Chemistry

I. F. LUTSENKO and M. KIRILOV

1960

SovietRxiv

Abstract

Full Text

Chemistry

I. F. LUTSENKO and M. KIRILOV

PHOSPHORYLATED CHLOROVINYL KETONES

PRIMARY PRODUCTS OF THE REACTION OF PHOSPHORUS PENTACHLORIDE WITH ENOL ACETATES

(Presented by Academician A. N. Nesmeyanov, January 7, 1960)

It was previously reported (1) that phosphorylated β-chlorovinyl ketones are obtained by the interaction of phosphorus pentachloride with enol acetates upon heating.

Further study of this reaction made it possible to find conditions under which it can be stopped at the initial stage, i.e., at the stage of addition of phosphorus pentachloride to the multiple bond of the unsaturated ester; moreover, two moles of PCl_5 are consumed per mole of ester:

$$\mathrm{R{-}C(OC(O)CH_3){=}CH_2 + 2PCl_5 \xrightarrow{\text{low temp.}} R{-}C(Cl)(OC(O)CH_3){-}CH_2PCl_4PCl_5} \qquad \text{(I)}$$

The composition given for the addition product was confirmed by analysis using vinyl acetate as an example. In view of the easy hydrolyzability of these products by atmospheric moisture and their instability at room temperature, they were further treated (without isolation from the reaction mixture) with sulfur dioxide at low temperature. In this way, the acid chlorides of β-acetoxy-β-chloroalkylphosphinic acids were obtained, which proved sufficiently stable to be isolated in pure form:

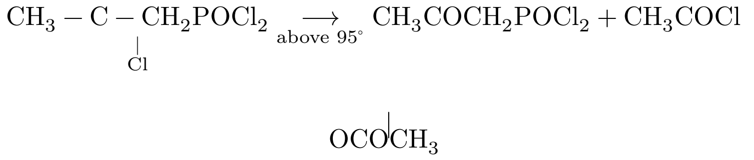
$$\mathrm{R{-}C(Cl)(OC(O)CH_3){-}CH_2{-}PCl_4PCl_5 \xrightarrow[\text{low temp.}]{SO_2} R{-}C(Cl)(OC(O)CH_3){-}CH_2{-}POCl_2 + POCl_3 + 2SOCl_2} \qquad \text{(II)}$$

The yields of the acid chlorides of β-acetoxy-β-chloroethyl- and β-acetoxy-β-chloropropylphosphinic acids are, respectively, 85 and 70%. When the ratio of enol acetate to phosphorus pentachloride is 1:1, the yield of acid chlorides in both cases does not exceed 40%. This is one more indirect proof that the addition product to vinyl acetate, and also, apparently, to isopropenyl acetate, has the composition shown in equation (I).

It should be noted that the conditions for carrying out the reaction for vinyl acetate and isopropenyl acetate are somewhat different. In the first case, the addition of phosphorus pentachloride must be carried out at 7–8°, in the second case at −25°, which is explained by the different stability of the addition products. Thus, raising the temperature by several degrees (respectively to +15 and −15°) leads to the formation of a mixture of products from which (after treatment with sulfur dioxide) individual substances cannot be isolated by simple distillation.

An analogous difference is observed in the stability of the acid chlorides obtained from the addition products. Thus, the acid chloride of β-acetoxy-β-chloroethylphosphinic acid distills in vacuo without decomposition,

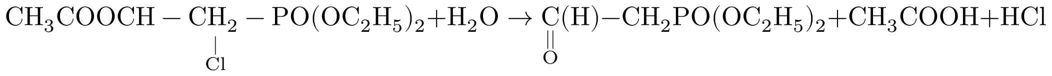
whereas the acid chloride of β-acetoxy-β-chloropropylphosphinic acid at a temperature above 95° eliminates acetyl chloride, giving, in 83% yield, crystalline acid chloride of acetonylphosphinic acid:



$$\mathrm{CH_3-\underset{\underset{Cl}{|}}{C}-CH_2POCl_2 \xrightarrow[\text{above } 95^\circ]{} CH_3COCH_2POCl_2+CH_3COCl} \qquad \text{(III)}$$

$$\mathrm{OCOCH_3}$$

On treatment with alcohol in the presence of pyridine, the acid chloride of β-acetoxy-β-chloroethylphosphinic acid gave the corresponding diethyl ester, which, under the action of water on heating for several hours, or at room temperature over 3-4 days, is hydrolyzed to give phosphonoacetaldehyde:



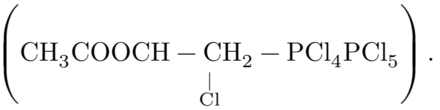
$$\mathrm{CH_3COOCH-\underset{\underset{Cl}{|}}{CH_2}-PO(OC_2H_5)_2+H_2O \rightarrow \underset{\underset{O}{\|}}{C}(H)-CH_2PO(OC_2H_5)_2+CH_3COOH+HCl} \qquad \text{(IV)}$$

Attempts to obtain the diethyl ester of β-acetoxy-β-chloropropylphosphinic acid both in the presence of pyridine and without it were unsuccessful: in both cases only phosphonoacetone was isolated from the reaction mixture. Phosphonoacetone was also obtained on treatment of the acid chloride of acetonylphosphinic acid with alcohol in the presence of pyridine.

The formation of the acid chloride of acetonylphosphinic acid, as well as the formation of phosphonoacetaldehyde, proves the hydrocarbon-radical structure of the addition products given above and, at the same time, is evidence that the addition occurs in accordance with Markovnikov’ s rule.

Experimental Part

Preparation of the product of addition of phosphorus pentachloride to vinyl acetate



$$\left(\mathrm{CH_3COOCH} - \underset{\overset{|}{\mathrm{Cl}}}{\mathrm{CH_2}} - \mathrm{PCl_4PCl_5}\right).$$

To a filtered solution of 41.6 g (0.2 mole) of phosphorus pentachloride in 250 ml of carbon tetrachloride, 8.6 g (0.1 mole) of vinyl acetate are added dropwise with stirring and cooling to 7-8°. Stirring is continued for another 6 hr (at the same temperature); part of the precipitated solid is filtered off through a glass filter, cooling it externally with dry ice. The precipitate is washed twice with carbon tetrachloride, then with isopentane, and analyzed immediately. (Residual isopentane is removed in vacuo, without allowing air to be drawn through the filter.)

Found, %:	C 9.22; 9.90;	H 1.16; 1.65;	P 12.25; 12.29
$C_4H_6O_2P_2Cl_{10}$. Calculated, %:	C 9.56;	H 1.20;	P 12.22

Acid chloride of β-acetoxy-β-chloroethylphosphinic acid. By the method described above, the addition product is obtained from 83.5 g (0.4 mole) of phosphorus pentachloride in 330 ml of carbon tetrachloride and 17.7 g (0.2 mole) of vinyl acetate. Then, without isolating it, sulfur dioxide gas is passed through the reaction mixture at 5-7° until the precipitate dissolves completely. Carbon tetrachloride, thionyl chloride, and phosphorus oxychloride are then distilled off in vacuo with a water-jet pump; the residue is distilled in vacuo. Obtained: 40.8 g (85% of theory) of acid chloride of β-acetoxy-β-chloroethylphosphinic acid. B.p. 99-100°/1.5 mm; n_D^{20} 1.4855, d_4^{20} 1.5035; MR_D found 45.68, calculated 45.25.

Found, %:	C 20.02; 20.36;	H 2.66; 2.78;	P 12.72; 12.71;	Cl 44.23; 44.27
$C_4H_6O_3PCl_3$. Calculated, %:	C 20.06;	H 2.53;	P 12.97;	Cl 44.42

Under analogous conditions, from 41.6 g (0.2 mole) of phosphorus pentachloride and 17.2 g (0.2 mole) of vinyl acetate, 20.8 g (40% of theory) of the acid chloride of β-acetoxy-β-chloroethylphosphinic acid was obtained.

Acetonylphosphinic acid chloranhydride. To a filtered solution of 83.5 g (0.4 mole) of phosphorus pentachloride in 650 ml of carbon tetrachloride, with stirring and cooling to −24-26°, 20 g (0.2 mole) of isopropenyl acetate is added dropwise over 20 min. After 2 hr of stirring at the same temperature, sulfurous gas is passed through (at −25°) until the precipitate has completely dissolved. The solvent, thionyl chloride, and phosphorus oxychloride are removed under the vacuum of a water-jet pump. During distillation of the residue in vacuo, decomposition of the substance is already observed at 60-70°. After complete decomposition, the residue distills at 89.5-90°/1.5 mm as a colorless liquid, which rapidly crystallizes in the receiver. Yield of acetonylphosphinic acid chloranhydride 21 g (60% of theory), m.p. 39-40°.

Found, %: C 21.02; 20.68; H 3.03; 2.99; P 17.18; 17.27
$C_3H_5O_2PCl_2$. Calculated, %: C 20.59; H 2.88; P 17.75

Under analogous conditions, from 83.5 g (0.4 mole) of phosphorus pentachloride and 40 g (0.4 mole) of isopropenyl acetate, 26 g (37% of theory) of acetonylphosphinic acid chloranhydride was obtained.

β-Acetoxy-β-chloropropylphosphinic acid chloranhydride. Under the conditions of the preceding experiment, an addition product is obtained from 83.5 g of phosphorus pentachloride and 20 g of isopropenyl acetate. After passing sulfurous gas (at −25°), the solvent, thionyl chloride, and phosphorus oxychloride are distilled off in the vacuum of a water-jet pump at 20-25°. On cooling with ice, the residue crystallizes completely. Yield of crude product 47 g (95% of theory). After crystallization from dry isopentane, 35.5 g (70% of theory) of β-acetoxy-β-chloropropylphosphinic acid chloranhydride is obtained in the form of colorless needles with m.p. 45.5-46.5°, sparingly soluble in isopentane and readily soluble in ordinary organic solvents.

Found, %: C 23.98; 23.96; H 3.26; 3.41; P 12.37; 12.42
$C_5H_8O_3PCl_3$. Calculated, %: C 23.67; H 3.18; P 12.21

Conversion of β-acetoxy-β-chloropropylphosphinic acid chloranhydride into acetonylphosphinic acid chloranhydride. 9.9 g of β-acetoxy-β-chloropropylphosphinic acid chloranhydride is heated on a bath at 95-105°. 2.7 g of acetyl chloride distills off (yield 88% of theory); acetanilide m.p. 114-115°, a mixed sample with an authentic specimen shows no depression. The residue is distilled in vacuo at 92-93°/2 mm. 5.0 g (83.8% of theory) of acetonylphosphinic acid chloranhydride is obtained in the form of colorless plates with m.p. 39-40°.

Diethyl ester of β-acetoxy-β-chloroethylphosphinic acid. To a solution of 47.9 g (0.2 mole) of β-acetoxy-β-chloroethylphosphinic acid chloranhydride in 150 ml of abs. ether, a mixture of 18.4 g (0.4 mole) of abs. ethyl alcohol, 31.6 g (0.4 mole) of pyridine, and 25 ml of ether is added dropwise with stirring and cooling to 0°. The mixture is stirred for another 1 hr, allowing the temperature to rise to room temperature, then boiled for 1 hr and filtered. The filtrate is concentrated and cooled to −10°. Colorless crystals with m.p. 62-63° separate. The precipitate, consisting of pyridine hydrochloride and the ester of phosphinic acid, is treated 3 times with abs. ether at boiling, and the ether extracts are combined and concentrated. On cooling, large colorless crystals with m.p. 64-65° separate. The total yield of the diethyl ester of β-acetoxy-β-chloroethylphosphinic acid is 41 g (79% of theory). In the open air the crystals slowly (after 10 days) melt, splitting off acetyl chloride.

Found, %: C 37.40; 37.18; H 6.42; 6.42; P 12.01; 11.99
$C_8H_{16}O_3PCl$. Calculated, %: C 37.15; H 6.23; P 11.98

Esterification of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid. A. In the absence of base. To a solution of 35.5 g of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid (immediately after its preparation) in 160 ml of dry ether, 12.9 g of absolute ethyl alcohol is added dropwise over 20 min with stirring, without external cooling (at −3° the reaction does not proceed for one and a half hours—the starting acid chloride is recovered). The mixture is heated for half an hour at 30°, the ether is distilled off together with hydrogen chloride, and the residue is distilled in vacuo. 16.3 g (60% of theory) of diethyl phosphonoacetone is obtained, b.p. 101-102°/2.5 mm; n_D^{20} 1.4364, d_4^{20} 1.1117; MR_D found 45.73, calculated 45.40.

Literature data: b.p. 106-106.5°/8.6 mm, n_D^{20} 1.4332, d_4^{20} 1.1127; b.p. 99-100°/1.5 mm, n_D^{20} 1.4355, d_4^{20} 1.1232 (2).

B. In the presence of pyridine. To a solution of 19.4 g of the acid chloride of β-acetoxy-β-chloropropylphosphinic acid in 120 ml of dry ether, a mixture of 7.1 g of absolute ethyl alcohol and 12.1 g of pyridine is added dropwise with stirring and cooling to 0°. The mixture is then heated for 1 hour at 35-40°, the precipitate is filtered off with suction and washed with ether. After 24 hours the precipitate that has again separated is filtered off with suction; from the filtrate, after fractionation, 6.8 g (47% of theory) of phosphonoacetone is obtained, b.p. 122°/8 mm; n_D^{20} 1.4370, d_4^{20} 1.1129.

Esterification of acetylphosphinic acid chloride. To a mixture of 10.2 g of absolute ethyl alcohol, 16.8 g of pyridine, and 60 ml of dry ether, a solution of 17.6 g of acetylphosphinic acid chloride in 40 ml of dry ether is added dropwise with stirring over the course of an hour. The mixture is then boiled for one hour, the precipitate is filtered off with suction, ether is distilled from the filtrate, and the residue is distilled in vacuo. 14.1 g (76.6% of theory) of phosphonoacetone is obtained, b.p. 94-95°/1 mm; n_D^{20} 1.4370, d_4^{20} 1.1131; MR_D found 45.70, calculated 45.40.

Found, %: C 43.34; H 7.79; P 15.88
$C_7H_{15}O_4P$. Calculated, %: C 43.30; H 7.79; P 15.96

Preparation of phosphonoacetaldehyde. A. In acetone at room temperature. 6 g of the diethyl ester of β-acetoxy-β-chloroethylphosphinic acid is dissolved in 10 ml of acetone, 1 g of water is added, and the mixture is left at room temperature. After 4 days the acetone and acetic acid are distilled off, and the residue is distilled in vacuo. 2.8 g (66.6% of theory) of the diethyl ester of phosphonoacetaldehyde is obtained, b.p. 92-93°/2 mm; n_D^{20} 1.4383, d_4^{20} 1.1476; MR_D found 41.23, calculated 40.79.

B. In dioxane with heating. 9 g of the diethyl ester of β-acetoxy-β-chloroethylphosphinic acid is dissolved in 25 ml of dioxane, 1.2 g of water is added, and the mixture is heated for 5 hours at 55-65°. The dioxane and acetic acid are distilled off, and the residue is distilled in vacuo. 4.2 g (67% of theory) of phosphonoacetaldehyde is obtained, b.p. 92-93°/2 mm; n_D^{20} 1.4382; d_4^{20} 1.1473; MR_D found 41.23, calculated 40.79.

Found, %: C 39.92; 39.96; H 7.27; 7.34; P 17.02; 17.01
$C_6H_{13}O_4P$. Calculated, %: C 40.01; H 7.27; P 17.20

Moscow State University
named after M. V. Lomonosov

Received
6 I 1960

CITED LITERATURE

1. I. F. Lutsenko, M. Kirilov, DAN, **128**, 89 (1959).

2. *Chemistry and Applications of Organophosphorus Compounds*, Moscow, 1957, p. 179.

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