## REACTION OF N-ARYLAMIDES OF DIALKYLPHOSPHOROUS AND DIARYLPHOSPHINOUS ACIDS WITH BENZIL

A. N. Pudovik, É. S. Batyeva, and V. D. Nesterenko UDC 542.91:547.1'118

In continuation of studying the reactions of the N-acrylamides of trivalent phosphorus acids with carbonyl-containing compounds [1-5] we investigated the reactions of the amides of dialkylphosphorous acids with benzil. It could be assumed that the reactions of the N-arylamidophosphites with  $\alpha$ -diketones will proceed with the initial involvement of either the phosphorus atom or the nitrogen atom according to the following directions (Scheme 1).

Compound (I) corresponds to the dioxaphospholene structure, the presence of which was established in the reactions of the fully substituted amides of dialkylphosphorous acids with  $\alpha$ -diketones [4]. It is possible to assume that in the case of secondary amidophosphites, due to the presence of involvement of the labile hydrogen atom of the amido group, both phospholene and the open bipolar form found in equilibrium with it, can change (Scheme 1) over to a compound containing the phosphimido linkage (structure II). Compounds of this type can also be formed by the initial attack of one of the carbons of the carbonyl groups by phosphorus, with subsequent phosphonate-phosphate rearrangement of the bipolar ion and transfer of the negative charge along the chain to the terminal oxygen atom. Compounds of the (III) type can be formed as the result of phosphonate-phosphate rearrangement of the initially formed bipolar ion (A), with subsequent intramolecular dealkylation of the new ion (B) by the Arbuzov scheme. Compound (IV) [3] can be formed by the direct stabilization of the bipolar ion, which is accomplished as the result of the migration of the hydrogen ion. The formation of compound (V) is postulated as the result of the initial attack of the carbonyl carbon by the nitrogen atom according to the scheme that was proposed earlier for aldehydes and ketones of the aliphatic and aromatic series [1].

The reactions of the anilide and p-toluidide of diethylphosphorous acid with benzil proceed in the absence of a catalyst and are accompanied by a substantial heat effect. The purest products are obtained when the reactions are run in diethyl ether at room temperature in a dry nitrogen atmosphere. These compounds are pale yellow viscous liquids that hydrolyze with ease and are unstable to the action of heat; because of this they were characterized in the undistilled form. Based on the elemental analysis data, they correspond to the 1:1 addition products of the amidophosphites to benzil.

Intense absorption in the 1380-1395 cm<sup>-i</sup> region is present in the IR spectra of the obtained compounds, which is characteristic for the P=N bond, and also absorption of the carbonyl group in the 1680 cm<sup>-1</sup> region. Absorption bands, characteristic for the phosphoryl, secondary amide and hydroxyl groups, are absent in the spectrum. As a result, the spectral data are found to be in agreement with the structure of imidophosphate (II), and contradict all of the other structures. The phosphate structure of the obtained compounds is also corroborated by the data of the <sup>31</sup>P NMR spectra. Intense absorption at  $\delta$  3 and 5 ppm is respectively present in the spectra of the reaction products of diethyl anilidophosphite and diethyl p-toluididophosphite with benzil. According to the data given in [6], upfield chemical shifts of ~2 ppm correspond to phosphate structures, containing strong electronegative substituents in the alkyl radical.

The imidophosphate structure of the (II) addition products was also corroborated by a number of chemical reactions. As is known, compounds containing the phosphimido linkage react with carbon disulfide and undergo hydrolysis [7]. These properties of phosphimido compounds are also inherent to the reaction products of the anilides of dialkylphosphorous acids with benzil.

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Scheme 1

Phenyl isothiocyanate was isolated as the result of the reaction of diethyl  $\alpha$ -benzoylbenzyl N-phenylimidophosphate with carbon disulfide, which was identified as the diphenylthiourea derivative

$$\begin{array}{cccc} C_{6}H_{5} & C_{6}H_{5} \\ | & | \\ (C_{2}H_{5}O)_{2}P-O-CH-C=O+CS_{2} \rightarrow (C_{2}H_{5}O)_{2}P-O-CH-C-C_{6}H_{5}+C_{6}H_{5}NCS \\ | & | \\ N-C_{6}H_{5} & C_{6}H_{5} & S & O \end{array}$$

The hydrolysis of the obtained imidophosphates proceeds with especial ease. They are gradually hydrolyzed when stored in the air under ordinary conditions, and they react with water very rapidly, in which connection the reaction is accompanied by an exothermic effect and the corresponding dialkyl anilidophosphates and benzoin are formed in nearly quantitative yields

 $\begin{array}{c} C_6H_5 & C_6H_5 \\ (RO)_2P - OCH - C = O + H_2O \rightarrow (RO)_2 P = O + CH - C = O \\ \parallel & \downarrow \\ N - Ar & C_6H_5 & NHAr & OH & C_6H_5 \end{array}$ 

As a result, both the physical and the chemical data testify in support of the imidophosphate structure for the addition products of the anilides of dialkylphosphorous acids to benzil. The formation of the dioxaphospholene structure as the intermediate product is postulated in scheme a and b, which is found in equilibrium with the open bipolar form. The presence of the phospholene structure in the reaction mixture was corroborated by the data of the NMR spectra on the  $P^{31}$  nuclei for the reaction of diethyl anilidophosphite with benzil; a peak with  $\delta$  55 ppm was detected when the reaction was run in benzene solution at low temperature, which peak gradually disappears during reaction with increase in the temperature. In harmony with the data given in [4], such a high positive value for  $\delta$  is in agreement with the dioxaphospholene structure.

The reactions of the anilides of diphenylphosphinous acid with benzil also proceed in a similar manner. However, the phosphimide that is formed in this case is stable only in an inert solvent. When the latter is removed the phosphimide decomposes with exceeding ease to give the anilide of diphenylphosphonic acid

 $\begin{array}{cccc} C_{6}H_{5} & C_{6}H_{6} & C_{6}H_{5} \\ | & | & | \\ (C_{6}H_{5})_{2}P-NHAr + C & C \rightarrow (C_{6}H_{5})_{2}P-O - CH - C - C_{6}H_{5} \\ | & | & | \\ O & O & N - Ar & O \end{array}$ 

The reactions of the N-phenyl-, p-tolyl-, and  $\alpha$ -naphthylaminodiphenylphosphine with benzil were run in either diethyl ether or benzene solution in a dry nitrogen atmosphere at room temperature. In the IR spectra of the reaction products, taken in benzene, is present intense absorption in the 1390 cm<sup>-1</sup> region, which is characteristic for the P=N bond, and also absorption of the P-O-C linkage in the 1030 cm<sup>-1</sup> region.

The presence of the phosphimido linkage is also corroborated by the chemical reactions run by us. As the result of reacting  $\alpha$ -benzoylbenzyl diphenyl N-phenylimidophosphinate with carbon disulfide we isolated phenyl isothiocyanate, which was identified as diphenylthiourea. In an analogous reaction with carbon dioxide we isolated  $\alpha$ -benzoylbenzyl diphenyl phosphinate, the structure of which was confirmed by the elemenetal analysis data and the IR spectra

 $\begin{array}{cccc} C_{6}H_{5} & O & C_{6}H_{5} \\ | & | \\ (C_{6}H_{5})_{2}P - O - C - C = O + CO_{2} \rightarrow (C_{6}H_{5})_{2}P - O - CH - C = O + C_{6}H_{5}NCS \\ | & | \\ N - C_{6}H_{5} & C_{6}H_{5} \\ \end{array}$ 

Absorption at 1230 cm<sup>-1</sup> is present in the IR spectrum, which is characteristic for the phosphoryl group in phosphinates, and there is also absorption at 980 cm<sup>-1</sup>, which belongs to the absorption of the P-O-C linkage, where a strong electronegative substituent is present in the alkyl radical. Also present is absorption of the carbonyl group in the 1680 cm<sup>-1</sup> region.

Consequently, as a result of the performed investigations it was established that the anilides of dialkylphosphorous and diphenylphosphinous acids react with benzil to form addition products that contain the phosphimido linkage.

## EXPERIMENTAL

Reaction of Diethylphosphorous Acid Anilide with Benzil. To 4.2 g of diethylphosphorous acid anilide in 50 ml of ether, with stirring, in a dry  $N_2$  stream, was added a solution of 4.2 g of benzil in 100 ml of ether. The mixture was stirred for 30 min at room temperature. The solvent was removed under reduced pressure. The residue was kept in vacuo (0.08 mm) for 30 min in order to remove traces of the solvent. We obtained 4.4 g of a pale yellow viscous liquid. Found: P 7.21; N 3.36%.  $C_{26}H_{26}NO_4P$ . Calculated: P 7.33; N 3.31%.

Reaction of Diethylphosphorous Acid p-Toluidide with Benzil. Similar to the above described, from 9 g of the p-toluidide and 8.4 g of benzil we obtained 17.3 g of diethyl  $\alpha$ -benzoylbenzyl N-tolylimidophosphate. Found: P 6.80; N 3.14%. C<sub>24</sub>H<sub>28</sub>NO<sub>4</sub>P. Calculated: P 7.09; N 3.23%.

<u>Reaction of Diethyl  $\alpha$ -Benzoylbenzyl N-Phenylimidophosphate with Carbon Disulfide</u>. To 8.4 g of the imidophosphate was added 10 ml of CS<sub>2</sub>. The mixture was kept for 3 days at room temperature, and then it was heated under reflux for 7 h. The excess CS<sub>2</sub> was removed in vacuo. From the residue by distillation was isolated 1.2 g (44%) of phenyl isothiocyanate with bp 52-55° (0.01 mm), which was identified as diphenylthiourea.

To 1.2 g of phenyl isothiocyanate was added 1 g of the anilide. The mixture crystallized completely with the formation of diphenylthiourea. Recrystallization from alcohol gave 1.1 g of product with mp 150-151°. The mixed melting point with the specially synthesized product was 152-153°.

<u>Reaction of Diethyl  $\alpha$ -Benzoylbenzyl N-Phenylimidophosphate with Water.</u> To 4.2 g of diethylphosphorous acid anilide in 20 ml of ether, in a dry N<sub>2</sub> stream, was added in drops a solution of 4.2 g of benzil in 50 ml of ether. The reaction mixture was stirred at room temperature for 30 min. Then 1 ml of water was added and the mixture was heated at 50° for 3 h. The solvent was removed in vacuo. From 7 g of the residue (0.03 M) by distillation and subsequent treatment with petroleum ether we isolated 3 g (88%) of diethyl anilidophosphate with mp 93°. From [8]: mp 93°. Found: P 13.08; N 6.00%. C<sub>10</sub>H<sub>6</sub>NO<sub>3</sub>P. Calculated: P 13.54; N 6.11%.

From 1.4 g of the residue, obtained after removal of the solvent, by treatment with ether we obtained 0.5 g (74%) of benzoin with mp 129-130°. The mixed melting point with benzoin was 130-131°.

<u>Reaction of  $\alpha$ -Benzoylbenzyl N-Phenylimidophosphinate with Carbon Dioxide</u>. A mixture of 7 g of diphenylphosphinous acid anilide and 5.3 g of benzil in 150 ml of ether was stirred at 35-40° in a dry N<sub>2</sub> stream for 30 min. Then CO<sub>2</sub> was passed into the solution for 20 h at room temperature. The obtained crystalline product (5.2 g) was filtered, washed with ether, and dissolved in hot benzene. The insoluble portion (0.7 g) was filtered. Recrystallization from alcohol gave 0.5 g of diphenyl anilidophosphate with mp 234°. Found: P 10.61; N 4.69%. C<sub>18</sub>H<sub>16</sub>NOP. Calculated: P 10.58; N 4.78%.

Treatment of the benzene filtrate with ether gave 4.5 g (42%) of  $\alpha$ -benzoylbenzyl diphenyl phosphinate with mp 128-130°. Found: P 7.93%. C<sub>26</sub>H<sub>21</sub>OP. Calculated: P 7.53%.

## CONCLUSIONS

The N-arylamides of dialkylphosphorous and diarylphosphinous acids react with benzil to give the corresponding imidophosphites and imidophosphonates.

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