching occurred at 1400 cm^{-1} in all the cases except **9** (R=3, 4-Me_2) where it was observed at 1406 cm^{-1}. All these peaks were having either medium or weak intensities. Apart from all these vibrations due to phosphorus nucleus, the aromatic C=C, aliphatic C-H and C-Cl stretching frequencies were observed at usual positions as shown in Table-2, but both the symmetric and asymmetric N-O stretching vibrations for NO_2 group substituted compounds were observed as medium or weak peaks.

TABLE-3
IR SPECTRAL DATA OF



(**1-15**)

Comp. No.	R	Medium	Stretching vibrations (cm^{-1})									
			P-Oalkyl	PO-alkyl	P-Oaryl	PO-Aryl	P=O	P-CH_2	Aromatic (C=C)	C-H	C-Cl	Others
1	H	LF	825.8 (m)	1024.9 (w)	926.5 (s)	1214.8 (s)	1262.9 (s)	1400.4 (m)	1489.4(s) 1592.3(m)	2927.2	765.4 (s)	–
2	4-Me	LF	825.8 (s)	1045.6 (s)	943.1 (s)	1216.0 (s)	1254.7 (s)	1400.4 (m)	1506.7(s) 1609.3(w)	2983.0	764.5 (m)	–
3	4-C(Me)$_3$	LF	840.9 (s)	1044.9 (s)	941.9 (s)	1218.1 (s)	1256.3 (s)	1400.4 (m)	1508.8(s) 1604.4(w)	2963.7	781.1 (m)	–
4	4-OMe	LF	834.4 (s)	1051.6 (s)	952.8 (s)	1202.9 (s)	1254.8 (s)	1400.4 (m)	1505.7(s) 1604.4(w)	2979.9	729.1 (m)	–
5	2-NO_2	LF	834.4 (m)	1038.4 (s)	952.8 (s)	1202.9 (s)	1249.0 (s)	1400.4 (m)	1505.7(w) 1605.8(w)	2987.0	781.1 (m)	1340.1(m) 1570.2(w)
6	4-NO_2	CCl_4	825.8 (s)	1038.4 (w)	952.8 (w)	1202.9 (s)	1249.0 (s)	1400.4 (w)	1518.8(m) 1604.4(w)	2966.7	765.4 (s)	1356.2(m) 1570.2(w)
7	2-Cl	LF	825.8 (w)	1038.4 (s)	926.5 (s)	1235.8 (s)	1254.6 (s)	1400.4 (w)	1479.3(s) 1584.6(w)	2993.1	768.6 (m)	–
8	4-Cl	LF	841.0 (s)	1038.4 (w)	933.1 (s)	1216.1 (s)	1254.6 (s)	1400.4 (s)	1485.9(s) 1597.8(m)	2979.9	781.7 (s)	–
9	3,4-Me$_2$	LF	887.0 (s)	1038.4(s) 1051.6(s)	966.0 (s)	1202.9 (s)	1255.6 (s)	1406.9 (m)	1505.7(m) 1617.6(w)	2979.9	764.5 (w)	–
10	3-Me,4-Cl	CCl_4	854.1 (m)	1038.6(s) 1051.6(s)	972.6 (m)	1235.8 (s)	1268.7 (s)	1400.4 (w)	1479.3(m) 1584.6(w)	2986.5	765.4 (s)	–
11	2-Cl,4-NO_2	LF	825.8 (w)	1038.6(s) 1051.6(s)	972.6 (m)	1216.1 (s)	1249.0 (s)	1400.4 (w)	1532.0(m) 1591.2(m)	2986.5	748.8 (m)	1340.1(s) 1570.2(w)
12	2,4-Cl_2	LF	818.1 (s)	1036.4 (s)	923.9 (s)	1235.2 (s)	1256.6 (s)	1400.4 (m)	1489.4(s) 1584.6(m)	2979.9	745.8 (w)	–
13	2,4,5-Cl_3	LF	854.1 (s)	1045.0 (s)	952.8 (s)	–	1255.6 (s)	1400.4 (m)	1479.3(s) 1584.6(w)	2979.9	781.1 (w)	–
14	2,4,6-Cl_3	KBr	825.8 (s)	1025.2(s) 1064.7(s)	985.7 (m)	1202.9 (m)	1249.0 (s)	1400.4 (w)	1453.0(s) 1558.3(m)	2960.1	781.1 (w)	–
15	Cl_5	KBr	847.5 (m)	1038.4 (s)	972.6 (m)	1235.6 (w)	1268.7 (m)	1400.4 (w)	1453.0(m) 1538.6(w)	2979.1	715.9 (m)	–

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