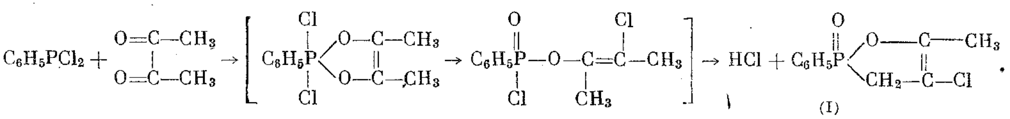
REACTION OF PHENYLDICHLOROPHOSPHINE WITH DIACETYL

A.N. Pudovik, V.K. Khairullin, and N.I. Kharitonova

UDC 542.91+661.718.1

In [1] we showed that alkyldichlorophosphines react with diacetyl to form 1:1 adducts, which by undergoing a rearrangement according to the second stage of the Arbuzov reaction lose hydrogen chloride and change into 2,5-dialkyl-4-chloro-2-oxo-1,2-oxaphosphol-4-ene.

We have extended the reaction to phenyldichlorophosphine. The reaction between phenyldichlorophosphine and diacetyl is exothermic, and the reaction mixture therefore forms a dark brown oily liquid. Vacuum distillation is accompanied by evolution of considerable quantities of hydrogen chloride and the formation of resinous products. By repeated distillation of the reaction products which came over without decomposition, 5-methyl-2-phenyl-4-chloro-2-oxo-1,2,-oxaphosphol-4-ene (I) was isolated in a yield of 16.2%. The reaction proceeds according to the following scheme:



A similar splitting off of hydrogen chloride from the methyl group of acetone by the action of pentachlorophenylbenzenesulfonyl chloride was observed by Yarmukhametova [2].

The structure of the oxaphospholene (I) agrees with its IR-spectrum (Fig. 1, curve 1): it contains the characteristic absorption bands of the C = C group (1685 cm^{-1}), the P = O group (1180 cm^{-1}), the O–C group (1140 cm^{-1}), and characteristic frequencies of the benzene ring (1445, 1588, and 3055 cm^{-1}).

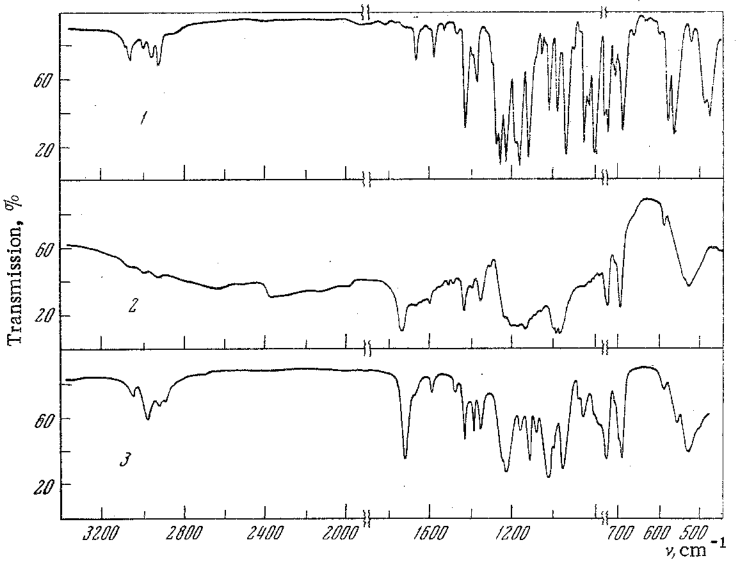
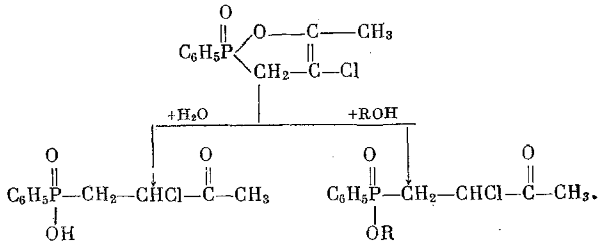


Fig. 1. IR-spectra: 1) 5-methyl-2-phenyl-4-chloro-2-oxo-1,2-oxaphosphol-4-ene (I); 2) phenyl(β-chloro-γ-oxo)butylphosphinic acid (II); 3) ethyl ester of phenyl-(β-chloro-γ-oxo)butylphosphinic acid (IV).

A.E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 466-468, February, 1969. Original article submitted July 29, 1968.

It is an extremely reactive compound. It is very sensitive to atmospheric moisture and reacts exothermically with water and alcohols according to the following scheme:



(II) (III) R=CH$_3$; (IV) R=C$_2$H$_5$

The IR-spectrum of phenyl-(β-chloro-γ-oxo)butylphosphinic acid (II) contains absorption bands of the following groups: C = O (1735 cm^{-1}), P(O)OH (2110-2380, 2600 cm^{-1}) (Fig. 1, curve 2). The IR-spectrum of the ethyl ester of phenyl-(β-chloro-γ-oxo)butylphosphinic acid (IV) (Fig. 1, curve 3) agrees with its structure: $\nu_{P=O}$ (1233 cm^{-1}), $\nu_{C=O}$ (1730 cm^{-1}), ν_{P-O-C} (1040 cm^{-1}), $\nu_{C_6H_5}$ (1440, 1592, 3055 cm^{-1}).

The structure of the oxaphospholene (I) is thus confirmed by its reaction with water and alcohols.

EXPERIMENTAL

Reaction of Phenyldichlorophosphine with Diacetyl. A four-necked flask fitted with a stirrer, a thermometer, a dropping funnel, and a reflux condenser was filled with dry CO$_2$, and 97.5 g phenyldichlorophosphine was added. A 47 g portion of diacetyl was added drop by drop over a period of 30 min with stirring. Dry CO$_2$ was then gradually passed through the dropping funnel. Heat was evolved during the reaction, and the flask was cooled periodically with water to keep the temperature of the reaction mixture between 30 and 42°C. After 7.5 h a dark brown viscous liquid was formed. After two successive distillations 20.1 g (16.2% theoretical) Compound I was obtained; bp = 129-131°C (0.01 mm); d_4^{20} = 1.2841; n_D^{20} = 1.5608. The product had the following composition: 52.86% C, 4.51% H, 14.86% Cl, 13.84% P; MR = 56.72; mol.wt. = 232.5. The theoretical composition for $C_{10}H_{10}ClO_2P$ is: 52.53% C, 4.72% H, 15.51% Cl, 13.56% P; MR = 57.63; mol. wt. = 228.61. Compound I is a liquid similar in appearance to glycerol, and becomes dark on storage.

Phenyl-(β-chloro-γ-oxo)butylphosphinic Acid (II). To 4.56 g oxaphospholene (I) was added 0.36 g water. The temperature of the reaction mixture increased, and 4.92 g Compound II was obtained; d_4^{20} = 1.2976; n_D^{20} = 1.5463. It had the following composition: 49.01% C, 5.01% H, 12.93% P; MR = 60.21. The theoretical composition of $C_{10}H_{11}ClO_3P$ is: 48.66% C, 4.86% H, 12.56% P; MR = 59.28. Compound II is a syrupy liquid.

Esters of Phenyl-(β-chloro-γ-oxo)butylphosphinic Acid. Into a flask cooled with ice 6.72 g oxaphospholene (I) and 1 g methanol were placed. Distillation of the reaction mixture gave 3.3 g (43%) methyl ester of phenyl-(β-chloro-γ-oxo)butylphosphinic acid (III); bp = 121-124°C (0.007 mm); d_4^{20} = 1.2120; n_D^{20} = 1.5210. The product had the following composition: 51.38% C, 5.95% H, 12.02% P; MR = 65.41. The theoretical composition of $C_{11}H_{14}ClO_3P$ is: 50.68% C, 5.37% H, 11.88% P; MR = 64.02. Compound III is an oily liquid.

In a similar manner the reaction of 6.72 g oxaphospholene (I) with 1.4 g ethanol gave 4.95 g (68.5%) ethyl ester of phenyl-(β-chloro-γ-oxo)butylphosphinic acid (IV); bp = 142-144°C (0.01 mm); d_4^{20} = 1.1921; n_D^{20} = 1.5205. It had the following composition: 53.05% C, 6.10% H, 11.51% P; MR = 69.75. The theoretical composition of $C_{12}H_{16}ClO_3P$ is: 52.45% C, 5.82% H, 11.27% P; MR = 68.64. Compound IV is an oily liquid.

CONCLUSIONS

Phenyldichlorophosphine reacts with diacetyl to form 5-methyl-2-phenyl-4-chloro-2-oxo-1,2-oxaphosphol-4-ene. Hydrolysis of this compound gives phenyl-(β-chloro-γ-oxo)butylphosphinic acid, and alcoholysis gives the ester of this acid.

LITERATURE CITED

1. A.N. Pudovik, V.K. Khairullin, Yu.Yu. Samitov, and R.R. Shagidullin, Zh. Obshch. Khim., 37, 865 (1967).
2. D.Kh. Yarmukhametova, Izv. Akad. Nauk SSSR, Ser. Khim., 1260 (1966).