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THE SYNTHESIS OF ESTERS OF ALPHA-AMINOALKYLTHIOPHOSPHONIC ACIDS

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Moscow, 11 Oct 1953

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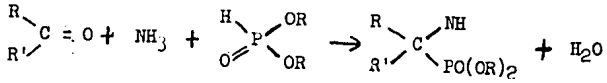
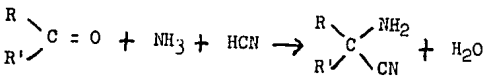
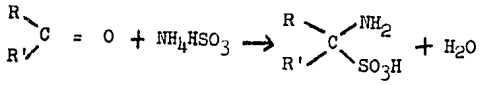
In our work (1) it was shown that alehydes and ketones react with dialkylphosphites in alcohol-ammonia solutions to form esters of α-aminoalkylphosphonic acids:



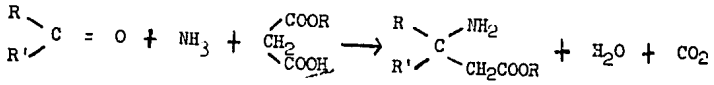
The reaction is carried out by heating the mixture to 100 degrees centigrade in sealed tubes for a period of several hours. The free acids are readily obtained by saponifying the esters of α-aminoalkylphosphonic acids. This reaction is similar to the well-known reaction for the preparation of aminonitriles from aldehydes or ketones, ammonia, and hydrocyanic acid (2), or according to N.D. Zelinskiy (3), from aldehydes or ketones, ammonium chloride, and potassium cyanide:



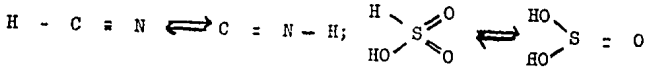
The synthesis of α-aminosulfonic acids from aldehydes and ammonium bisulfite is also related to this type of reaction (4):

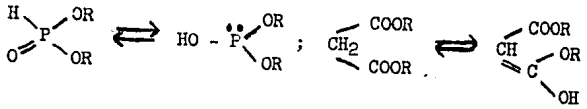


V.M. Rodionov's reaction is also related, i.e., the synthesis of β-aminoacids (5):

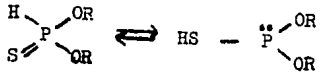


A common characteristic of the above reactions is that the ammonium salts participating in them are salts of acids which are capable of tautomeric conversions of either the diad or triad type:

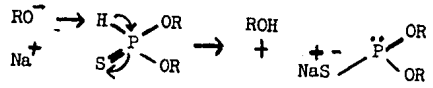




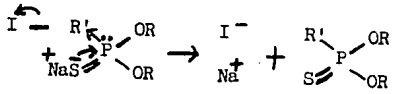
M. I. Kabachnik and T. A. Mastryukova (6) pointed out that dialkylthiophosphites also belong to this category:



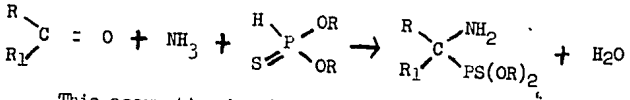
The tautomeric equilibrium in these substances is strongly shifted to the side having the pentavalent phosphorus. However, under the action of sodium alcoholate, for example, these substances form salts having trivalent phosphorus:



Upon alkylation, these salts form derivatives of alkylphosphonic acid with a pentavalent phosphorus atom:



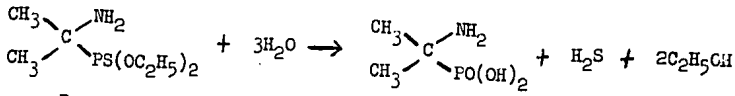
These properties of dialkylthiophosphites permitted us to assume that in reactions with carbonyl compounds and ammonia, they must form esters of the corresponding aminothiophosphonic acids:



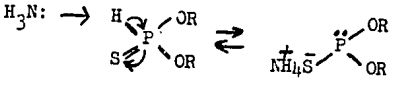
This assumption has been fully confirmed by experiment. The reaction of dialkylthiophosphites with aldehydes or ketones and ammonia takes place more smoothly than the reaction of dialkylphosphites. We accomplished it by heating a mixture of equivalent amounts of aldehyde or ketone, dialkylthiophosphite, and a 10% ammonia solution in absolute alcohol (a 50% excess of ammonia) in a sealed glass tube on a boiling water bath for a period of 3 hours. Then the alcohol and the excess ammonia were distilled off and the residue distilled under vacuum. In the reaction with benzaldehyde or acetophenone, the heating was continued for 6 hours; the reaction product was separated in the form of its picrate. The initial dialkylthiophosphites were synthesized through the reaction of phosphorus hexasulfide with alcohols, according to the method proposed by M.I. Kabacknik and T.A. Mastryukova (7)

Listed in tables 1 and 2 (appended) are the substances synthesized by the reaction of dialkylthiophosphites with ammonia and aldehydes or ketones, together with their constants and the data of analysis.

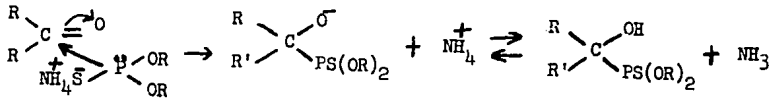
We proved the structure of the substances prepared by using α-aminoisopropylphosphonic acid as an example. Saponification of the ester of this acid by heating it with hydrochloric acid (1:1) in a sealed tube yielded α-aminoisopropylphosphonic acid which was synthesized earlier by T. Ya. Medved' and M. I. Kabachnik.(8) Both preparations proved to be identical.

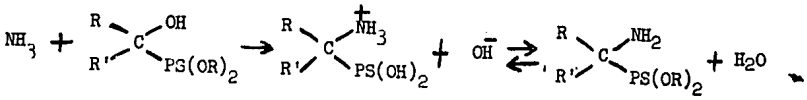


In regard to the mechanism of the reaction, it may be assumed that the dialkylthiophosphite forms the corresponding ammonium salt in the alcohol-ammonia solution:

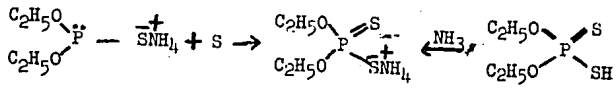


This salt reacts with the carbonyl compound with a transfer of the reaction center in a manner similar to that which takes place during the alkylation of sodium dialkylthiophosphite. An exchange reaction with ammonia completes the formation of the ester of α-aminothiophosphonic acid:





The presence of an ammonium salt having the structure $\dot{N}H_4\bar{S}\text{-}P(OR)_2$ in the alcohol-ammonia solution of dialkylthiophosphite is proved by the fact that sulfur is soluble in this solution after it has been heated to 100 degrees centigrade; ammonium salt of dialkyldithiophosphoric acid then forms, which has been isolated and described:



We prepared this salt from dialkyldithiophosphate of known composition and ammonia. In both cases, and in a mixed test, the melting point was 162-163 degrees centigrade.

[Table follows on next page.]

Table 1. Esters of alpha-Aminoalkylthiophosphonic Acids

Formula	Boiling Point (degrees)	Pressure (mm. Hg)	d_4^{20}	n_D^{20}	MR_D Found	MR_D Calculated
$CH_3C(NH_2)(CH_3)PS(OC_2H_5)_2$	83-84	5	1.0543	1.4760	56.3	56.4
$CH_3C(NH_2)(CH_3)PS(OC_3H_7\text{-}i)_2$	87-88	4	0.0108	1.4665	65.5	65.4
$CH_3C(CH_3)(NH_2)PS(OC_4H_9)_2$	120-122	5	1.0019	1.4722	74.8	74.7
$C_2H_5C(NH_2)(CH_3)PS(OC_2H_5)_2$	95-96	6	1.0492	1.4808	60.9	61.0
$C_2H_5C(NH_2)(CH_3)PS(OC_3H_7\text{-}i)_2$	101-103	3	1.0204	1.4740	70.1	69.7
$C_4H_9C(NH_2)(CH_3)PS(OC_2H_5)_2$	99-101	4	1.0255	1.4798	70.2	70.1
$C_4H_9C(NH_2)(CH_3)PS(OC_3H_7\text{-}i)_2$	107-108	3	0.9931	1.4745	79.4	79.6

[Adjoins page 5 here.]

Yield (%)	Analysis (in %) C Found	C Calculated	H Found	H Calculated	N Found	N Calculated	P Found	P Calculated
53	39.8 40.1	39.8	8.8 6.6	8.5	6.4	6.6	14.4 14.2	14.7
80	45.1 45.2	45.2	8.8 8.9	9.2	6.6		12.9 13.0	13.0
24							11.8 11.7	11.6
38	43.1 43.1	42.7	9.3 9.2	9.9	6.2 6.1	6.2	13.8	13.8
56					5.4 5.6	5.5	12.3 12.2	12.2
26	47.9 48.0	47.4	9.9 9.8	9.5			12.1 12.1	12.3
45					4.4 4.3	5.0	11.0 11.1	11.1

[Adjoins page 4 here.]

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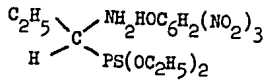
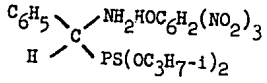
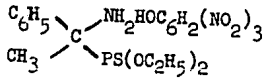
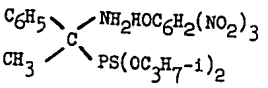
Table 2. Esters of alpha-Aminoalkylthiophosphonic Acids

Formula	Melting Point (degrees)	Yield (%)	P Valnes (%) Found	P Valnes (%) Calculated	N Valnes (%) Found	N Valnes (%) Calculated
	175-178	41	6.4;6.3	6.4	2.9;2.7	2.9
	174	33	5.9;5.8	6.0	2.8;2.8	2.7
	169-171	42	6.2;6.3	6.2	2.7;2.9	2.8
	170	31	5.6;5.6	5.8	---	---

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4. H. Backer, H. Mulder, Rec., Vol 52, 454 (1933); Vol 53, 1120 (1934).
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7. M.I. Kabachnik, T.A. Mastryukova, ibid., No 4, 727 (1952).
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