Chemistry

1960

SovietRxiv

Abstract

Full Text

Chemistry

A. I. Razumov and B. G. Liorber

Studies in the Series of Derivatives of Phosphinic and Phosphonous Acids

Synthesis and Properties of the Dibutyl Ester of Allylphosphonous Acid

(Presented by Academician A. E. Arbuzov, June 29, 1960)

Esters of unsaturated phosphonous acids have been almost unstudied. Of these, only a small number of esters of vinyl-, ethynyl-, and *p*-vinylphenylphosphonous acids are known (^{1}). The study of such compounds is, in our view, of considerable interest. They may serve as starting products for the synthesis of various substances, including biologically active and high-molecular-weight compounds, and also as convenient objects for studying the mutual influence of a multiple bond and a trivalent phosphorus atom on the reactivity of the molecule.

The present work, in which the dibutyl ester of allylphosphonous acid and some of its transformations are described, is a continuation of the investigations of our laboratory in the field of the synthesis of esters of phosphonous acids and their various derivatives (^{2,3}). The dibutyl ester of allylphosphonous acid was obtained by the interaction of allylmagnesium bromide with dibutyl chlorophosphite at a temperature of −60° (^{1}).

$$\mathrm{CH_2{=}CH{-}CH_2MgBr} + \mathrm{(C_4H_9O)_2PCl} \xrightarrow[-60^\circ]{} \mathrm{CH_2{=}CH{-}CH_2P(OC_4H_9)_2} + \mathrm{MgClBr}.$$

The reaction was carried out in dry ether. In this case no formation was observed of a complex compound of the synthesized ester with magnesium halide salts, which occurs in the preparation of the dibutyl ester of vinylphosphonous acid.

The isolated ester is a colorless liquid with a characteristic phosphine odor; it combines avidly with oxygen from the air, and, when applied to cotton wool or paper, oxidizes with evolution of a large amount of smoke. To confirm its structure, we studied several addition reactions at phosphorus and at the double bond and compared them with those for the dibutyl ester of vinylphosphonous acid (^{1}) (the difference in the behavior of the two esters is apparently due to the position of the double bond relative to the phosphorus atom).

The dibutyl ester of allylphosphonous acid reacts with one equivalent of cuprous iodide on heating. It reacts vigorously with sulfur and selenium, forming the corresponding esters of allylthio- and allylselenophosphonic acids.

In contrast to the dibutyl ester of vinylphosphonous acid, where the Arbuzov rearrangement is complicated by condensation reactions, isomerization of the allyl analogue, as was to be expected, proceeds readily. On heating with butyl iodide in a sealed tube at 117°, the rearrangement is complete within 20 min. These facts indicate a trivalent structure of phosphorus. The presence of a double bond in the ester is demonstrated by chlorination of the isomerized product at a temperature of -5 to $0°$, as a result of which the butyl ester of butyl-β,γ-dichloropropyl-

phosphinic acid. The latter is insufficiently stable to heating and during distillation partially decomposes with elimination of hydrogen chloride. A tendency toward elimination of hydrogen chloride in phosphinous and phosphinic derivatives containing 2 chlorine atoms in the molecule has also been observed by other authors ([4,5,6]).

The yields, constants, and analytical data of the synthesized compounds are given in Table 1.

Experimental Part

All operations connected with the preparation and reactions of dibutyl allylphosphinous acid ester were carried out in an atmosphere of purified nitrogen.

Dibutyl ester of allylphosphinous acid I. A solution of allylmagnesium bromide ([7]) (63 g (2.62 g-at.) of magnesium, 106 g (0.87 mole) of allyl bromide, and 850 ml of ether) was added to a solution of 186 g (0.82 mole) of dibutyl chlorophosphite in 400 ml of ether at a temperature of -65 to $-55°$. After the addition was complete, the ether was removed in vacuo; the residue was washed by decantation with petroleum ether (4×200 ml). The latter was removed, and the residue was distilled.

Dibutyl ester of allylthiophosphinic acid II. 0.65 g (0.02 g-at.) of sulfur was added, with stirring, to a solution of 4.33 g (0.019 mole) of dibutyl ester of allylphosphinous acid in 20 ml of benzene. After the sulfur had dissolved, the mixture was heated for 2 hours. The benzene was removed, and the residue was distilled in vacuo.

Table 1

Compound	B.p., °C/mm	n_D^{20}	d_{20}^{20}	MR_D, found	MR_D, calc.	P, %, found	P, %, calc.	S (Cl), %, found	S (Cl), %, calc.	Yield, %
I. $CH_2=CH-CH_2P(OC_4H_9)_2$	102.4–103°/10	1.4465	0.9006	64.61	64.65	13.99; 14.41; 12.35; 12.08	14.22	–	–	33.0
II. $CH_2=CH-CH_2\overset{S}{\overset{\|}{P}}(OC_4H_9)_2$	133–135°/10	1.4717	0.9865	70.92	70.86	12.4	12.4	12.74; 12.70	12.8	63.0
III. $CH_2=CH-CH_2\overset{Se}{\overset{\|}{P}}(OC_4H_9)_2$	145–147°/10	1.4889	1.1457	74.80	74.52	10.7; 10.83	10.43	–	–	61.0
IV. $CH_2=CH-CH_2-\overset{O}{\overset{\|}{\underset{C_4H_9}{P}}}OC_4H_9$	139–140°/12	1.4522	0.9480	62.27	62.05	13.5; 13.9	14.22	–	–	64.0
V. $CH_2Cl-CHCl-CH_2-\overset{O}{\overset{\|}{\underset{C_4H_9}{P}}}OC_4H_9$	145–148°/10.3	1.4765	1.1209	72.47	72.78	11.19	10.72	22.95; 22.86	24.56	21.0

Dibutyl ester of allylselenophosphinic acid III. 1.75 g (0.022 g-atom) of selenium was added to 4.8 g (0.022 mole) of dibutyl ester of allylphosphinous acid. The mixture was heated for 3 hours at 90–100°, and after cooling it was distilled in vacuo.

Butyl ester of allylbutylphosphinous acid IV. 12.5 g (0.057 mole) of dibutyl ester of allylphosphinous acid and 10.13 g (0.055 mole) of butyl iodide were heated in a sealed tube in a dilatometer in vapors of *n*-butyl alcohol (117°). After 20 min, the decrease in the volume of the mixture ceased. A control two-hour heating did not lead to any further change in volume. The product was distilled in vacuo.

Butyl ester of butyl-β,γ-dichloropropylphosphinic acid V. Chlorine was passed into a solution of 15 g (0.07 mole) of butyl ester of butylallylphosphinous acid in 20 ml of carbon tetrachloride at $-5 \div 0°$ until the theoretical weight gain was reached (4.8 g). The solvent was removed. The residue was distilled in vacuo.

Kazan Chemical-Technological Institute
named after S. M. Kirov

Received
27 VI 1960

CITED LITERATURE

1. M. I. Kabachnik, E. N. Tsvetkov, Chzhan-Zhui-Yui, DAN, **131**, 1334 (1960).

2. A. I. Razumov, O. A. Mukhacheva, Sim-Do-Khen, Izv. AN SSSR, OKhN, 1952, 894.
3. A. I. Razumov, O. A. Mukhacheva, ZhOKh, **26**, 2463 (1956).
4. V. S. Tsivunin, G. Kamai, DAN, **131**, 1113 (1960).
5. Yu. M. Zinov’ ev, L. Z. Soborovskii, ZhOKh, **30**, 1571 (1960).
6. Yu. M. Zinov’ ev, L. Z. Soborovskii, ZhOKh, **29**, 615 (1959).
7. H. Gilman, G. H. McGlumpry, Bull. Soc. Chim., **43**, 1322 (1928); Chem. Abstr., **23**, 1870 (1929).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.