## SYNTHESIS OF DERIVATIVES OF N-PHOSPHORYLIMINOTHIOCARBAMIC ACID AND N-PHOSPHORYLIMIDOUREA

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We have previously reported some derivatives of iminocarbonic acid phosphorylated at the nitrogen atom in the imino group [1, 2]. In the present paper we give the conditions for obtaining derivatives of N-phosphorylated iminothiocarbamic acid, imidourea, and formimine.

The derivatives of N-diethylphosphoryliminothiocarbamic acid were obtained by the action of ammonia and primary and secondary amines on monochlorides of N-diethylphosphorylimino-S-alkylthiocarbonic acids by the following reactions

$$(C_{2}H_{5}O)_{2}P(O)N = C \begin{pmatrix} SR \\ Cl \end{pmatrix} + 2NH_{3} \rightarrow (C_{2}H_{5}O)_{2}P(O)N = C \begin{pmatrix} SR \\ NH_{2} \end{pmatrix} + NH_{4}Cl$$
(1)  
(I)-(II)

where  $R = C_2H_5$  (I) and  $i-C_3H_7$  (II), and

$$(C_{2}H_{5}O)_{2}P(O)N = C \begin{pmatrix} SR \\ CI \end{pmatrix} + 2R'R''NH \rightarrow (C_{2}H_{5}O)_{2}P(O)N = C \begin{pmatrix} SR \\ NR'R'' \end{pmatrix} + R'R''NH \cdot HCI(2)$$

$$(III) - (VI) \qquad (2)$$

where  $R = C_3H_7$ , R' = H,  $R'' = CH_3$  (III);  $R = C_4H_9$ . R' = H;  $R'' = CH_3$  (IV);  $R = C_4H_9$ ; R' = H,  $R'' = C_2H_5$  (V);  $R' = C_3H_7$ ,  $R' = C_3H_7$ ,  $R' = R'' = C_2H_5$  (VI) (III) - (VI).

(I) and (II) are crystalline substances soluble in organic solvents and practically insoluble in water. (III) - (VI) are liquids that can be distilled in vacuum. The action of the monochloride of N-diethylphosphorylimino-S-propylthiocarbonic acid on sodium ethoxide forms a mixed ester of the corresponding carbonic acid

$$(C_{2}H_{5}O)_{2} P(O) N = C \begin{pmatrix} SC_{3}H_{7} \\ Cl \end{pmatrix} + C_{2}H_{5}ONa \rightarrow (C_{2}H_{5}O)_{2}P(O) N = C \begin{pmatrix} SC_{3}H_{7} \\ OC_{2}H_{5} \end{pmatrix} + NaCl$$
(VII)

In addition to (VII), we also isolated the iminoether of dithiocarbonic acid  $(C_2H_5O)_2P(O)N = C(SC_3H_7)_2$ . It may be formed by the redistribution of the ester groups in the mixed iminoether

$$2 (C_2H_5O)_2P (O) N = C \begin{pmatrix} SC_8H_7 \\ OC_2H_5 \end{pmatrix}$$
  

$$\rightarrow (C_2H_5O)_2P (O) N = C (SC_3H_7)_2 + (C_2H_5O)_2 P (O) N = C (OC_2H_5)_2$$

We have been unable to isolate the latter compound formed in this reaction. It has a boiling point very close to that of the first two [1] and it was therefore washed out with water from the mixture obtained.

The dichloride of N-diethylphosphoryliminocarbonic acid [1] readily reacts with trialkyl phosphites forming bis-C-[0,0-dialkylphosphoryl]-methyleneamides of diethylphosphonic acid (VIII) and (IX)

$$\begin{array}{l} (C_2H_5O)_2P(O)N = CCl_2 + 2(RO)_3P \longrightarrow \\ \longrightarrow (C_2H_5O)_2P(O)N = C[P(O)(OR_2)]_2 + 2RCl \\ (VIII) - (IX) \end{array}$$

where  $R = C_2H_5$  (VIII) and  $C_3H_7 _{0}IX$ ; (VIII) is a pale yellowish viscous liquid and (IX) a crystalline substance.

The action of amines on the dichlorides of N-[N',N",N",N"-tetramethyldiaminophosphoryl-iminocarboxylic acid forms the corresponding derivatives of imidourea (X) and (XI)

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Com-	B.p., °C (p, mm Hg) or m.p., °C	$n_D^{20}$	d <sub>4</sub> <sup>2)</sup>	MR		P, %		%
pound				found	calcu- lated	found	calcu- lated	Yield,
I II III IV V	TM.p 85-86 T.M.p 73-74 128 (1) 116-118 (1)	 1,4954 1,4938	 1,1329 1,1135	 69,02 73,72 78,12	69,32 73,94 78,55	13,20 12,74 11,87 11,45 11,06	12,90 12,20 11,56 10,99 10,47	39,5 39,8 30,8 31,6 41 3
VI VII VIII IX	$\begin{array}{c} 120-12435 \\ 130-133 \\ 112-114 \\ 103-164 \\ 10,1) \\ 174-175 \\ 175 \\ 10,1) \\ 174-61 \\ 175 \\ 10,1) \\ 174-61 \\ 175 \\ 10,1) \\ 174-61 \\ 100 \\ 10$	1,4882 1,5002 1,4880 1,4566 	1,0939 1,1300 1,2347 	83,39 72,16 96,29	83,28 71,74 96,65	10,17 10,88 20,74 18,71	10,0 10,95 21,12 18,86	41,7 14,1 41,3 36,0
X XI	104—106 (0,015) 120 (0,02)	$1,5052 \\ 1,4915$	$1,0790 \\ 1,0205$	68,41 86,64	$     \begin{array}{r}       68,47 \\       86,88     \end{array}   $	$12,63 \\ 10,10$	12,45 10,16	$26,8 \\ 30,0$

Derivatives of Iminothiocarbamic Acid, Imidourea, and Forminine

where  $R = CH_3$  (X) or  $C_2H_5$  (XI). Substances (X) and (XI) are mobile red liquids soluble in water and organic solvents. The physical constants of the compounds synthesized are given in the table.

## EXPERIMENTAL

<u>N-Diethylphosphoryliminoethers of thiocarbamic acids</u>. Ammonia was passed through an ethereal solution of 0.035 mole of the monochloride  $(C_2H_5O)_2P(O)N = C(SAlk)Cl$ , obtained by the reaction of an alkyl mercaptan with the dichloride of N-diethylphosphoryliminocarbonic acid [2], at 20-30° until the reaction ceased. The precipitate of NH<sub>4</sub>Cl was separated off by centrifuging. The crude product in the form of a semicrystalline mass was pressed out on the filter and was recrystallized from ether [see table, compounds (I) and (II)].

An ethereal solution of 0.07 mole of amine was gradually added to an ethereal solution of 0.035 mole of  $(C_2H_5O)_2P(O)N = C(SAlk)Cl$  at 0°. The reaction mixture was stirred for an hour at room temperature. After the hydrochloride of the amine and the solvent had been eliminated, the substance obtained was distilled [see Table, compounds (III)-(VI)].

<u>N-Diethylphosphorylimine of S-propyl-O-ethylthiocarbonic acid</u>. An ethereal solution of 0.07 mole of  $(C_{2}H_{5}O)_{2}P(O)N = C(SC_{3}H_{7})Cl$  was added at room temperature to an alcoholic solution of 0.07 mole of sodium ethoxide, and then the mixture was stirred for 2 h. After the NaCl and the solvent had been eliminated, the residue was dissolved in ether, washed with water, and dried with MgSO<sub>4</sub>. Distillation yielded two fractions: 2.8 g (14.1%) of fraction I with b.p. 112-114° (0.1 mm) [see table, compound (VII)] and 2.5 g of fraction (II) with b.p. 134° (0.1 mm);  $nD^{20}$  1.5162. Found %: P 9.92.  $C_{11}H_{24}NO_3PS_2$ . Calculated %: P 9.9. The substance was identical with the N-diethylphosphorylimine of S, S-dipropyldithiocarbonic acid obtained previously [2].

 $\frac{\text{Bio-C-[O,O-dialkylphosphenyl]-methyleneamides of diethylphosphenic acid.}}{\text{With stirring at 0°, 0.02 mole of (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>P(O)N = CCl<sub>2</sub> [1] was added slowly to 0.04 mole of a trialkyl phosphite. The temperature of the mixture was raised to room temperature during an hour and then it was heated for 30 min at 35-40°. The amount of alkyl chloride liberated corresponded to theory. The crude product was distilled twice [see table, compounds (VIII) and (IX)].$ 

 $\frac{N-(N, N', N'', N''-tetramethyldiamidophosphonyl); iminotetraalkylureas. 0.06}{Mole of [(CH_3)_2N]_2P(O)NCS obtained by the reaction of the chloride [(CH_3)]_2N]_2P(O)Cl with potassium thiocyanate [3] was chlorinated in the unpurified state at -5 to +5° until the reaction ceased [1]. After the elimination of the excess of chlorine and the sulfur chloride, the crude product was dissolved in ether and to this solution was slowly added at -5 to 0° an ethereal solution of 0.12 mole of an amine. The mixture was stirred at room temperature for 2 h and then the crude product was isolated and was twice distilled [see table, compound (X) and (XI)].$ 

## SUMMARY

1. Derivatives of N-diethylphosphoryliminothiocarbamic acid have been obtained by the action of ammonia and methylamine, ethylamine, and diethylamine on the monochlorides of N-diethylphosphorylimino-S-alkylcarbonic acids (alkyl groups:  $C_2H_5$ , i- $C_3H_7$ ,  $C_3H_7$ ,  $C_4H_9$ ) and have been characterized.

2. The reaction of triethyl and tripropyl phosphites with the dichloride of N-diethylphosphoryliminocarbonic acid has given the corresponding bis-C-[O,O-dialkylphosphoryl]-methyleneamides of diethylphosphoric acid.

3. The reaction of dimethylamine and diethylamine with the dichloride of N-[N', N", N", N"-tetramethyldiamidophosphoryl]-iminocarbonic acid forms the corresponding N-phosphorylimidotetraalkylureas.

## LITERATURE CITED

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