REACTION OF SUBSTITUTED 2,5-DIOXO-1,2-OXAPHOSPHOLANES WITH MERCAPTANS

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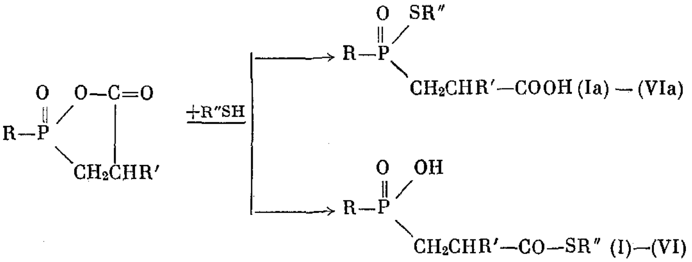
UDC 542.91:661.718.1

Alcohols react readily with 2-ethyl-2,5-dioxo-1,2-oxaphospholane at the phosphorus atom to form esters of ethyl-β-carboxyethylphosphinic acid [1]. When substituted 2,5-dioxo-1,2-oxaphospholanes are reacted with mercaptans, which are even milder bases [2], it could be expected that the phosphorus atom will also be the reaction center in them. The reaction of substituted 2,5-dioxo-1,2-oxaphospholanes with mercaptans proceeds when the reaction mixture is heated at 150-180°C for several hours. Here a mixture is formed, which consists of two isomers: the ethyl- or phenyl-(β-carbalkylthioalkyl)phosphinic acids (I)-(VI) and the thioalkyl esters of the ethyl- or phenyl-β-carboxyalkylphosphinic acids (Ia)-(VIa)



(I, Ia) $R = C_2H_5$, $R' = H$, $R'' = C_3H_7$; (II, IIa) $R = C_2H_5$, $R' = H$, $R'' = C_4H_9$;
(III, IIIa) $R = C_2H_5$, $R' = CH_3$, $R'' = C_4H_9$; (IV) $R = C_2H_5$, $R' = CH_3$, $R'' = C_4H_9\text{-}i$;
(V) $R = C_6H_5$, $R' = H$, $R'' = C_4H_9$; (VI, VIa) $R = C_6H_5$, $R' = H$, $R'' = C_4H_9\text{-}i$.

In Fig. 1a are shown the IR spectra of the reaction product of 2-ethyl-2,5-dioxo-1,2-oxaphospholane with butyl mercaptan. In the spectrum is present the absorption band of the $P=O$ group (1170 cm^{-1}), and an intense band with a maximum at 1690 cm^{-1}, which corresponds to the stretching vibration of the $C=O$ in the $COSC_4H_9$ group, with a shoulder at 1735 cm^{-1}, which indicates the presence of a carboxyl group. The diffuse broad absorption bands at 2150-2320 and 2500-2700 cm^{-1} correspond to the vibrations of the P(O)OH and COOH groups. Thus, the product formed as a result of the reaction consists of a mixture of isomeric compounds (II) and (IIa), in which connection a comparison of the intensities of the absorption bands at 1690 and 1735 cm^{-1} indicates that compound (II) is present in larger amount. The presence of the isomeric (II) and (IIa) and their quantitative ratios are both manifested more distinctly in the IR spectrum of the reaction mixture after the latter has been treated with thionyl chloride (Fig. 1b). The absorption band at 1690 cm^{-1} of the carbonyl in the $COSC_4H_9$ group is retained, while the absorption band at 1735 cm^{-1} of the $C=O$ of the carboxyl group is shifted to 1795 cm^{-1} due to its conversion to the CO–Cl group.

As the result of successive distillations we were able to isolate the ethyl-(I)-(IV) or the phenyl-(β-carbalkylthioalkyl)phosphinic acids (V) in a fairly pure state. Here the isomeric products, as the result of the cleavage of mercaptan, are partially converted to the corresponding substituted 2,5-dioxo-1,2-oxaphospholanes. We attempted to separate the mixture of isomers (II) and (IIa) chemically. By treating the mixture with aqueous $FeCl_3$ solutions we obtained the crystalline iron salt of ethyl-(β-carbobutylthioethyl)phosphinic acid. The other isomer (IIa) does not react with $FeCl_3$. Its aqueous solution was evaporated and vacuum-distilled. However, instead of the expected (IIa) we isolated the anhydride of ethyl-β-carboxyethylphosphinic acid (VII), which is probably formed as the result of the hydrolysis of the $P(O)SC_4H_9$ group and the subsequent cleavage of water on heating

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A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1722-1726, August, 1971. Original article submitted October 20, 1969.

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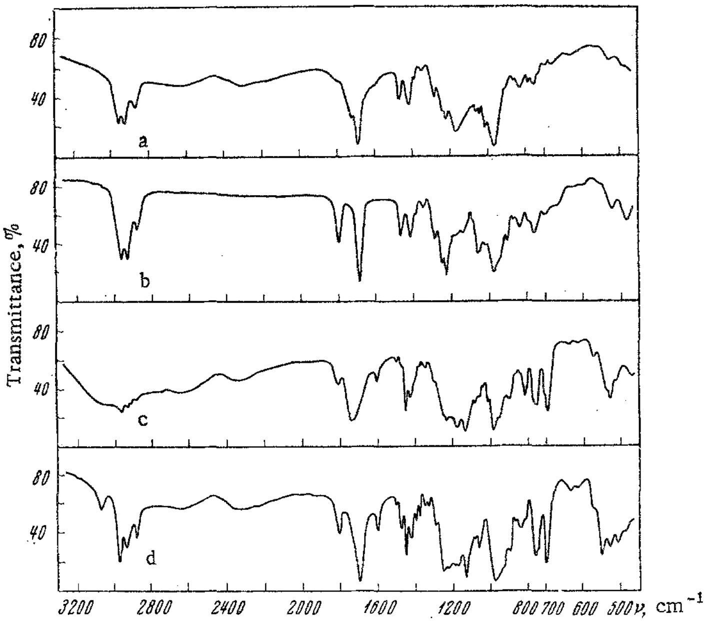
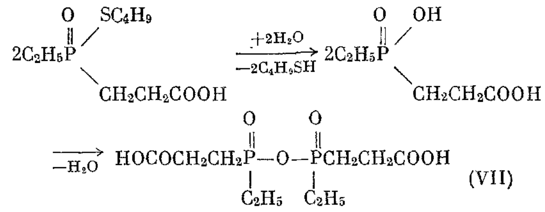


Fig. 1. Infrared spectra: a) reaction product of 2-ethyl-2,5-dioxo-1,2-oxaphospholane with butyl mercaptan [mixture of (II) and (IIa)]; b) mixture of (II) and (IIa) after treatment with thionyl chloride; c) thioisobutyl ester of phenyl-β-carboxyethylphosphinic acid (VIa); d) phenyl-(β-carbisobutylthioethyl)phosphinic acid (VI).



$$2C_2H_5P(=O)(SC_4H_9)CH_2CH_2COOH \xrightarrow[-2C_4H_9SH]{+2H_2O} 2C_2H_5P(=O)(OH)CH_2CH_2COOH \xrightarrow[-H_2O]{} HOCOCH_2CH_2\overset{O}{\overset{\|}{\underset{C_2H_5}{\underset{|}{P}}}}-O-\overset{O}{\overset{\|}{\underset{C_2H_5}{\underset{|}{P}}}}CH_2CH_2COOH \quad (VII)$$

The reaction product of 2-phenyl-2,5-dioxo-1,2-oxaphospholane with isobutyl mercaptan was separated into the isomers (VI) and (VIa) by vacuum-distillation. The low-boiling isomer (VIa) (17.6%) is the thioisobutyl ester of phenyl-β-carboxyethylphosphinic acid [$\nu_{C=O}$ in the COOH grouping = 1735 cm^{-1} (Fig. 1c)], while the high-boiling isomer (VI) (58.8%) is phenyl-(β-carboisobutylthioethyl)phosphinic acid [$\nu_{C=O}$ in the COSC$_4$H$_9$-i group = 1690 cm^{-1} (Fig. 1d)]. The presence of absorption bands in the 1795 cm^{-1} region in the spectrograms of compounds (VI) and (VIa) (see Fig. 1c and d) is due to their being slightly contaminated with 2-phenyl-2,5-dioxo-1,2-oxaphospholane, which is formed when the compounds are heated during the distillation process. Actually, as the result of the repeated distillation of (V) we obtained 2-phenyl-2,5-dioxo-1,2-oxaphospholane in 89% yield.

As a result, the reaction of substituted 2,5-dioxo-1,2-oxaphospholanes with mercaptans goes to a large degree contrary to the principle of hard and soft acids and bases [2], with attack of the mercaptan on the carbonyl group of 2,5-dioxophospholanes. This anomalous progress of the reaction can probably be explained by steric hindrance: the atomic radius of the sulfur in the mercaptan, which is greater than the atomic radius of oxygen, makes it difficult for the sulfur to approach the phosphorus atom.

EXPERIMENTAL METHOD

The constants and analyses of the synthesized compounds are given in Table 1. The IR spectrograms were obtained on a UR-10 spectrometer. Here a drop of the substance was pressed between two KBr plates. The layer thickness of the substance was not controlled.

TABLE 1

Compound Number	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found Calcd.		
					MR	P, %	S, %
I	30,0	220—222 (0,08)	1,1782	1,5060	56,50 56,59	13,97 13,82	13,80 14,28
II	29,8	200—201 (0,04)	1,1652	1,5010	60,24 60,21	13,40 13,01	12,98 13,47
III	29,1	192—194 (0,03)	1,1191	1,4990	66,21 65,82	12,88 12,28	12,99 12,69
IV	30,1	222—223 (0,04)	1,1270	1,4960	65,36 65,82	12,39 12,28	12,69 12,69
V	61,3	260—263 (0,04)	1,2115	1,5500	75,26 76,08	11,05 10,83	10,55 11,19
VI	58,8	280—283 (0,06)	1,2109	1,5550	75,84 76,08	11,25 10,83	10,48 11,19
VIa	17,6	230—233 (0,04)	—	1,5550	—	11,25 10,83	10,65 11,19

Ethyl-(β-carbopropylthioethyl)phosphinic acid (I). In an ampul were sealed 6.1 g of 2-ethyl-2,5-dioxo-1,2-oxaphospholane and 3.1 g of propyl mercaptan; the mixture was heated at 150° for 18 h. As the result of distillation we isolated 6.5 g (70%) of a fraction with bp 227-229° (0.04 mm), which is a mixture of the isomeric (I) and thiopropyl ester of ethyl-β-carboxyethylphosphinic acid (Ia). Redistillation of this fraction gave 2.8 g (46%) of 2-ethyl-2,5-dioxo-1,2-oxaphospholane with bp 125-127° (0.04 mm); d_4^{20} 1.2908; n_D^{20} 1.4860 [1] and 3 g of (I).

Compounds (II), (III), and (IV) were obtained in a similar manner.

Iron Salt of Ethyl-(β-carbobutylthioethyl)phosphinic acid. To a solution of 3.8 g of the freshly distilled reaction product of 2-ethyl-2,5-dioxo-1,2-oxaphospholane with butyl mercaptan, which represented a mixture of the isomeric (II) and (IIa), in 20 ml of water was added a solution of 0.8 g of $FeCl_3$ in 10 ml of water. The obtained iron salt of ethyl-(β-carbobutylthioethyl)phosphinic acid was filtered, washed with water, and dried in a vacuum-desiccator. We obtained 2 g (52%) of the salt with mp 248-249°. Found: C 41.80; H 7.09; P 12.85; S 12.95%. $C_{27}H_{54}FeO_9P_3S_3$. Calculated: C 42.27; H 7.09; P 12.11; S 12.56%.

Evaporation of the filtrate, followed by distillation, gave 0.8 g (21.3%) of the anhydride of ethyl-β-carboxyethylphosphinic acid (VII) with bp 160-162° (0.04 mm); n_D^{20} 1.4945; mp 85-87°. Found: C 38.77; H 6.66; P 20.09%. $C_{10}H_{20}O_7P_2$. Calculated: C 38.22; H 6.41; P 19.72%.

Reaction of Mixed (II) and (IIa) with Thionyl Chloride. In a four-necked flask, fitted with a stirrer, thermometer, dropping funnel, and a reflux condenser, was placed 5.6 g of the freshly-distilled reaction product of 2-ethyl-2,5-dioxo-1,2-oxaphospholane with butyl mercaptan [mixture of (II) and (IIa)]. With water cooling, 2.8 g of thionyl chloride was added in drops at such a rate that the temperature of the reaction mixture did not exceed 30°. After removal of the voltatile products in vacuo, the reaction product was distilled through a molecular still at a heater temperature of 180° and a pressure of 0.04 mm. We obtained 4 g (66.5%) of a product with d_4^{20} 1.1500 and n_D^{20} 1.5080, which represented a mixture of the thiobutyl ester of ethyl-β-chloroformylethylphosphinic acid and the acid chloride of ethyl-(β-carbobutylthioethyl)phosphinic acid [3].

Reaction of 2-Phenyl-2,5-dioxo-1,2-oxaphospholane with Isobutyl Mercaptan. A mixture of 2-phenyl-2,5-dioxo-1,2-oxaphospholane and 3 g of isobutyl mercaptan was sealed in an ampul and heated at 160-180° for 20 h. As the result of distillation we obtained 1.8 g (17.6%) of the thioisobutyl ester of phenyl-β-carboxyethylphosphinic acid (VIa) and 6 g (58.8%) of phenyl-(β-carboisobutylthioethyl)phosphinic acid (VI).

Phenyl-(β-carbobutylthioethyl)phosphinic Acid (V). A mixture of 7.85 g of 2-phenyl-2,5-dioxo-1,2-oxaphospholane and 3.6 g of butyl mercaptan was sealed in an ampul and heated at 160-180° for 20 h. As the result of distillation we obtained 7 g (61.3%) of (V). As the result of the repeated distillation of 7 g of (V) we obtained 4.3 g (89%) of 2-phenyl-2,5-dioxo-1,2-oxaphospholane with bp 173° (0.04 mm) and mp 74-75° [4].

CONCLUSIONS

The reaction of substituted 2,5-dioxo-1,2-oxaphospholanes with mercaptans goes to a large degree contrary to the principle of hard and soft acids and bases, with attack of the mercaptan on the carbonyl group.

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