

M. El-Deek, K. El-Badry and S. M. Abdel-Wahhab

Departments of Chemistry, Faculty of Science and University College for Women, Ain-Shams University, Cairo, Egypt

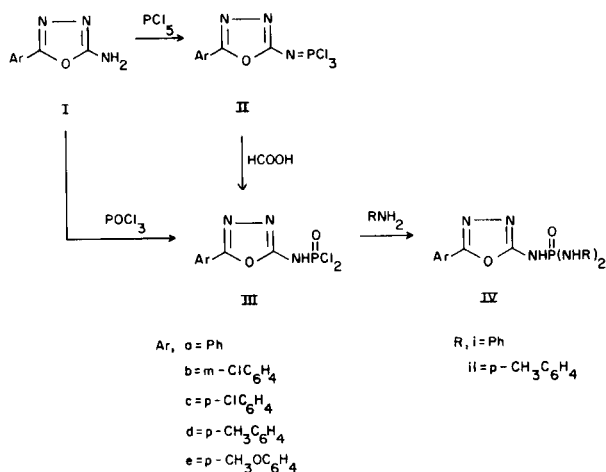
Received March 15, 1979

Stable *N*-(5-aryl-1,3,4-oxadiazol-2-yl)phosphorimidic trichlorides (II) are obtained by refluxing 2-amino-5-aryl-1,3,4-oxadiazoles (I) with one equivalent of phosphorus pentachloride in dry benzene. The reactions of the phosphorimidic trichlorides were also studied.

J. Heterocyclic Chem., 16, 1097 (1979).

The reaction of aromatic amines with phosphorus pentachloride leads to arylphosphorimidic trichlorides and has been reported by Kirsanov, *et. al.* (1). Recorded in the literature are also a number of reactions, *e.g.*, diazotization of aminooxadiazoles (I) (2), which have been used to demonstrate the aromatic nature of the oxadiazole ring. The success of the diazotization of I coupled with our interest in heterocyclic systems bearing phosphorus substituents led us to investigate the reaction of the five-membered heteroarylamines (I) with phosphorus pentachloride.

When I was heated under reflux in dry benzene with an equal amount of phosphorus pentachloride until the evolution of hydrogen chloride gas ceased (6-8 hours), phosphorylation of the amino group occurred, yielding *N*-(5-aryl-1,3,4-oxadiazol-2-yl)phosphorimidic trichlorides (II). Structural assignments were based mainly on ir spectroscopic data and chemical reactions of the phosphorimidic trichloride group.



Ir Spectra.

The ir spectra of all the compounds (IIa-e) display a band at 1260-1300 cm^{-1} due to the $\text{P}=\text{N}$ stretching vibration (3a) with the concomitant disappearance of the NH stretching vibration at 3300 cm^{-1} which appeared in the ir spectra of the aminooxadiazoles (I). The band at 570 cm^{-1}

is assigned to the P-Cl vibration (3b). The ir spectra also show cyclic $\text{C}=\text{N}$ stretching bands at 1640-1690 cm^{-1} . The position of absorption in this region appears at higher frequencies than the corresponding absorption at 1590-1640 cm^{-1} in the parent aminooxadiazoles (I). This shift may be due to the conjugation of the strong electron-attracting $\text{N}=\text{PCl}_3$ group with the oxadiazole ring.

Reactions.

Two reactions were investigated and are discussed below.

Formolysis (4).

With one mole of anhydrous formic acid, the oxadiazolylphosphorimidic trichlorides (II) reacted readily in dry benzene at room temperature yielding the corresponding *N*-(5-aryl-1,3,4-oxadiazol-2-yl)phosphoramidic dichlorides (III). These products precipitated almost immediately. These same derivatives (III) have also been obtained by refluxing the aminooxadiazoles (I) for 6 hours in phosphoryl chloride. The ir spectra of III show a strong band at 1220-1250 cm^{-1} , attributable to $\text{P}=\text{O}$ stretching (3c) and a broad band at 3300 cm^{-1} (NH).

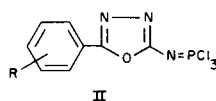
Reaction of the Dichlorides (III) with Aromatic Amines.

When four moles of aniline or *p*-toluidine were allowed to react with one mole of phosphoramidic dichlorides (III), nucleophilic displacement of the two chlorine atoms occurred, yielding stable dianilides (IV; R = Ph) and di-*p*-toluidides (IV; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$). The ir spectra of IV show two bands at 3430 and 3240 cm^{-1} due to NH stretching and a sharp band at 1210 cm^{-1} attributed to $\text{P}=\text{O}$ stretching (3c).

EXPERIMENTAL

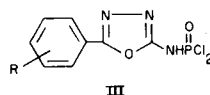
Because of the moisture sensitivity of phosphorimidic trichlorides and phosphoramidic dichlorides, all transfers and handling of these compounds were conducted in a dry box. Anhydrous solvents such as ether and benzene were dried over sodium and filtered prior to use. Elemental analyses for carbon, hydrogen and phosphorus were performed by Alfred Bernhardt, West Germany. Nitrogen analyses were carried out by El-Nasr Pharmaceutical Chemical Company, Cairo, Egypt. Chlorine analyses were determined for freshly prepared samples using mercuric nitrate as described by Vogel (5). Infrared spectra were recorded on a

Table 1

N-(5-Aryl-1,3,4-oxadiazol-2-yl)phosphorimidic Trichlorides

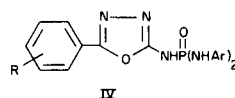
Compound No.	R	M.p., °C	Formula	Cl	Analysis %		Found	
					Calcd.	N	Cl	N
1	H	170	C ₈ H ₅ Cl ₃ N ₃ OP	35.91	14.16	35.72	14.09	
2	<i>m</i> -Cl	132	C ₈ H ₄ Cl ₄ N ₃ OP	42.90	12.68	42.74	12.45	
3	<i>p</i> -Cl	176	C ₈ H ₄ Cl ₄ N ₃ OP	42.90	12.68	42.68	12.70	
4	<i>p</i> -CH ₃	172	C ₉ H ₆ Cl ₃ N ₃ OP	34.29	13.52	34.38	13.36	
5	<i>p</i> -CH ₃ O	155	C ₉ H ₇ Cl ₃ N ₃ O ₂ P	32.61	12.86	32.49	13.04	

Table 2

N-(5-Aryl-1,3,4-oxadiazol-2-yl)phosphorimidic Dichlorides

Compound No.	R	M.p., °C	Formula	Calcd. Cl	Analysis %		Calcd. Cl	Found N
					Found N	Found N		
1	H	175	C ₈ H ₆ Cl ₂ N ₃ O ₂ P	25.53	15.10	25.63	14.83	
2	<i>m</i> -Cl	143	C ₈ H ₅ Cl ₃ N ₃ O ₂ P	34.08	13.44	34.30	13.34	
3	<i>p</i> -Cl	183	C ₈ H ₅ Cl ₃ N ₃ O ₂ P	34.08	13.44	34.21	13.32	
4	<i>p</i> -CH ₃	185	C ₉ H ₆ Cl ₂ N ₃ O ₂ P	24.31	14.38	24.26	14.27	
5	<i>p</i> -CH ₃ O	156	C ₉ H ₆ Cl ₂ N ₃ O ₃ P	23.05	13.63	22.98	13.40	

Table 3

N-(5-Aryl-1,3,4-oxadiazol-2-yl)phosphoramidic Dianilides and Di-*p*-toluidides

Compound No.	R	Ar	M.p. °C	Formula	Analysis % (a)	
					Calcd. N	Found N
1	H	C ₆ H ₅	218	C ₂₀ H ₁₆ N ₅ O ₂ P	17.90	17.70
2	<i>m</i> -Cl	C ₆ H ₅	220	C ₂₀ H ₁₇ ClN ₅ O ₂ P	16.45	16.52
3	<i>p</i> -Cl	C ₆ H ₅	233	C ₂₀ H ₁₇ ClN ₅ O ₂ P	16.45	16.25
4	<i>p</i> -CH ₃	C ₆ H ₅	225	C ₂₁ H ₂₀ N ₅ O ₂ P	17.28	17.34
5	<i>p</i> -CH ₃ O	C ₆ H ₅	222	C ₂₁ H ₂₀ N ₅ O ₃ P	16.62	16.45
6	H	<i>p</i> -tolyl	217	C ₂₂ H ₂₂ N ₅ O ₂ P	16.70	16.52
7	<i>m</i> -Cl	<i>p</i> -tolyl	212	C ₂₂ H ₂₁ ClN ₅ O ₂ P	15.43	15.64
8	<i>p</i> -Cl	<i>p</i> -tolyl	234	C ₂₂ H ₂₁ ClN ₅ O ₂ P	15.43	15.39
9	<i>p</i> -CH ₃	<i>p</i> -tolyl	230	C ₂₂ H ₂₄ N ₅ O ₂ P	16.17	16.10
10	<i>p</i> -CH ₃ O	<i>p</i> -tolyl	216	C ₂₃ H ₂₄ N ₅ O ₃ P	15.59	15.34

(a) The composition and purity of compounds 4 and 9 were also checked by analysis for C, H and P. Compound 4 requires: C, 62.2; H, 4.9; P, 7.6. Found: C, 62.1; H, 5.0; P, 7.5. Compound 9 requires: C, 63.7; H, 5.6; P, 7.2. Found: C, 63.5; H, 5.7; P, 7.4.

Beckman IR-5A unit as potassium bromide pellets.

The key starting 2-amino-5-aryl-1,3,4-oxadiazoles (I) were obtained by oxidative cyclization of the corresponding aldehyde semicarbazones (6,7). *N*-(5-Aryl-1,3,4-oxadiazol-2-yl)phosphorimidic Trichlorides (II) (Table 1).

A suspension of the appropriate aminooxadiazole (10 mmoles) in dry benzene (25 ml.) was refluxed with phosphorus pentachloride (10 mmoles) until the evolution of hydrogen chloride ceased (6-8 hours). On cooling, the phosphorimidic trichlorides (II) which separated were crystallised from benzene as fine needles, yield 60-70%.

N-(5-Aryl-1,3,4-oxadiazol-2-yl)phosphoramidic Dichlorides (III). (Table 2).

a) Formolysis of the Phosphorimidic Trichlorides (II).

A solution of the appropriate trichlorides (II) in benzene was treated with anhydrous formic acid (10 mmoles) and the mixture was kept at room temperature for 6 hours. The precipitated solid was filtered and crystallised from benzene, yield 80-90%.

b) Reaction of Compounds I with Phosphoryl Chloride.

The dichlorides (III) were also prepared by refluxing the aminooxadiazoles (10 mmoles) with phosphoryl chloride (50 ml.) for 5 hours. Excess phosphoryl chloride was removed under vacuum and the resulting residues were treated with petroleum ether to give III, yield 75-80%.

N-(5-Aryl-1,3,4-oxadiazole-2-yl)phosphoramidic Dianilides and Di-*p*-toluidides (IV) (Table 3).

A solution of aniline (4 mmoles) or *p*-toluidine in benzene (10 ml.) was gradually added to a suspension of the dichlorides (1 mmole) in benzene (25 ml.). The mixture was stirred at room temperature for 6 hours and then refluxed two hours. The solids which separated were filtered, washed well with dilute hydrochloric acid, water and dried. They crystallised from ethanol colorless prisms, yield 85-90%.

REFERENCES AND NOTES

- (1) I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **30**, 3044 (1960).
- (2) R. N. Butler, T. M. Lambe, J. C. Tobin and F. L. Scott, *J. Chem. Soc., Perkin Trans. 1*, 1357 (1973).
- (3) L. C. Thomas, "Interpretation of the Infrared Spectra of Organophosphorus Compounds", Heyden, London, 1974; (a) p. 105; (b) p. 71; (c) p. 21.
- (4) I. N. Zhmurova and A. V. Kirsanov, *J. Gen. Chem. USSR*, **30**, 4048 (1960).
- (5) A. I. Vogel, "A Text Book of Quantitative Inorganic Analysis", Longmans, London, 1966.
- (6) M. S. Gibson, *Tetrahedron*, **18**, 1377 (1962).
- (7) H. N. Bandey, V. J. Ram and L. Mishra, *J. Indian Chem. Soc.*, **53**, 520 (1976).