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1957

SovietRxiv

Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR M. I. Kabachnik and V. A. Gilyarov

ON IMIDES OF PHOSPHORUS ACIDS

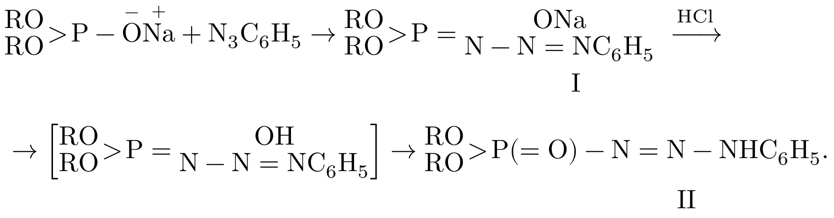
DIALKYLPHOSPHORYL-*N*-PHENYLTRIAZENES AND THEIR SALTS

We have shown that complete esters of trivalent phosphorus acids react with phenyl azide, forming imidophosphates ($^{1-3}$):

$$(RO)_3P + N_3C_6H_5 \rightarrow (RO)_3P = NC_6H_5 + N_2$$

The reaction with phenyl azide was proposed as one characteristic of derivatives of trivalent phosphorus acids (^{3}).

It was of interest to study this reaction with salts of dialkyl phosphites, in which, according to many data, phosphorus is trivalent (^{4}). We found that free dialkyl phosphites do not react with phenyl azide; salts of dialkyl phosphites (triethylammonium and sodium), on the contrary, readily enter into the reaction, forming salts of dialkyl-*N*-phenylphosphoryltriazenes (I), from which free dialkylphosphoryl-*N*-phenyltriazenes (II) can be isolated—representatives of a new class of phosphorus-nitrogen compounds:



$$\begin{matrix}\mathrm{RO}\\\mathrm{RO}\end{matrix}{>}\mathrm{P}-\overset{-}{\mathrm{O}}\overset{+}{\mathrm{Na}} + \mathrm{N_3C_6H_5} \rightarrow \begin{matrix}\mathrm{RO}\\\mathrm{RO}\end{matrix}{>}\mathrm{P} = \underset{\mathrm{I}}{\overset{\mathrm{ONa}}{\mathrm{N}-\mathrm{N}=\mathrm{NC_6H_5}}} \xrightarrow{\mathrm{HCl}}$$

$$\rightarrow \left[\begin{matrix}\mathrm{RO}\\\mathrm{RO}\end{matrix}{>}\mathrm{P} = \overset{\mathrm{OH}}{\mathrm{N}-\mathrm{N}=\mathrm{NC_6H_5}}\right] \rightarrow \begin{matrix}\mathrm{RO}\\\mathrm{RO}\end{matrix}{>}\mathrm{P}(=\mathrm{O})-\mathrm{N}=\mathrm{N}-\underset{\mathrm{II}}{\mathrm{NHC_6H_5}}.$$

The formation of triazene salts in the reaction of dialkyl phosphite salts with phenyl azide may serve as confirmation of the previously expressed assumption that triazenes III are formed as intermediate products in the reaction of trialkyl phosphites with phenyl azide (^{2})

$$(RO)_3P + N_3C_6H_5 \rightarrow [(RO)_3P = N - N = NC_6H_5] \rightarrow (RO)_3P = NC_6H_5 + N_2.$$

III

The reaction with phenyl azide proceeds at the unshared electron pair of phosphorus; in this sense it is analogous to the reaction with sulfur. However, in the case of phenyl azide the sodium salts react considerably faster than the triethylammonium salts. Such a difference is not observed in the reaction with sulfur (^{5}).

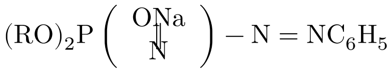
Sodium salts of dialkylphosphoryltriazenes are crystalline substances of light-yellow color, not hydrolyzed by atmospheric moisture, soluble in some organic solvents and in water (aqueous solutions decompose on standing); on melting they decompose with evolution of nitrogen. They probably have structure I, in which the Na^+ ion is located at oxygen. The yields and constants of these salts are given in Table 1.

From the triethylammonium salts, the free triazenes are isolated by distilling off triethylamine in vacuum (method A), and from the sodium salts—by the action of hydrochloric acid in aqueous solution or of a calculated amount of acetic acid in ethereal solution (method B).

Yields, properties, and analytical results for dialkylphosphoryl-*N*-phenyltriazenes are given in Table 2.

Table 1

Sodium salts of dialkylphosphoryltriazenes



$$(RO)_2P\left(\begin{matrix} ONa \\ \Downarrow \\ N \end{matrix}\right) - N = NC_6H_5$$

R	Yield, %	M.p., °C (un-corr.)	C, % found	C, % calc.	H, % found	H, % calc.	N, % found	N, % calc.
C_2H_5	62.8	147.5 – 148.5	43.0843.21	43.02	5.515.39	5.41	15.2415.34	15.05
C_3H_7	32.5	142.0 – 142.5	–	–	–	–	13.3213.32	13.63
u-C_3H_7	47.8	142.0 – 143.0	–	–	–	–	14.1414.38	13.63
C_4H_9	46.7	145.0 – 146.0	49.8949.87	50.14	6.746.51	6.91	12.6512.61	12.50

Dimethyl-, diethyl-, and diisopropylphosphoryl *N*-phenyltriazenes are crystalline substances that decompose on melting with evolution of nitrogen.

Table 2

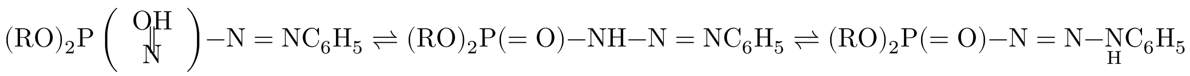
Dialkylphosphoryltriazenes

$$(RO)_2P(=O)-N=N-NHC_6H_5$$

R	Method of synthesis	Yield, %*	M.p., °C	C, % found	C, % calc.	H, % found	H, % calc.	P, % found	P, % calc.	N, % found	N, % calc.
CH_3	A	24.0	94.5–95.0	41.90 42.04	41.93	5.39 5.43	5.24	13.41 13.33	13.54	17.89 17.80	18.34
C_2H_5	A	38.6	83.0–83.5	46.96 47.02	46.70	6.32 6.23	6.22	11.61 11.39	12.07	16.21 16.18	16.34
C_2H_5	B	57.7	84.0–85.0								
u-C_3H_7	A	17.5	64.0–65.0	50.66 50.61	50.53	7.14 7.08	7.02	11.38 10.98	10.87	14.80 14.92	14.74
u-C_3H_7	B	26.3									
C_4H_9	B	90.0**	–	53.52 53.61	53.67	7.75 7.74	7.67	9.38 9.31	9.91	–	–

* Calculated on the dialkyl phosphite.
** Calculated on the sodium salt of the phosphoryltriazene.

They are soluble in most organic solvents and insoluble in water. The structure of dialkylphosphoryl-*N*-phenyltriazenes probably corresponds to formula II, since, of the possible tautomeric forms:



$$(RO)_2P\left(\begin{matrix}OH\\ \Downarrow\\ N\end{matrix}\right)-N=NC_6H_5 \rightleftharpoons (RO)_2P(=O)-NH-N=NC_6H_5 \rightleftharpoons (RO)_2P(=O)-N=N-\underset{H}{N}C_6H_5$$

II

the substance of formula II should have the least acidic properties, and, consequently, the equilibrium should be shifted toward this form (6). These substances do not possess basic properties (they do not form picrates or hydrochlorides) and in this respect differ sharply from triazenes of the type $RN = N—NHAr$.

As regards the acidic properties, dialkylphosphoryl-N-phenyltriazenes are soluble in solutions of alkalis, forming salts identical with salts I obtained from dialkyl phosphites and phenyl azide. From solutions of the salts, the free triazenes are readily isolated on acidification with hydrochloric acid.

Apparently, dialkylphosphoryl-N-phenyltriazenes are stronger acids than dialkyl phosphites. This follows from the fact that the reaction of diethyl phosphite with phenyl azide in the presence of catalytic amounts of alkoxide does not occur.

Experimental Part

Sodium salts of dialkylphosphoryl-N-phenyltriazenes (I) were obtained by adding phenyl azide dropwise to sodium dialkyl phosphite in ether. Warming of the reaction mixture was observed, and the color of the solution became light brown. After one day, in the case of dipropyl- or dibutylphosphoryltriazenes, the ethereal solutions of the sodium salts were evaporated in vacuo. In the case of diethyl- or diisopropylphosphoryltriazenes, on addition of phenyl azide to the Na salt of the dialkyl phosphite in ether, a homogeneous solution is first formed, from which after 1–2 hours a precipitate of the sodium salt separates.

Example. The sodium salt of diethylphosphoryl-N-phenyltriazene was obtained from 13.8 g (0.1 mole) of diethyl phosphite, 2.3 g (0.1 mole) of sodium, and 11.9 g (0.1 mole) of phenyl azide in 30 ml of ether. The separated crystals were filtered off and washed with ether; weight 19.2 g (68.5%; m.p. 145.0–145.5°). The salt was purified by reprecipitation with petroleum ether (b.p. 37–62°) from dry chloroform. It is soluble in alcohol, dioxane, water (the solution has an alkaline reaction), and hot benzene, and insoluble in petroleum ether.

The sodium salts of dipropyl- and diisopropylphosphoryltriazenes were purified analogously. The sodium salt of dibutylphosphoryl-N-phenyltriazene was recrystallized from petroleum ether.

Preparation of free dialkylphosphoryl-N-phenyltriazenes (II). Method A (via triethylammonium salts of dialkyl phosphites). On addition of phenyl azide to a mixture of dialkyl phosphite and triethylamine, no visible changes are observed. Only in the case of dimethyl phosphite does a vigorous reaction take place (5–10 min after mixing the reagents). Therefore phenyl azide was added dropwise to a solution of dimethyl phosphite and triethylamine in ether. After standing for 1–2 days, the volatile products were removed in vacuo.

Dimethylphosphoryl-N-phenyltriazene was obtained from 2.2 g (0.02 mole) of dimethyl phosphite, 2.0 g (0.02 mole) of triethylamine in 5 ml of absolute ether, and 2.4 g (0.02 mole) of phenyl azide. The crystalline residue obtained after removal of the volatile products was pressed on a porous plate. 1.4 g (30.4%) of colorless needle-shaped crystals was obtained. The substance was precipitated with petroleum ether from chloroform. In determining the melting point, the capillary containing the substance was immersed in sulfuric acid heated to 90°.

Diethylphosphoryl-*N*-phenyltriazene was obtained from 4.1 g (0.03 mole) of diethyl phosphite, 3.0 g (0.03 mole) of triethylamine, and 3.6 g (0.03 mole) of phenyl azide. The crystals were pressed on a porous plate (3.0 g, 50%); m.p. 81–83°. After two reprecipitations with petroleum ether from chloroform, the pure substance was obtained—colorless pentagonal plates, soluble in ether, alcohol, and aqueous caustic potash solution, insoluble in water, aqueous potash solution, and petroleum ether.

Diisopropylphosphoryl-*N*-phenyltriazene was obtained from 3.3 g (0.02 mole) of diisopropyl phosphite, 2.0 g (0.02 mole) of triethylamine, and 2.4 g (0.02 mole) of phenyl azide. The oily residue was crystallized by partial evaporation of the solution in petroleum ether and purified by recrystallization from chloroform while evaporating over paraffin.

Method B. Ethereal solutions of the sodium salts of dialkylphosphoryl-*N*-phenyltriazenes were evaporated in vacuo, the residue was dissolved in water, and impurities were extracted with benzene. The free phosphoryltriazenes were isolated by acidification with dilute hydrochloric acid to a weakly acid reaction to Congo red.

Dibutylphosphoryl-*N*-phenyltriazene was obtained from 1.340 g of the Na salt of dibutylphosphoryl-*N*-phenyltriazene and 0.247 g of glacial acetic acid (equimolar amounts) in 8 ml of ether. The precipitated sodium acetate was separated after 4 hours; the ether and volatile impurities were removed in vacuo (at the end, 2 mm, 40°). This gave 1.128 g of a thick liquid of light-brown color; n_D^{20} 1.5220; soluble in organic solvents, insoluble in water.

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Received
28 II 1957

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

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