AN INVESTIGATION IN THE FIELD OF THE UNSATURATED PHOSPHINIC ACIDS

COMMUNICATION 23. ADDITION OF PHOSPHORUS PENTACHLORIDE TO ETHYNYLCYCLOHEXENE-1

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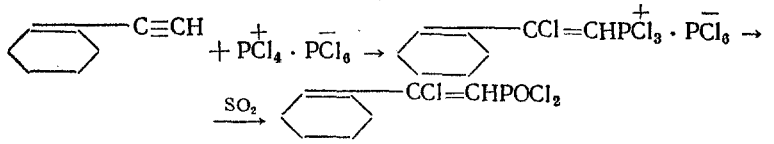
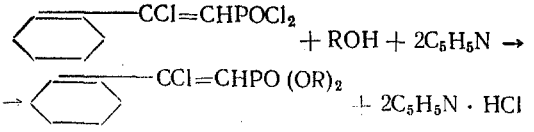
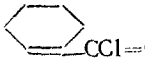
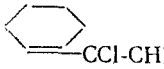
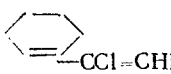
Continuing our work in the field of derivatives of unsaturated phosphinic acids, in the present communication we describe the addition of phosphorus pentachloride to ethynylcyclohexene-1.



The resulting acid chloride readily reacts with alcohols.



By this reaction [1], we have prepared the ethyl and n-propyl esters of β,β'-cyclohexenylchlorovinylphosphinic acid. Constants of the compounds obtained are given in the table.

Formula	B.p., °C mm Hg	$n^{20}D$	d^{20}_4	Yield, %	MR found	MR calcd.	C=C cm^{-1}	P=O cm^{-1}
 Acid chloride of β,β'-cyclohexenylchlorovinylphosphinic acid	132 (2)	1.5808	1.4103	54	61.35	58.93	1620 med. 1558 v.s.	1275 v.s.
 Diethyl ester of β,β'-cyclohexenylchlorovinylphosphinic acid	132 (1)	1.5142	1.1688	90.5	71.98	70.204	1625 s. 1570 s.	1260 v.s.
 Di-n-propyl ester of β,β'-cyclohexenylchlorovinylphosphinic acid	131 (1)	1.5083	1.1235	56	71.38	79.44	1625 s. 1570 s.	1260 v.s.

With the aim of studying their structure, the infrared spectra of the acid chloride (Fig. 1) and the esters of β,β'-cyclohexenylchlorovinylphosphinic acid (Fig. 2) were measured. Frequencies serving as a basis for analysis of infrared spectra are shown in the table.

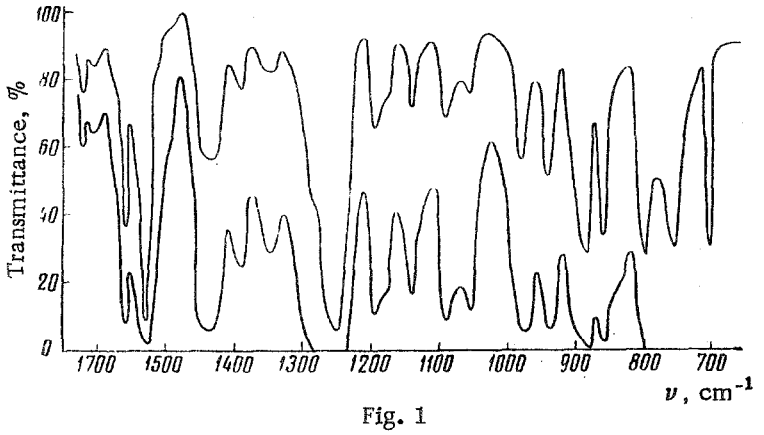


Fig. 1

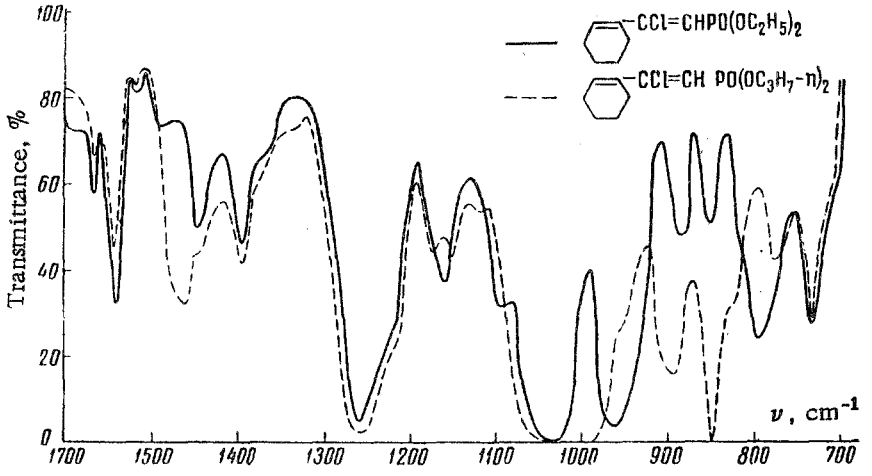


Fig. 2

In the region of valence vibrations of the C=C bond in the spectrum of our compounds there are two bands 1625, 1620 cm^{-1} and 1570, 1558 cm^{-1}, which confirms the presence in the molecules of a conjugated system of double bonds [2, 3]. Absorption bands 1275, 1260 cm^{-1} are valence vibrations of P=O bonds [4, 5].

EXPERIMENTAL

Acid chloride of β,β'-cyclohexenylchlorovinylphosphinic acid. To a solution of 83.3 g (0.4 M) of phosphorus pentachloride in 150 ml of absolute benzene was added with stirring 21.2 g (0.2 M) of ethynylcyclohexene-1. Further treatment of the product was carried out according to the method described previously [6]. 26.0 g of acid chloride was obtained; yield 54%; b. p. 132° (2 mm); $n^{20}D$ 1.5808; d^{20}_4 1.4103; MR found 61.35; MR calculated 58.93; mol. wt. 259.5. Found: C 36.91, 36.69; H 3.96, 3.93; Cl 41.38, 41.38; P 12.05, 11.73%. $C_8H_6POCl_3$. Calculated: C 37.00; H 3.85; Cl 41.08; P 11.96%.

Esters of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid. To prepare the diethyl ester, to a solution of 4.6 g (0.1 M) of absolute ethyl alcohol and 7.9 g (0.1 M) of absolute pyridine in 100 ml of absolute benzene was added with stirring 12.98 g (0.05 M) of the acid chloride of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid. As a result of the reaction, 12.6 g (90.5% theoretical) of the diethyl ester of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid was obtained. Constants: b. p. 132° (2 mm); $n^{20}D$ 1.5142; d^{20}_4 1.1688. MR found 71.98; MR calculated 70.20. Found:

C 50.90, 50.84; H 7.04, 7.05; P 11.44, 11.18%. $C_{12}H_{16}PO_3Cl$. Calculated: C 50.50; H 7.18; P 11.27%. On mixing the substance in the same molar proportions with n-propynyl alcohol* 7.9 g (56% theoretical) of the n-propyl ester of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid was obtained with b. p. 131°; $n^{20}D$ 1.5083; d^{20}_4 1.123; MR found 81.38; MR calculated 79.44. Found: P 10.01, 9.78; Cl 11.07, 11.34%. $C_{14}H_2OPOCl_3$. Calculated: P 10.104; Cl 11.57%.

Measurement of infrared spectra. Measurement of absorption spectra in the infrared region was carried out on a Hilger (model 209) infrared spectrometer, using the single beam variant of this model. A Nernst Lamp was used as the light source. Measurements in the region from 4.0 to 15 μ were carried out with a rock salt prism. Rock salt plates were used as cells. Layer thickness of the substance being investigated was regulated with aluminum foil packing and was 10.30 and 70 μ. Accuracy in determination of position of maxima of the absorption bands was 2 cm^{-1}.

SUMMARY

1. The acid chloride of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid was prepared.
2. The diethyl and di-n-propyl esters of β,β'-cyclohexenyl-1-chlorovinylphosphinic acid were synthesized.
3. The structure of the substances obtained was studied with the help of infrared spectroscopy.

LITERATURE CITED

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* Publishers note: n-propynyl alcohol, although indicated as such in the Russian, is probably n-propyl alcohol.