ORGANOPHOSPHORUS DERIVATIVES

OF METHYLURETHAN

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Previously we had studied the reaction of the acid chlorides of carboxylic acids with the dialkylamido esters of phosphorus acids, which proceeds by either one or two schemes [1]. As a continuation of these studies we investigated the reaction of the acid chlorides with the amido esters of phosphorus acid where one of the substituents in the amido group was an electron-acceptor group, for example, an ester group.

We studied the reaction of the acid chlorides of acetic, benzoic, ethylcarbonic and N-diethylaminosulfenic acids with the diethyl ester of methylurethanphosphorous acid(diethyl N-methyl-N-carbethoxyamidophosphite). The acid chlorides of carboxylic and ethylcarbonic acids react with the ester of urethanphosphorous acid [2] by the scheme of the Arbuzov rearrangement, with the formation of the corresponding phosphonic acid derivatives.



methylurethan (I)-(IV).

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$$\begin{array}{c} C_2 H_5 O \\ (C_2 H_5 O)_2 P - N - COOC_2 H_5 + RCOCl \rightarrow P - N - COOC_2 H_5 + C_2 H_5 Cl \\ \downarrow \\ CH_3 \\ R = CH_3 (I); C_9 H_5 (II); C_9 H_5 O (III) \end{array}$$

The reaction of the acid chlorides with the given amido ester proceeds at higher temperature than when using dialkyl N-dialkylamidophosphites, and with better yields of the reaction products [1]. N-Diethylaminosulfenyl chloride reacts with the ester of methylurethanphosphorous acid also by the scheme of the Arbuzov rearrangement, but, in contrast to the indicated acid chlorides, the reaction proceeds with the evolution of heat.

The structure of compounds (I)-(IV) was corroborated by the IR spectra, which are shown in Fig.1. For compound (I) absorption bands are present in the regions $1300 (\nu_{P=O})$ (cf. [3]), $1035 (\nu_{P-O-C})$, and an intense absorption band with two maxima at 1705 and 1740 cm⁻¹ ($\nu_{C=O}$). For compound (II) are observed absorption bands at 1300 ($\nu_{P=O}$), $1045 (\nu_{P-O-C})$, and at 1665 and 1740 cm⁻¹ ($\nu_{C=O}$). The presence of an aromatic group is shown by bands at 1450, 1600, and 3060 cm⁻¹. For compound (III) absorption bands are present at 1300 ($\nu_{P=O}$), $1030 (\nu_{P-O-C})$ and $1730 \text{ cm}^{-1} (\nu_{C=O})$. For compound (IV) absorption bands are characteristic in the regions 1310 ($\nu_{P=O-C}$), $1050 (\nu_{P-O-C})$ and $1750 \text{ cm}^{-1} (\nu_{C=O})$.

When the N-methylamide of ethylcarbonic and O-ethylbenzoylphosphonic acids (II) is treated with aqueous ammonia solution at room temperature the P - C and P - N bonds are cleaved and benzamide, the ammonium salt of monoethylphosphorous acid and methylurethan are formed.



For identification, the ammonium salt of ethylphosphorous acid was obtained by another method, specifically, by the action of aqueous ammonia solution on diethylphosphorous acid [4].



The ammonium salt of ethylphosphorous acid formed in both cases has identical IR spectra; the mixed melting point of the salts is not depressed.

A factor which influences a weakening and cleavage of the P - N bond in the monoethyl ester of urethanphosphorous acid when it is treated with aqueous ammonia solution is apparently the presence of hydrogen, which is attached to the phosphorus atom as P - H (cf. [4]). In order to check this assumption, we treated the diethyl ester of N-methylurethanphosphoric acid $(C_2H_5O)_2P(O)N(CH_3)COOC_2H_5$ [5] with aqueous ammonia solution under the same conditions: the substance was recovered unchanged.

The ester of methylurethanphosphorous acid adds either sulfur or selenium under the same conditions as do trialkyl phosphites.

Com-	nd Bp, °C (p, mm of Hg)	n ²⁰ n _D	d ²⁰	MR		Found/calculated, %		Yield,
No.				found	calc.	N	P	%
I	9899 (1,5)	1,4455	1,1661	54,15	53,87	$\frac{6,29}{5,91}$	$\frac{13,04}{13,08}$	62
11	148 (1,5)	1,5136	1,2003	74,96	73,36	$\frac{4,82}{4,68}$	$\frac{10,6}{10,36}$	71
III	115—116,5(1,5)	1,4430	1,1713	60,45	60,13	5,23 5,24	$\frac{11,86}{11,61}$	68
IV	116 (1,5)	1,4693	1,1169	74,34	74,94	$\frac{10,43}{10,74}$	$\frac{10,58}{10,40}$	43
v	94—95 (2)	1,4660	1,1388	62,01	62,47	$\frac{5,73}{5,4}$	$\frac{12,33}{12,16}$	68
VI	91—93 (2)	1,4860	1,3175	65,79	65,92		$\frac{10,6}{10,26}$	75

TABLE 1. Organophosphorous Derivatives of Methylurethan

 $(C_{2}H_{3}O)_{2} P-N-COOC_{2}H_{5}- \overbrace{CH_{3}}^{+S} (C_{2}H_{5}O)_{2} P-N-COOC_{2}H_{5} \\ \overbrace{CH_{3}}^{+Se} (C_{2}H_{5}O)_{2} P-N-COOC_{2}H_{5} \\ \overbrace{Se}^{+Se} (C_{2}H_{5}O)_{2} P-N-COOC_{2}H_{5} \\ \overbrace{Se}^{\parallel} CH_{3} (VI)$

It is known that the esters of urethanphosphoric acids possess insecticidal properties [6]. Insecticidal action could also be expected from the esters of the urethanthiophosphoric and urethanselenophosphoric acids (V) and (VI). The preliminary testing of compound (VI) disclosed that it possesses systemic insecticidal action, but it is toxic to animals (white mice) and, in addition, it causes leaf blight of the plants. Compound (V) is much less toxic than (VI), but it lacks insecticidal action (flies, spider mites).

In Table 1 are given the formulas and constants of the synthesized compounds.

EXPERIMENTAL

<u>N-Methylamide of Ethylcarbonic and O-Ethylacetylphosphonic Acids</u>. To 0.03 mole of $(C_2H_5O)_2PN(CH_3)$ -COOC₂H₅ (bp 108-109° (9 mm) [2]) was added at room temperature 0.03 mole of CH₃COCl; here the temperature of the reaction mixture failed to rise. The mixture was heated at 55-90° for 1.5 h until the evolution of C_2H_5Cl ceased. Then the reaction product was distilled twice [see Table 1, compound (I)]. Compounds (II) and (III), listed in Table 1, were obtained in a similar manner.

<u>N-Methylamide of Ethylcarbonic and O-Ethyl-N-diethylaminosulfenophosphonic Acids</u>. To 0.03 mole of $(C_2H_5O)_2PN(CH_3)COOC_2H_5$ was added in drops, at 20-65°, 0.03 mole of $(C_2H_5)NSC1$ (the reaction was exothermic, and the flask was cooled with water). After the evolution of C_2H_5C1 had ceased the product was distilled twice [compound (IV)].

Action of Aqueous Ammonia Solution on N-Methylamide of Ethylcarbonic and O-Ethylbenzoylphosphonic Acids. To 5 ml of aqueous NH₃ solution, with cooling in an ice – salt mixture, was added 3.83 g of $(C_2H_5O) \cdot (C_8H_5CO)P(O)N(CH_3)COOC_2H_5$. A white crystalline precipitate was obtained immediately. The mixture was allowed to stand at room temperature for 24 h. The crystalline precipitate was filtered, washed with water, and recrystallized from water; mp 127–128°. Found: C 69.52; 69.61; H 6.21; 5.95; N 11.63; 11.77%. C_7H_7NO . Calculated: C 69.42; H 5.78; N 11.57%.

As a result, based on the analysis data and the melting point, the substance is benzamide. The mixed melting point with authentic benzamide was not depressed. The yield of the obtained benzamide was 1.16 g (76%). After removal of the benzamide, the low-boiling substances were removed in vacuo from the filtrate by heating the flask in a bath whose temperature was 40°. The residue represented 1.12 g of a crystalline substance, which after two recrystallizations from an alcohol – acetone mixture was obtained as tiny white needles with mp 103–104°. Found: C 18.38; 18.60; H 7.44; 7.44; N 11.26; 11.30; P 24.56; 24.7%. $C_2H_{10}NO_3P$. Calculated: C 18.89; H 7.87; N 11.02; P 24.4%.

The substance is readily soluble in water and in alcohol, and is insoluble in nonpolar organic solvents. As a result, based on the elemental analysis data and the melting point, the obtained substance is the ammonium salt of the monoethyl ester of phosphorous acid. The mixed melting point with the ammonium salt of the ethyl ester of phosphorous acid, obtained by the action of aqueous ammonia solution on diethylphosphorous acid [4], was not depressed. Methylurethan, which should have been formed in the hydrolysis of the monoethyl ester of methylurethanphosphorous acid, was not isolated by us, since it was removed in vacuo along with the water.

<u>N-Methylamide of Ethylcarbonic and Diethylthiophosphoric Acids</u>. To a solution of 0.034 mole of $(C_2H_5O)_2PN(CH_3)COOC_2H_5$ in 7 ml of benzene was added 0.03 atom of powdered sulfur, and the mixture was heated at 60° for 1 h. Then the product was distilled. Compound (V) was obtained.

<u>N-Methylamide of Ethylcarbonic and Diethylselenophosphoric Acids</u>. To 0.03 mole of $(C_2H_5O)_2PN(CH_3) \cdot COOC_2H_5$ was added at room temperature 0.03 g-atom of powdered selenium (gray). Here the temperature of the mixture rose from 20° to 45°. The mixture was heated at 85-90° for 30 min, and then the product was distilled twice. Compound (VI) was isolated.

CONCLUSIONS

1. A study was made of the reaction of the acid chlorides of acetic, benzoic, ethylcarbonic and Ndiethylaminosulfenic acids with the diethyl ester of methylurethanphosphorous acid. In all cases the reaction proceeds by the scheme of the Arbuzov rearrangement, with the formation of the corresponding phosphonic acid derivatives.

2. The action of aqueous ammonia solution on the N-methylamide of ethylcarbonic and O-ethylbenzoylphosphonic acids at room temperature results in cleavage of the P-C and P-N bonds, and benzamide, the ammonium salt of ethylphosphorous acid and methylurethan are formed.

3. The reaction of sulfur or selenium with the N-methylamide of ethylcarbonic and diethylphosphorous acids gave the N-methylamides of the corresponding acids, namely of ethylcarbonic and diethylthiophosphoric acids, and of ethylcarbonic and diethylselenophosphoric acids.

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