AMIDES OF PHENYLVINYLPHOSPHINIC ACID

I. A. Nuretdinov, R. R. Shagidullin,
Yu. Ya. Shamonin, and N. P. Grechkin

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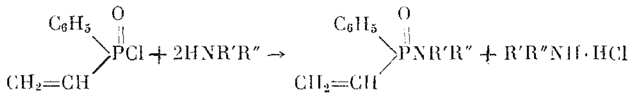
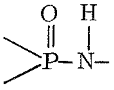
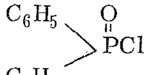
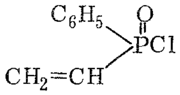
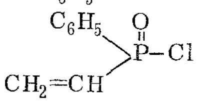
Recently several researchers produced phenylvinylphosphinic acid and its esters [1, 2]. This communication presents the properties of amides of phenylvinylphosphinic acid (PVPA), which were produced according to the usual method

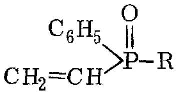


All the amides obtained, except for the piperidide of PVPA, are crystalline substances. The analyses, yields, melting points, and boiling points of the amides obtained are cited in Table 1.

An attempt was made to produce the ethyleneimide of phenyl-β-ethylene-iminoethylphosphinic acid by the reaction of the chloride of phenyl-β-chloroethylphosphinic acid (one mole) with ethyleneimine (two moles) in the presence of triethylamine (two moles) as a hydrogen chloride acceptor. Judging by the data of analysis, IR and NMR spectra, the basic reaction product under these conditions is the ethyleneimide of phenyl-β-chloroethylphosphinic acid.

The IR spectra of the compounds obtained were studied. The absorption frequencies of certain characteristic groups are cited in Table 2. From the peculiarities of the IR spectra of the amides of PVPA obtained, we can note the substantially reduced ν (P=O) for the allylamide of PVPA (by approximately 35 cm^{-1}) (Fig. 1). This is evidently due to the presence of a hydrogen bond $\gt N-H\ldots O=P-$; moreover, ν (NH) 3150 cm^{-1} indicates a "cis," i. e.,  configuration of these groups in the molecule. The PVPA derivatives obtained are interesting in that they contain two π-electronic systems, which may interact with the phosphoryl group. Kabachnik et al. [3], considering the question of π-π conjugation in systems with a tetrahedral phosphorus atom, found in a determination of the dissociation constants of phosphinic acids that two vinyl or vinyl and phenyl groups on the phosphorus atom exert an additive effect. In the case of diarylphosphinic acids, no such additivity was observed. The disturbance of additivity in diarylphosphinic acids is explained by the authors by steric hindrances, interfering with the formation of molecular π-orbitals, including the two aryl rings and the P=O group. On the IR spectra of derivatives of diphenyl-, phenylvinyl-, and vinylphosphinic acids, the influence of steric factors upon the interaction of π-electronic systems with the phosphoryl group is not manifested. Actually, ν (P=O) in  and  is equal to 1234 [4] and 1234/1243 cm^{-1}, respectively; ν (C=C) in  and $CH_2{=}CH\overset{\overset{O}{\|}}{P}Cl_2$ are also practically the same (1600-1610 cm^{-1} in both cases). These facts are in better agreement with the hypothesis of the interaction of the π-electrons of the aryl and vinyl groups with the d-orbitals of phosphorus, i. e., of p_π-d_π conjugation.

Institute of Organic Chemistry, Academy of Sciences of the USSR, Kazan'. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp. 839-843, May, 1966. Original article submitted December 28, 1963.

TABLE 1. Amides of Phenylvinylphosphinic Acid 
$(C_6H_5)(CH_2{=}CH)P(O)-R$

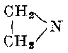
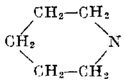
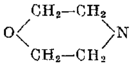
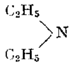
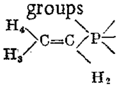
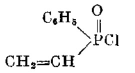
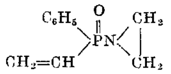
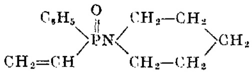
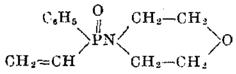
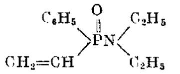
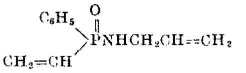
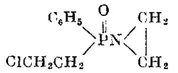
R	M.p., °C and b.p., °C (p, mm Hg)	Found %		Calculated %		Yield, %
		P	N	P	N	
	31—33 94—95 (0,09)	15,90 15,85	7,03 6,90	16,06	7,25	69,1
	114—115 (0,05)	12,89 12,78	5,90 5,77	13,19	5,96	51,7
	63—64	13,02 12,86	6,07 5,83	13,08	5,90	68,3
 $(C_2H_5)_2N$	41—42 108—109 (0,06)	13,80 13,71	6,27 6,25	13,90	6,28	71,8
$CH_2{=}CH{-}CH_2{-}NH$	91—92	14,63	6,68 6,59	14,97	6,76	86,2

TABLE 2. Data of IR and PMR Spectra

Formula of compound	ν (C=C), cm^{-1}	ν (P=O), cm^{-1}	Chemical shift with respect to benzene (δ), millionths*			
			Protons of amide groups	Protons of vinyl groups 		
				H_3	H_4	H_2
 $C_6H_5(CH_2{=}CH)P(O)Cl$	1610	1234/1243	—	1,9	1,29	0,47
	1605	1196	5,08 J (P—H)12 Hz	1,8	1,19	0,48
	1600	1198	5,59 $(\beta,\gamma_N CH_2)$ 4,27 $(\alpha_N CH_2)$	1,9	1,24	0,47
	1603	1170/1207	4,33 $(\alpha_N CH_2)$ 3,84 $(\beta_N CH_2)$	1,6	1,16	0,48
 $C_6H_5(CH_2{=}CH)P(O)N(C_2H_5)_2$	1605	1174/1210	5,83 (CH_3) 4,27 (CH_2)	1,7	1,25	0,47
 $C_6H_5(CH_2{=}CH)P(O)NHCH_2CH{=}CH_2$	1605/1637	1153/1168	—	—	—	—
	—	1176/1218	5,10 J (P—H)12Hz	—	—	—

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* The indicated values of δ for H_3 and H_4 pertain to the centers of multiplets; δ for H_2 pertains to the most intensive signal, although it is possible that the signal of the phenyl group is superimposed upon the multiplet from H_2 (the assignment was made by analogy with other vinyl systems; more detailed data will be published later).

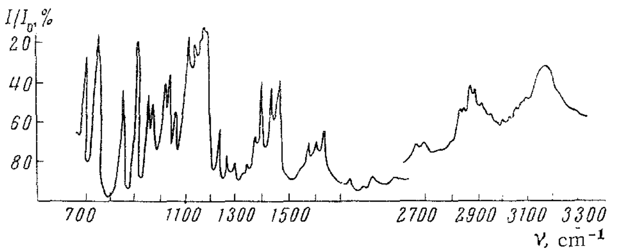


Fig. 1. IR spectrum of allylamide of phenylvinylphosphinic acid.

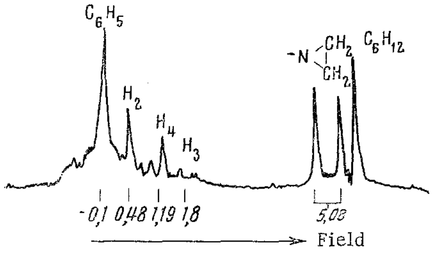


Fig. 2. PMR spectrum of the ethyleneimine of phenylvinylphosphinic acid

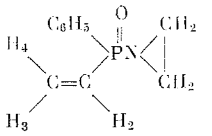
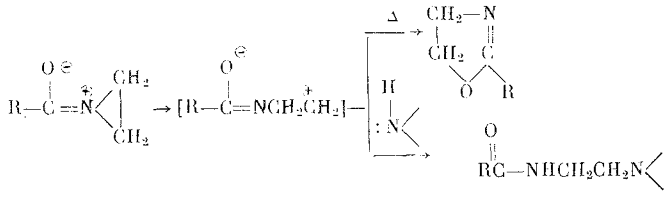


Table 2 presents the data of the proton magnetic resonance (PMR) spectra. On all the spectra, the signals can be divided into two groups. The protons of the amide groups give distinct, well resolved signals, the chemical shifts of which are cited in Table 2. The PMR spectra of various ethyleneimine derivatives are described in the literature [5, 6]. The authors of [6], on the basis of the data of the PMR spectra of N-acylethyleneimines, on which a single signal from the protons of the ring was observed, proposed that the reaction of N-aminoethylation in the case of ethyleneimines of carboxylic acids proceeds according to the scheme



The authors also propose an analogous scheme for the corresponding derivatives of phosphorus acids.

Without going into a discussion of the proposed mechanism of the reaction of opening of the ring of ethyleneimides of acids, we might note that the rate of inversion of nitrogen in ethyleneimides of PVPA and phenyl-β-chloroethylphosphinic acid is rather high. In the PMR spectra of these compounds, two peaks with spin-spin interaction constants J(P–H) equal to 12 Hz belong to the protons of the ethyleneimine group (Fig. 2). In the region of weak fields, the PMR signals belong to the protons of the vinyl and phenyl groups. The chemical shift of the protons of the phenyl group and that of benzene differ little. The protons of the vinyl group give three groups of signals. Since the signal from the phenyl group is superimposed upon the multiplets from the protons of the vinyl group, it is difficult to determine accurately the chemical shifts and spin-spin interaction constants of the protons of the vinyl group. Hence, the values of the chemical shifts of the protons of the vinyl group cited in Table 2 correspond to the centers of the multiplets, whose assignment was made by analogy with other vinyl systems [7].

EXPERIMENTAL

Synthesis of the Diethylamide of Phenylvinylphosphinic Acid. To a solution of 6.28 g of diethylamine in 50 ml of dry benzene, with cooling in the range – 5 to 5°, mixing, and protection from atmospheric moisture, we added dropwise a solution of 8.0 g of the chloride of PVPA [2]. After the reaction, the precipitate of diethylamine hydrochloride was filtered off, and the filtrate was removed under water jet pump vacuum. The residue was distilled under high vacuum. Yield 6.85 g of the diethylamide of PVPA (71.8% of the theoretical) with b.p. 108-109 (0.006 mm). The substance crystallizes upon standing m.p. 41-42°. The allylamide, piperidide, and morpholide of PVPA were produced analogously. The ethyleneimide of PVPA was produced using triethylamine as the base.

Interaction of the Chloride of Phenyl-β-Chloroethylphosphinic Acid with Ethyleneimine in the Presence of Triethylamine. The conditions of the reaction were analogous to those cited above. From 7.2 g of the chloride of phenyl-β-chloroethylphosphinic acid [2], 2.8 g of ethyleneimine, and 6.9 g of triethylamine we obtained 4.3 g of triethylamine hydrochloride and 3.19 g of a crystalline substance with m.p. 44-45°. Found%: C 52.11; H 6.06; P 13.39; N 6.21, $C_{10}H_{13}NOPCl$. Calculated%: C 52.28; H 5.66; P 13.50; N 6.10. A band ν (C–Cl) 791 cm^{-1} is observed in the IR spectrum, and the absorption band of the vinyl group in the region of 1600 cm^{-1} is absent.

The signals of the phenyl ring, a multiplet with $\delta = 5 \cdot 10$ J (P–H) = 12 Hz, belonging to the protons of the ethyleneimine ring, connected to phosphorus, are observed in the PMR spectrum.

The IR spectra were obtained on the UR-10 spectrophotometer; a drop of the test liquid or suspension of the crystalline substance in liquid petrolatum was pressed between plates of KBr.

The PMR spectra were obtained on a spectrometer with resolving power $\sim 5 \cdot 10^{-8}$ at a frequency of 30 MHz. The stability of the permanent magnet during the measurement was $\sim 5 \cdot 10^{-8}$. The chemical shifts were determined relative to the shift of benzene, using benzene and cyclohexane as the internal standards, according to the formula $\delta = \Delta f/30$ millionths, where Δf is the distance between the signal of benzene and the given signal in Hz. The accuracy of the measurement of the chemical shift was ± 0.03 millionth.

CONCLUSIONS

1. Amides of phenylvinylphosphinic acid and the ethyleneimide of phenyl-β-chloroethylphosphinic acid were produced.

2. The IR spectra of the substances obtained were studied. On the basis of the values of the frequencies of the P=O and C=C groups, the presence of p_π-d_π-conjugation in the systems considered was hypothesized.

3. The rate of inversion of nitrogen in the ethyleneimides of phenylvinylphosphinic and phenyl-β-chloroethylphosphinic acids, according to the PMR data, is very high.

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