# REACTION OF VINYLDICHLOROPHOSPHINE WITH ACRYLIC AND PROPIOLIC ACIDS

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Previously it was shown [1-3] that different chlorophosphines, depending on the character of the substituent at the phosphorus atom, react with  $\alpha,\beta$ -unsaturated acids with variable ease. The most active in these reactions are the dichlorophosphines that contain electron-donor substituents; electron-acceptor aromatic radicals in the chlorophosphines retard the reaction with  $\alpha,\beta$ -unsaturated acids. A reaction scheme is given on the basis of these data, which includes direct nucleophilic attack of the  $\beta$ -carbon atom of the unsaturated acid by the phosphorus atom.

In order to further elucidate the effect of the nature of the substituent at the phosphorus atom on the intensity of the reaction a study was made of the reaction of vinyldichlorophosphine with acrylic and propiolic acids.

In contrast to the previously studied exothermic reactions of the alkyl- or aryldichlorophosphines with acrylic acid, vinyl-dichlorophosphine reacts with it endothermally, giving in high yield the acid chloride of vinyl-( $\beta$ -chloroformylethyl)phosphinic acid (II), the structure of which was confirmed by the IR spectrum (Fig. 1a). Infrared spectrum of (II) ( $\nu$ , cm<sup>-1</sup>): 1240 (P=O); 1615 and 970 (C=C); 1740 (C=O); 3080 (=CH).



Fig. 1. Infrared spectra: a) acid chloride of vinyl-( $\beta$ -chloroformylethyl)phosphinic acid (II); b) ethyl ester of vinyl-( $\beta$ -carboethoxyethyl)phosphinic acid (III); c) ethyl ester of vinyl-( $\beta$ -carboxyethyl)phosphinic acid (VI).

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No.6, pp.1386-1390, June, 1972. Original article submitted October 30, 1970.

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Com- pound	Formula	Yield, %	.Bp, °C(p,	$d_4^{20}$	$n_D^{20}$	Found/Calculated			
			mm of Hg)			MR	C, %	Н, %	P, %
I	O CH₂=CH−PCH₂CH₂COOH OH	57,0	158—1€0 (0,05)				$\frac{36,64}{36,60}$	5,57 5,53	<u>19,18</u> 18,88
11	O CH2=CH-PCH2CH2CO-Cl * I Cl	96,7		1,3439	1,5059	44,36 43,40	<u>30,22</u> 29,88	$\frac{3.79}{3,51}$	15,10 15,46
uı	$CH_2 = CH - PCH_2CH_2CH_2COOC_2H_3$	39,0	97—98 (0,06)	1,1044	1,4542	54,02 54,69	<u>48,70</u> 49,09	8,01 7,68	<u>14,03</u> 14,07
tv	$CH_2 = CH - P \begin{pmatrix} O &C = O \\ CH_2 - CH_2 \end{pmatrix}$	66,6	Mp 53-58				41,50 41,95	4,62 4,79	$\frac{21,01}{21,23}$
v	$\begin{array}{c} 0 \\ \overset{\parallel}{}_{\text{CH}_2 \subset \text{H}_2 \subset \text{H}_2 \subset \text{H}_2 \subset \text{COOH}} \\ \overset{\mid}{}_{\text{OC}_2 \in \text{H}_5} \end{array}$	81,0		1,2087	1,4748	<u>44,74</u> 45,33	43,55 43,70	$\frac{6,68}{6,82}$	16,00 16,12
VI	O CH₂=CH−PCH₂CH₂CONHC₅H₅ ↑ OH	83,0	_		1,5143				<u>12,32</u> 12,55
<b>v</b> 11	$\begin{array}{c} C, H_s \\ O & i \\ H_s = CH_s = CH_s = CH_s \\ CH_s = CH_s = CH_s \\ CH_s = CH_s \end{array}$	40,0	92—93 (0,04)	1,0929	1,4930	53,51 53,15			15,46 15,40
VIII	$\begin{array}{c} O \\ \parallel \\ CH_2 = CH - PCH = CH - COOC_2H_5 \\ \downarrow \\ OC_2H_5 \end{array}$	32,3	92 (0,06)	1,1666	1,4790	53,02 54,22	49,67 49,53	$\frac{6,40}{6,93}$	<u>14,29</u> 14,21
ıx	$CH_2-CH-P < CH=CH$	14,0	92 (0,04)	<b>1,344</b> 2	1,5124	32,18 31,91	42,92 41,68	$\frac{3,29}{3,50}$	$\frac{21,01}{21,50}$

<sup>\*</sup>Found: Cl 34,08%. C<sub>5</sub>H<sub>7</sub>Cl<sub>2</sub>O<sub>2</sub>P. Calculated: Cl 35,2%. <sup>†</sup> Found: N 5,60%. C<sub>11</sub>H<sub>14</sub>NO<sub>3</sub>P. Calculated: N 5,82%.

‡Found: N 7,23%. C9H16NO2P. Calculated: N 6,96%.

When compared with the alkyldichlorophosphines, the lower reactivity of vinyldichlorophosphine toward acrylic acid can be explained by the nature of the vinyl group in that it decreases the nucleophilicity of the phosphorus atom, which is in agreement with the mentioned reaction scheme. Possible alternate schemes, in which the acid chlorides of trivalent phosphorus acids enter into the reaction with acrylic acid as electrophiles, require for the alkyldichlorophosphines the acknowledgement of the existence of the

hypothetical alkylchlorophosphinous acid RP, and also they are not in agreement with our experimental results.

The hydrolysis of acid chloride (II) gave vinyl- $(\beta$ -carboxyethyl)-phosphinic acid (I), while the reaction of (II) with alcohol gave the ethyl ester (III). Infrared spectrum of (III) (Fig.1b) ( $\nu$ , cm<sup>-1</sup>): 1040 (P-O-C); 1240 (P=O); 1620 (C=C); 1730 (C=O). The acid chloride (II) when heated with acetic anhydride is easily converted to 2-vinyl-2, 5-dioxo-1, 2-oxaphospholane (IV).

The reactions of oxaphospholane (IV) with alcohol and with aniline go differently. When reaction is with alcohol the P-O bond in the ring is cleaved with the formation of the ethyl ester of vinyl-( $\beta$ -carboxy-ethyl)phosphinic acid (V), in the IR spectrum of which (Fig.1c) is observed a distinct peak at 1040 cm<sup>-1</sup>, which is characteristic for the P-O-C group. When reaction is with aniline the bond between the O of the oxaphospholane ring and the C of the carbonyl group is cleaved with the formation of vinyl-( $\beta$ -phenylcarba-moylethyl)phosphinic acid (VI).

The reaction of acid chloride (II) with butylamine, when run in the presence of triethylamine, gave 2-vinyl-1-butyl-2, 5-dioxo-1, 2-azaphospholane (VII).

The reaction of vinyldichlorophosphine with propiolic acid proceeds vigorously with the formation of the acid chloride of vinyl-( $\beta$ -chloroformylvinyl)phosphinic acid, which could not be isolated in the pure state. The formation of the acid chloride was corroborated by the fact that the ethyl ester of vinyl-( $\beta$ carboethoxyvinyl)phosphinic acid (VIII) was obtained and characterized as the result of treating it with alcohol, while treatment with acetic anhydride gives 2-vinyl-2, 5-dioxo-1, 2-oxa-3-phospholene (IX). The yields and constants of the obtained compounds are given in Table 1.

### EXPERIMENTAL SECTION

The spectra were obtained on a spectrometer of the UR-10 type. A drop of the substance was pressed between two KBr plates. The layer thickness of the substance was not controlled.

Vinyldichlorophosphine was obtained as described in [4], from phenyldichlorophosphine and vinyldichlorophosphine sulfide; yield 63.8%; bp 104-105°. From [5]: bp 104°.

Acid Chloride of Vinyl-( $\beta$ -chloroformylethyl)phosphinic Acid (II). To a mixture of 50 ml of absolute benzene and 31.5 g of vinyldichlorophosphine, with stirring, in drops, was added 19.5 g of acrylic acid. Here the temperature of the reaction mixture dropped from 24 to 18°C. Then the mixture was heated at 60° for 1.5 h, and the benzene was removed in vacuo. After keeping the residue in vacuo at 0.05 mm of Hg we obtained 46.8 g of the acid chloride of vinyl-( $\beta$ -chloroformylethyl)phosphinic acid (II) as a clear liquid that fimes in the air.

<u>Vinyl-( $\beta$ -carboxyethyl)phosphinic Acid (I)</u>. With shaking, to 30 ml of distilled water was added 8.8g of acid chloride (II) in portions. The HCl and excess water were removed in vacuo. Distillation of the residue gave 4 g of acid (I) as a thick syrup.

Ethyl Ester of Vinyl-( $\beta$ -carboethoxyethyl)phosphinic Acid (III). To 9 g of acid chloride (II), contained in an Arbuzov flask that was cooled in ice, was added 6.5 g of absolute alcohol in portions. The liberated HCl and excess alcohol were removed in vacuo. Distillation of the residue gave 3.5 g of ethyl ester (III).

<u>2-Vinyl-2, 5-dioxo-1, 2-oxaphospholane (IV)</u>. A mixture of 12.1 g of acid chloride (II) and 5 g of acetic anhydride was stirred at 60° for 1 h. We obtained 4.4 g of  $CH_3COC1$  (bp 51°,  $n_D^{20}$  1.3920) and 5.8 g of oxaphospholane (IV) as a thick liquid, which solidified to crystals.

Ethyl Ester of Vinyl- $(\beta$ -carboxyethyl)phosphinic Acid (V). To 1.6 g of the oxaphospholane was added 0.8 g of absolute alcohol. After 15 h the excess alcohol was removed at 0.05 mm of Hg. The residue represents ester (V).

<u>Vinyl-( $\beta$ -phenylcarbamoylethyl)phosphinic Acid (VI)</u>. To 2 g of the oxaphospholane was added 1.2 g of anhydrous aniline; a rise in the temperature of the reaction mixture was observed. After 15 h the mixture was kept in vacuo at 0.05 mm of Hg. We obtained 2.5 g of acid (VI) as a thick yellowish syrup.

<u>2-Vinyl-1-butyl-2, 5-dioxo-1, 2-azaphospholane (VII)</u>. To a stirred mixture of 2 g of butylamine and 5 g of triethylamine in 20 ml of absolute ether, with cooling in ice, in an argon stream, was added 5 g of acid chloride (II) in drops. The reaction mixture was stirred at room temperature for 3 h. The precipitate  $(C_2H_5)_3N$  HCl was filtered, and the ether was distilled off. Distillation of the residue gave 2 g of azaphospholane (VII).

Reaction of Vinyldichlorophosphine with Propiolic Acid. To a solution of 21.5 g of vinyldichlorophosphine in 50 ml of absolute benzene, with cooling in ice, in an argon atmosphere, was added 13 g of propiolic acid in drops. The next day the benzene was removed in vacuo. The residue, a thick dark brown liquid, contains the acid chloride of vinyl-( $\beta$ -chloroformylvinyl)phosphonic acid. It decomposes when distilled.

Ethyl Ester of Vinyl-( $\beta$ -carboethoxyvinyl)phosphinic Acid (VIII). In a distillation flask was placed 12 g of the reaction product of vinyldichlorophosphine with propiolic acid and, with cooling in ice, 7 g of absolute alcohol was added. We obtained 3.2 g of ester (VIII).

<u>2-Vinyl-2, 5-dioxo-1, 2-oxa-3-phospholene (IX)</u>. In a distillation flask with a low takeoff was placed 16 g of the reaction product of vinyldichlorophosphine with propiolic acid, and 13 g of acetic anhydride was added in drops. The reaction mixture was heated at 50° for 1 h. Distillation gave 1.8 g of CH<sub>3</sub>COCl and 2 g of the oxa-3-phospholene (IX).

### CONCLUSIONS

The reaction of vinyldichlorophosphine with acrylic acid, accompanied by the initial attack of the phosphorus atom on the  $\beta$ -carbon atom of the acid, leads to the formation of the acid chloride of vinyl-( $\beta$ -chloroformylethyl)phosphinic acid.

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