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Abstract

Full Text

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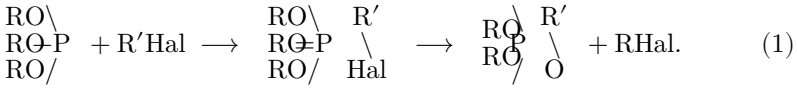
INTERACTION OF INTERMEDIATE PRODUCTS OF THE ARBUZOV REARRANGEMENT WITH AMINES

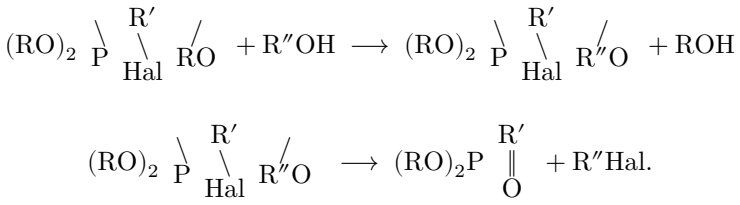
In 1905, one of us ([1]) discovered a reaction that subsequently received the name of the Arbuzov rearrangement. Its general scheme is as follows:



(1)

For phosphites in which R is an aliphatic radical, the intermediate complex is an unstable substance; it readily splits off an alkyl halide and is converted into an ester of an alkylphosphinic acid. For phosphites in which R is an aromatic radical, the intermediate complex can be isolated in analytically pure form ([2], [3]).

The intermediate products of the Arbuzov rearrangement are reactive substances. They react vigorously with water and with various alcohols ([2],). Landauer and Rydon ( ) give the following scheme for the reaction of intermediate complexes with alcohols:



(2)

Since the first phase of this reaction, in all probability, proceeds at the expense of the active hydrogen of the alcohol, the same reaction may also be expected with other substances having active hydrogen. In place of the alcohol we used secondary amines. The following complexes obtained by us (Nos. 1–in Table 1) were taken into reaction with dialkylamines (diethylamine and dimethylamine).

Table 1

No.	Complex	Formation: time, h	Formation: temp., °C	M.p., °C	Hal, % calc.	Hal, % found	Yield, %
1	$(C_6H_5O_3PCH_3)J$	8–10	100	130		25.29	quant.
2	$(o\text{-}CH_3C_6H_4O)_3PCH_3J$	7	100	135–136	25.7	25.72	quant.
3	$(o\text{-}ClC_6H_4O)_3PCH_3J$	7	100–110	49	22.86	22.64	75
4	$(n\text{-}ClC_6H_4O)_3PCH_3J$	13	100	104	22.86	22.56	quant.
5	$(o\text{-}CH_3C_6H_4O)_3PC_2H_5J$	10	100–120	107–108	25	24.84	70
6	$(o\text{-}CH_3C_6H_4O)_3PC_4H_9J$	10	100–120	oil	oil	oil	oil

Intermediate products of the Arbuzov rearrangement were obtained by heating equimolecular amounts (of the phosphite and the alkyl halide) in sealed tubes.

Initially, some of the intermediate complexes were subjected to a decomposition reaction with ethyl alcohol, and as a result esters of alkylphosphinic acids were isolated (Nos. 1–4 in Table 2).

Table 2

No.	Ester	B.p., °C / mm Hg	d_0^{20}	n_D^{20}	P (N), %, calc.	P (N), %, found	Yield, %	$\frac{MR_{\text{calc}}}{MR_{\text{found}}}$
1	$(o\text{-}CH_3C_6H_4O)_2P(=O)CH_3$	215/10	m.p. 64		11.23	11.08–11.05	74.6	
2	$(o\text{-}CH_3C_6H_4O)_2P(=O)C_2H_5$	213–214/12	1.1410	1.5415	10.69	10.48–10.59	38.8	79.75–79.92
3	$(o\text{-}ClC_6H_4O)_2P(=O)CH_3$	176–177/3	1.3350	1.5560	9.78	9.91–10.06	30	75.63–76.32
4	$(o\text{-}CH_3C_6H_4O)_2P(=O)C_4H_9$	216–217/11	1.1071	1.5321	9.74	9.66–9.78	30.2	88.99–89.02
5	$(C_6H_5O)_2P(=O)N(C_2H_5)_2$	176–178/4	1.0902	1.5532	10.72	10.74–10.86	62.8	84.85–44

As is known, the reaction of intermediate complexes with alcohols is accompanied by the evolution of a large amount of heat. The same phenomenon is observed upon their decomposition by amines.

As a result of the reaction of the products 1–5 of Table 1 with amines, phenol or, respectively, its analog was always liberated quantitatively. The second product

of this reaction could be obtained in crystalline form in only four cases and purified by recrystallization from an acetone–ether mixture (Nos. 1–4 in Table 3).

Table 3

No.	Substance	M.p., °C	P, %, calc.	P, %, found	Yield, %	Appearance
1	$CH_3(C_6H_5O)_2P^+=N(C_2H_5)_2J^-$	126	7.19	7.06	56	needles
2	$CH_3(C_6H_5O)_2P^+=N(CH_3)_2J^-$	109	7.69	7.58	26	needles
3	$CH_3(CH_3C_6H_4O)_2P^+=N(C_6H_5)_2J^-$	111	6.59	6.54	41.1	needles
4	$CH_3(CH_3C_6H_4O)_2P^+=N(CH_3)_2J^-$	136.5	7.37	7.19	28.8	needles

The remaining products were viscous, slightly brown-colored liquids which, on standing in air, underwent saponification with liberation of the hydroiodide salt of the dialkylamine.

In an attempt to isomerize the ester of diethylamidodiphenylphosphorous acid with methyl iodide, a product was obtained identical with the product of the interaction of methyltriphenoxyphosphonium with diethylamine. The amidophosphite (No. 5 in Table 2), as a compound with trivalent phosphorus, reacts vigorously with bromine in quantitative proportions and also enters into reaction with cuprous iodide, forming a crystalline complex with m.p. 111° and molecular weight 1443, as against the calculated 479.5×3 (1438.5).

The amidophosphite was obtained from diphenylphosphorous acid chloride and diethylamine in ether medium

$$P(OC_6H_5)_2Cl + 2NH(C_2H_5)_2 = P(OC_6H_5)_2N(C_2H_5)_2 + NH(C_2H_5)_2 \cdot HCl.$$

When equimolecular amounts of the amidophosphite and methyl iodide were heated at 100° for half an hour and then cooled, the entire mass in the tube crystallized completely. For the principal reaction product we propose the formula:

$$\begin{matrix} RO \\ RO \end{matrix} > P = \overset{+}{N}\begin{matrix} R'' \\ R' \\ R'' \end{matrix} J^-$$

We assume that its formation proceeds according to the following schemes.

$$(RO)_2P\begin{pmatrix} R' \\ J \end{pmatrix} + NH_2R'' \longrightarrow \left[(RO)_2\overset{+}{P} - \overset{\curvearrowleft}{N}R''_2\right] J^- + ROH \longrightarrow (RO)_2P = \overset{+}{N}R''J^- \tag{3}$$

$$(RO)_2P-\ddot{N}R''_2 \longrightarrow \left[(RO)_2\overset{+}{P}-NR''_2\right]J^- \longrightarrow (RO)_2P=\overset{+}{N}R''_2J^- \qquad (4)$$

To confirm the proposed structure of products Nos. 1-4 in Table 3, a number of chemical reactions were carried out.

Saponification of product No. 1 of Table 3 gave methylphosphinic acid with m.p. 102° and the hydriodide salt of diethylamine in quantitative yield. This fact indicates that the methyl group is bonded to phosphorus.

The iodine in this product is present as an ion. This is confirmed by quantitative precipitation of AgJ with silver nitrate in ethyl alcohol medium. Only such a structure of the product can explain the absence in them of reactions according to schemes (1) and (2).

The scheme proposed by us for the formation of products Nos. 1-4 from Table 3 is confirmed in a number of studies on the isomerization of amidophosphites. Earlier, authors [5–7] showed that, as a result of the isomerization of amidophosphites by alkyl halides, in contrast to the isomerization of diamidophosphites, where a normal isomerized product is formed [8], a nondistillable mass and a dialkylamine salt are obtained.

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29 IV 1957

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Note: Figure translations are in progress. See original paper for figures.