

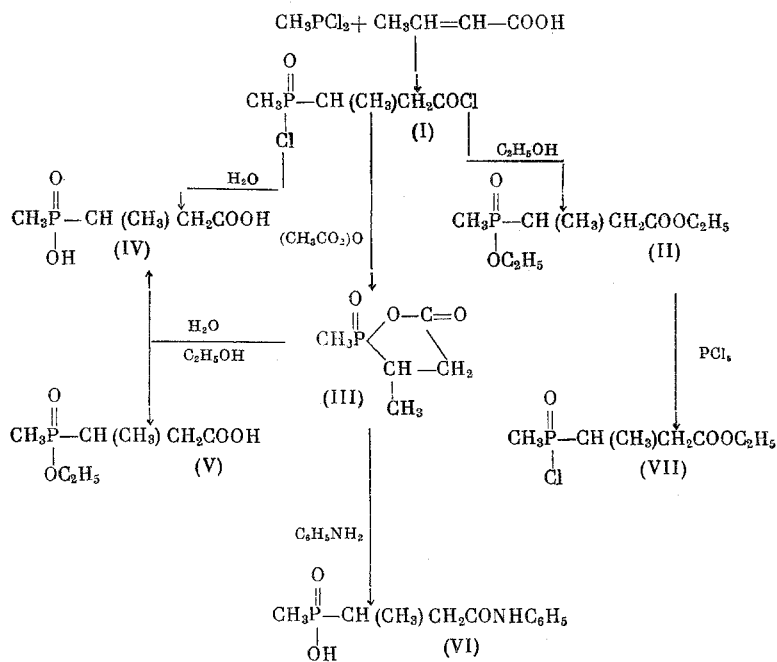
THE REACTION OF METHYLDICHLOROPHOSPHINE
WITH CROTONIC ACID

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UDC 542.91+661.718.1

We have reported earlier on the reaction of methyldichlorophosphine with acrylic [1], methacrylic, and propiolic [2] acids. Continuing our study in this direction we have now studied the reaction of methyldichlorophosphine with α -crotonic acid.

As product of the exothermal reaction of methylchlorophosphine with α -crotonic acid methyl-(β -chloroformylisopropyl)phosphinic acid chloride (I) is formed with 62% yield. The IR spectrum of the acid chloride (I) (Fig. 1, (1)) shows characteristic absorption bands of the following groups: P—Cl (555 cm^{-1}), P = O (1230 cm^{-1}), and C = O (1810 cm^{-1}). In hydrolysis the acid chloride (I) is converted to methyl-(β -carboxyisopropyl)phosphinic acid (IV), in heating with acetic anhydride 2, 3-dimethyl-2, 5-dioxo-1, 2-oxaphospholane (III) is formed. Reaction of the acid chloride (I) with ethanol gives the ethyl ester of methyl-(β -carbethoxyisopropyl)phosphinic acid (II). Its IR spectrum (2) contains the absorption bands of the following groups: R—OC₂H₅ (1045 cm^{-1}), P = O (1230 cm^{-1}), and C = O (1740 cm^{-1}). In the reaction phos-



phorus pentachloride with the ester (II) methyl-(β -carbethoxyisopropyl)phosphinic acid chloride (VII) is formed. The ethoxyl group next to the carbonyl group is not replaced by a chlorine atom. The IR spectrum (3) of the acid chloride (VII) is in agreement with the proposed structure: P—Cl (550 cm^{-1}), P = O (1250 cm^{-1}), and C = O (1740 cm^{-1}).

Phospholane (III) as a typical ambidentic reagent reacts differently with ethanol and aniline. The less nucleophilic ethanol in comparison with aniline attacks the less electrophilic center: the phosphorus atom. The product of this reaction is the ethyl ester of methyl-(β -carboxyisopropyl)phosphinic acid (V). The IR spectrum (4) of

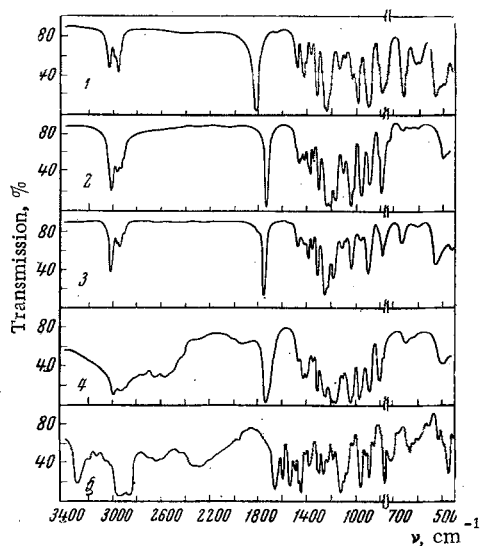


Fig. 1. IR spectra of (1) methyl-(β -chloroformylisopropyl) phosphinic acid chloride (I), (2) ethyl ester of methyl-(β -carbethoxyisopropyl)phosphinic acid (II), (3) methyl-(β -carbethoxyisopropyl)phosphinic acid chloride (VII), (4) ethyl ester of methyl-(β -carboxyisopropyl)phosphinic acid (V), (5) methyl-(β -phenylcarbamoylisopropyl)phosphinic acid (VI).

the ester (V) is in agreement with the proposed structure: $\text{P}-\text{OC}_2\text{H}_5$ (1045 cm^{-1}), $\text{P}=\text{O}$ (1170 cm^{-1}), $\text{C}=\text{O}$ (1730 cm^{-1}), and COOH ($2380\text{--}2680\text{ cm}^{-1}$). The more nucleophilic aniline in comparison with ethanol attacks the more electrophilic carbonyl ring carbon atom. The product of the reaction is methyl-(β -phenylcarbamoylisopropyl) phosphinic acid (VI). In the IR spectrum (5) of the acid (VI) the absorption band in the 1130 cm^{-1} region must be ascribed to $\text{P}=\text{O}$ vibration, the bands at 1450 , 1540 , and 1600 cm^{-1} are characteristic for the benzene ring, the band at 1640 cm^{-1} for the $\text{C}=\text{O}$ group of the carbonic acid amide, the broad bands at $2100\text{--}2400\text{ cm}^{-1}$ and $2500\text{--}2750\text{ cm}^{-1}$ are connected with the presence of the $\text{P}(\text{O})\text{OH}$ grouping, and the band at 3280 cm^{-1} is related to the NH -group. The acid (IV) is formed in the hydrolysis of phospholane (III).

EXPERIMENTAL METHOD

The IR spectra were obtained on a UR-10 spectrometer, by placing a drop of the sample between two KBr discs. The layer thickness was not measured.

Methyl-(β -Chloroformylisopropyl)phosphinic Acid Chloride (I). 50 g methyl dichlorophosphine was added dropwise in a stream of dry CO_2 to 36.7 g α -crotonic acid. The reaction temperature decreased from 23 to 20° . After formation of a homogeneous solution the temperature was slowly increased to 30° . By periodic cooling of the reaction vessel with cold water the reaction temperature was maintained at $45\text{--}50^\circ$, and then the reaction mixture kept at 60° for 4 h. Distillation of the reaction product gave 53.8 g (62%) of the acid chloride (I) with a bp of 120° (0.06 mm), d_4^{20} 1.3610, n_D^{20} 1.4960. Found: C 30.06, H 4.45, Cl 34.35, P 15.35%; MR 43.55. $\text{C}_5\text{H}_9\text{Cl}_2\text{O}_2\text{P}$. Calculated: C 29.58, H 4.47, Cl 34.93, P 15.25%; MR 43.87. The chloroanhydride (I) represents a liquid fuming in air. In a liquid nitrogen trap 6 g of α -crotonic acid chloride was collected, d_4^{20} 1.2940, n_D^{20} 1.4650 [3].

Ethyl Ester of Methyl-(β -Carbethoxyisopropyl)phosphinic Acid (II). 7 g ethanol were added dropwise to 15 g of acid chloride (I), cooled with an ice and salt mixture. Distillation of the reaction product yielded 8.7 g (53%) ester (II), bp 110° (0.06 mm) d_4^{20} 1.0845, n_D^{20} 1.4490. Found: C 48.32, H 8.63, P 13.67%; MR 54.96. $\text{C}_9\text{H}_{19}\text{O}_4\text{P}$. Calculated: C 48.64, H 8.62, P 13.93%, MR 55.16. A fraction with bp $125\text{--}128^\circ$ (0.06 mm), d_4^{20} 1.2542, n_D^{20} 1.2542, n_D^{20} 1.4800 of 3.1 g (28.5%) was found to be 2,3-dimethyl-2,5-dioxo-1,2-oxaphospholane (III).

2,3-Dimethyl-2,5-Dioxo-1,2-Oxaphosphospholane (III). 10.5 g Ac_2O were added dropwise to 20 g acid chloride (I). The reaction mixture was kept 1 h at 60° . After removal of acetyl chloride by distillation (bp $50\text{--}52^\circ$, d_4^{20} 1.1050, n_D^{20} 1.3900) the remaining 13.6 g were distilled. Obtained 10 g (69%) of phospholane (III), bp 125° (0.06 mm); d_4^{20} 1.2548, n_D^{20} 1.4800. Found: C 40.75, H 6.48, P 21.28%; MR 33.55. $\text{C}_5\text{H}_9\text{O}_3\text{P}$. Calculated: C 40.54, H 6.12, P 20.91%; MR 32.85. Phospholane (III) forms deliquescent crystals.

Methyl-(β -Carboxyisopropyl)phosphinic Acid (IV). An excess of water was added to 1.5 g acid chloride (I). After removal of the water in vacuo 1.25 g (100%) of acid (IV) was obtained, d_4^{20} 1.2810, n_D^{20} 1.4750. Found: C 36.04, H 6.73, P 18.19%; MR 36.40. $\text{C}_5\text{H}_{11}\text{O}_4\text{P}$. Calculated: C 36.14, H 6.67, P 18.06%; MR 36.45.

0.5 g water was added to 1.5 g phospholane (III). After removal of excess water 1.68 g (100%) of acid (IV) was obtained, having the same constants.

Ethyl Ester of Methyl-(β -Carboxyisopropyl)phosphinic Acid (V). When mixing 2.5 g of phospholane (III) with 1 g ethanol the temperature of the reaction mixture increased to 55°. The excess ethanol was removed under vacuum without heating. Obtained 3.3 g (100%) ester (V), d_4^{20} 1.1594, n_D^{20} 1.4610. Found: C 43.07, H 7.82, P 15.15%; MR 44.96. $C_5H_{15}O_4P$. Calculated: C 43.30, H 7.70, P 15.95%; MR 45.81.

Methyl-(β -phenylcarbamoylisopropyl)phosphinic Acid (VI). The crystals formed when mixing 3 g of phospholane (III) with 1.9 g aniline were recrystallized from acetone-dioxane. Obtained 4.5 g (92.6%) acid (VI), mp 143-144°. Found: C 54.80, H 6.75, N 5.90, P 13.00%. $C_{11}H_{16}NO_3P$. Calculated: C 54.79, H 6.69, N 5.86, P 12.84%.

Methyl-(β -Carbethoxyisopropyl)phosphinic Acid Chloride (VII). 7.5 g PCl_5 was added in small portions to 8 g of ester (II) in 50 ml CCl_4 and the reaction mixture kept 1 h at 60°. After removal of CCl_4 and the phosphorus oxychloride formed, the remaining substance was distilled. Obtained 6.5 g (85.5%) of acid chloride (VII), bp 110° (0.06 mm); d_4^{20} 1.2066, n_D^{20} 1.4732. Found: C 38.45, H 6.31, Cl 17.95, P 15.15%; MR 49.34. $C_7H_{14}ClO_3P$. Calculated: C 39.54, H 6.63, Cl 16.67, P 14.57%; MR 49.52.

CONCLUSIONS

1. Methylchlorophosphine reacts with α -crotonic acid and gives methyl-(β -chloroformylisopropyl)phosphinic acid chloride.
2. The hydrolysis of methyl-(β -chloroformylisopropyl)phosphinic acid chloride gives methyl-(β -carboxyisopropyl)phosphinic acid, the alcoholysis gives the complete ester of this acid; its reaction with acetic anhydride leads to the formation of 2,3-dimethyl-2,5-dioxo-1,2-oxaphospholane.
3. The reaction of 2,3-dimethyl-2,5-dioxo-1,2-oxaphospholane with ethanol gives the ethyl ester of methyl-(β -carboxyisopropyl)phosphinic acid, the reaction with aniline gives methyl-(β -phenyl-carbamoyl-isopropyl)phosphinic acid.
4. The ethyl ester of methyl-(β -carbethoxyisopropyl)phosphinic acid with PCl_5 gives methyl-(β -carbethoxyisopropyl)phosphinic acid chloride.

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