Chemistry

1960

SovietRxiv

Abstract

Full Text

Chemistry

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ESTERS OF UNSATURATED PHOSPHINOUS ACIDS

Esters of unsaturated phosphinous acids (not described in the literature up to the present time) combine in the molecule an unsaturated grouping and an atom of trivalent phosphorus linked by a C—P bond. This accounts for the high reactivity of the indicated compounds, the diversity of their chemical transformations, and thereby opens up possibilities for the synthesis, on their basis, of various organophosphorus substances, including polymeric ones.

Investigation of the reactivity of esters of unsaturated phosphinous acids is also of interest in connection with the study of the mutual influence of unsaturated carbon—carbon bonds and the trivalent phosphorus atom, and with elucidation of the nature of orientation in π—p-conjugated systems containing phosphorus.

In the present work the synthesis and some transformations of derivatives of vinyl-, ethynyl-, and *n*-vinylphenylphosphinous acids are described.

Dibutyl esters of vinyl- and ethynylphosphinous acids (I and II, see Table 1) were obtained by means of the method developed earlier (^{1}), by interaction of the corresponding organomagnesium compounds with dibutyl chlorophosphite in tetrahydrofuran.

$$\mathrm{RMgX} + \mathrm{ClP(OR')_2} \xrightarrow[-60^\circ]{} \mathrm{RP(OR')_2} + \mathrm{MgXCl}.$$

Analogously, from vinylmagnesium bromide and phenylbutoxychlorophosphine (III), the butyl ester of secondary vinylphenylphosphinous acid (IV) was synthesized. From chloro-*n*-vinylphenylmagnesium and diethyl chlorophosphite, a styrene derivative (V) was obtained. Since esters of unsaturated phosphinous acids proved to be relatively strong complexing agents, in order to isolate them from the reaction mixture it was necessary to use substances displacing the phosphinous esters formed from complex compounds with magnesium halide salts. Pyridine was used as such a complexing agent; as E. L. Gefter showed (^{2}), it gives good results in the isolation of phenyldichlorophosphine from a complex compound with aluminum chloride. The relative stability of esters of unsaturated phosphinous acids toward hydrolysis also makes it possible to use washing with water or with a solution of sodium bicarbonate to destroy the indicated complex compounds with magnesium halide salts.

The substances obtained are readily oxidized in air, but apparently less vigorously than the corresponding alkylphosphinous esters, since, in contrast to alkyl derivatives, esters of unsaturated phosphinous acids do not "smoke" when applied to cotton wool or paper. We investigated some reactions of esters of vinyl- and ethynylphosphinous acids (I) and (II), confirming the structure of these compounds as unsaturated derivatives of trivalent phosphorus.

It had previously been shown that hydrolysis of full esters of phosphinous acids leads to the corresponding acid esters of these acids ([3]). Analogously, butyl esters of vinyl- and ethynylphosphinous acids (I) and (II), on reaction with the theoretical amount of acidified water in dioxane, gave readily polymerizing monobutyl esters of these acids (VI) and (VII).

The trivalency of phosphorus in the dibutyl ester of vinylphosphinous acid (I) was also proved by sulfur-addition reactions and by the Arbuzov rearrangement with methyl iodide, as a result of which the dibutyl ester of vinylthiophosphinous acid (VIII) and the butyl ester of vinylmethylphosphinic acid (IX), respectively, were obtained. It should be noted that, when an attempt was made to carry out the Arbuzov rearrangement of the dibutyl ester of vinylphosphinous acid (I) by boiling in an excess of methyl iodide, mainly polymeric products were isolated. Polymerization also occurred when the reaction was conducted in acetonitrile at 0°. A positive result was obtained only when petroleum ether was used as the solvent. However, in this case the rate of the process was greatly slowed, and rather severe conditions (100–110°, 4 hr) were required to carry out the reaction.

The dibutyl ester of vinylphosphinous acid (I), as a dienophile, enters into a diene-synthesis reaction with cyclopentadiene and forms the corresponding adduct—the dibutyl ester of bicyclo-(1,2,2)-heptene-2-yl-6-phosphinous acid (X). The latter contains in the molecule a trivalent phosphorus atom, as shown by the sulfur-addition reaction. The yields, constants, and analytical data of all the compounds obtained are given in Table 1.

Experimental Part

All operations were carried out in an atmosphere of purified nitrogen; the solvents were carefully dried.

Dibutyl ester of vinylphosphinous acid (I). A solution of vinylmagnesium bromide ([4]) (0.65 g-at. magnesium, 0.67 mole of vinyl bromide, 500 ml of tetrahydrofuran) was added dropwise to 0.60 mole of dibutyl chlorophosphite in 200 ml of tetrahydrofuran with vigorous stirring and at a reaction-mixture temperature of −60°. After the addition was complete, the tetrahydrofuran was removed in vacuo, 300 ml of petroleum ether and 1.3 mole of pyridine were added to the residue, the precipitate was filtered off and washed with petroleum ether (5 × 100 ml), the solvent was removed, and the residue was distilled in vacuo in the presence of hydroquinone.

Dibutyl ester of ethynylphosphinous acid (II) was synthesized analogously from ethynylmagnesium bromide (5) (from 0.12 mole of ethyl bromide, 0.12 g-at. magnesium, and acetylene in 80 ml of tetrahydrofuran) and 0.10 mole of dibutyl chlorophosphite in 50 ml of tetrahydrofuran.

Phenylbutoxychlorophosphine (III). 0.3 mole of butyl alcohol and 0.3 mole of diethylaniline in 50 ml of petroleum ether were added dropwise, with stirring, to 0.3 mole of phenyldichlorophosphine (2) in 300 ml of petroleum ether at −30°; the mixture was stirred for 1 hr, the precipitate was filtered off, washed with petroleum ether, the solvent was removed, and the residue was distilled in vacuo.

Butyl ester of vinylphenylphosphinous acid (IV) was synthesized analogously to the dibutyl ester of vinylphosphinous acid (I) by reaction of vinylmagnesium bromide (0.12 mole of vinyl bromide, 0.11 g-at. magnesium, 60 ml of tetrahydrofuran) with 0.10 mole of phenylbutoxychlorophosphine in 50 ml of tetrahydrofuran.

Diethyl ester of *p*-vinylphenylphosphinous acid (V) was obtained from chloro-*p*-vinylphenylmagnesium (6) (0.06 mole of *p*-chlorostyrene, 0.06 g-at. magnesium, 40 ml of tetrahydrofuran) and 0.06 mole of diethyl chlorophosphite in 40 ml of tetrahydrofuran. Sodium nitrite was used as a polymerization inhibitor.

Acid esters of vinyl- and ethynylphosphinous acids (VI), (VII). A mixture of 0.03 mole of the corresponding full ester of phosphinous acid (I) or (II), 0.033 mole of water, containing 0.4% ser-

Table 1

Formula	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.	S (Cl), % found	S (Cl), % calc.
I. $CH_2=CHP(OC_4H_9)_2$	71	49–51.5/2	1.4471	0.9039	60.39	60.04	58.7 58.6	58.8	10.5 10.5	10.4	15.0 15.1	15.2		
II. $CH\equiv C-P(OC_4H_9)_2$	74	58.8–60/2	1.4520	0.9289	58.73	58.50	59.0 59.3	59.4	9.6 9.6	9.5	15.2 15.5	15.3		
III. $C_6H_5P(OC_4H_9)Cl$	62	77–78/2	1.5352	1.1049	61.08		55.7 55.7	55.4	6.6 6.5	6.5	14.1 14.0	14.3	16.2 16.4	16.4
IV. $CH_2=CH(C_6H_5)POC_4H_9$	66.4	76–77/2	1.5310	0.9762	66.00		69.2 69.4	69.2	8.2 8.2	8.2	14.9 14.6	14.9		
V. *p*-$CH_2=CHC_6H_4P(OC_2H_5)_2$	33	96.5–97/2	1.5398	1.0251	68.61		63.9 64.1	64.3	7.6 7.8	7.6	13.9 14.0	13.8		
VI. $CH_2=CHPH(O)OC_4H_9$	92	50–51/2	1.4479	1.0040	39.50	39.40	48.7 48.6	48.6	9.1 8.9	8.8	20.8 20.8	20.9		

Formula	Yield, %	b.p., °C/mm	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.	S (Cl), % found	S (Cl), % calc.
VII. $CH\equiv CPH(O)OC_4H_9$	78	65–66/1.5	1.4492	1.0322	38.00	37.86	49.4 49.3	49.3	7.6 7.5	7.6	21.1 20.9	21.2		
VIII. $CH_2=CH-P(S)(OC_4H_9)_2$	88.2	96.2–96.8/2.5	1.4730	0.9954	66.61	66.27	51.2 51.0	50.8	9.0 9.0	9.0	12.9 13.1	13.1	13.6 13.7	13.6
IX. $CH_2=CH(CH_3)P(O)OC_4H_9$	84	64–64.2/2	1.4452	0.9862	43.78	43.80	52.1 52.0	51.8	9.3 9.4	9.3	18.9 19.0	19.1		
X. [[structural formula: bicyclic diene ring]]$-P(OC_4H_9)_2$	55.5	99.7–101/1.5	1.4792	0.9696	79.12	78.73	66.5 66.8	66.6	10.2 10.0	10.1	11.6 11.5	11.5		
XI. [[structural formula: bicyclic diene ring]]$-P(S)(OC_4H_9)_2$	63.5	139–139.2/2	1.4961	1.0425	84.87	84.96					10.0 10.1	10.2		

acid, and 10 ml of dioxane were left to stand at room temperature (in the case of the ethynyl derivative, at 40°) for 30 min; the dioxane was removed in vacuo, and the residue was distilled in the presence of hydroquinone.

Dibutyl ester of vinylthiophosphinic acid (VIII). 0.017 g-at. of sulfur was added, with stirring, to 0.017 mole of dibutyl ester of vinylphosphinic acid (I) in 15 ml of absolute ether at 0°. After the sulfur had dissolved, the ether was removed and the residue was distilled in vacuo.

Butyl ester of methylvinylphosphinic acid (IX). 0.03 mole of dibutyl ester of vinylphosphinic acid (I) and 0.09 mole of methyl iodide in 100 ml of petroleum ether were heated for 4 h in an autoclave in the presence of hydroquinone at 100–110°. The solvent was then removed, and the residue was distilled in vacuo.

Dibutyl ester of bicyclo-(1,2,2)-hepten-2-yl-6-phosphinic acid (X). 0.03

mole of dibutyl ester of vinylphosphinic acid (I) and 0.015 mole of cyclopentadiene dimer were heated for 13 h in a sealed tube in the presence of hydroquinone at 190–200°. The reaction mixture was fractionated in vacuo.

Dibutyl ester of bicyclo-(1,2,2)-hepten-2-yl-6-thiophosphinic acid (XI). 0.0094 g-at. of sulfur was added to 0.0094 mole of adduct (X) at room temperature. The reaction product was distilled in vacuo.

Institute of Organoelement Compounds
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Received
22 I 1960

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Note: Figure translations are in progress. See original paper for figures.