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Abstract

Full Text

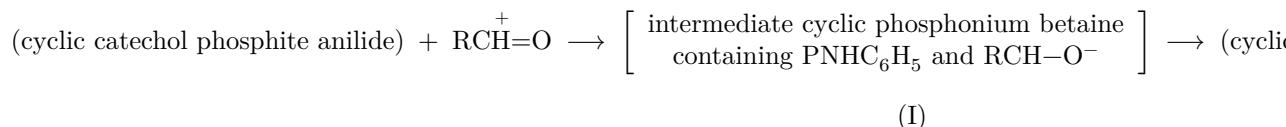
CHEMISTRY

V. S. ABRAMOV and N. A. IL' INA

REACTIONS OF ALDEHYDES AND KETONES WITH AMIDES OF PHOSPHOROUS ACIDS

(Presented by Academician B. A. Arbuzov, January 23, 1960)

Aldehydes and ketones react with esters of phosphorous acids and with dialkylphosphorous acids and form esters of α -alkoxyalkylphosphinic acids in the first case ⁽¹⁾ and esters of α -oxyalkylphosphinic acids in the second ⁽²⁾. Recently the reaction of aldehydes and ketones was extended to amides of phosphorous acids, and it was shown that anilides of phosphorous acids react with aldehydes and ketones with the formation of anilido esters of α -alkoxyalkylphosphinic acids ⁽³⁾ according to the scheme:

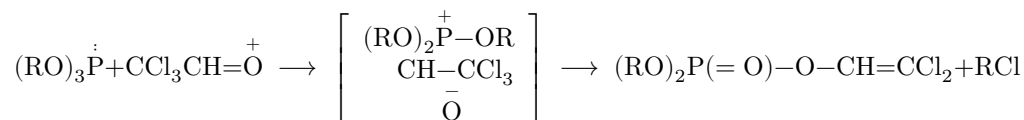


This course of the reaction is confirmed by data from the saponification of product I, as a result of which pyrocatechol, aniline, and the corresponding α -oxyalkylphosphinic acid are obtained.

Another possible reaction of aldehydes or ketones with the amido group of amides of phosphorous acids apparently does not occur, since no other products, apart from small amounts of resin, were obtained. However, in order to check the latter assertion, it was desirable to study the reactions of aldehydes and ketones with disubstituted amides of phosphorous acids. It turned out that aldehydes and ketones enter into reaction with diethylamides of phosphorous acids ⁽⁴⁾. Dialkylamides of phosphorous acids react especially readily, with evolution of heat, with halogen-substituted carbonyl compounds such as chloral, chloroacetone, symmetrical dichloroacetone, etc.

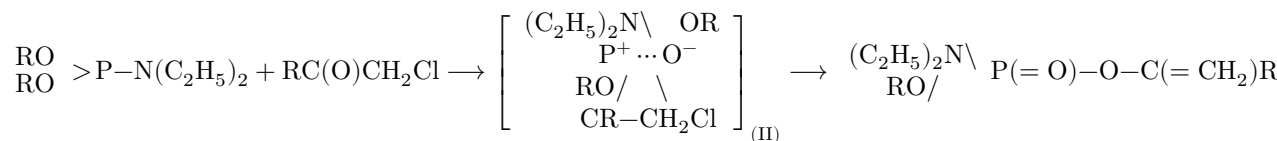
Esters of phosphorous acid with halogen-substituted aldehydes and ketones, as was shown by a number of chemists ⁽⁵⁾, react with the formation of mixed esters of phosphoric acid. The primary attack of the phosphite is effected on the electrophilic carbon atom of the carbonyl group, with the formation of an intermediate three-membered cyclic compound, which decomposes with elimination

of a halogen alkyl and formation of mixed dialkylvinyl esters of phosphoric acid according to the scheme:



Chloral, chloroacetone, α -chlorocyclohexanone, and others readily enter into reaction with diethylamides of phosphorous acids and form amidoalkylvinyl esters of phosphoric acid. The reaction proceeds analogously to the reaction of esters of phosphorous acid and, apparently, begins with attack by the phosphorus atom, bearing an unshared pair of electrons, on the electrophilic carbon atom of the carbonyl group, with formation of an intermediate compou-

of compound (II) and ends with conversion into an amido ester of phosphoric acid with elimination of an alkyl halide.



Amidoalkylvinyl esters of phosphoric acid are colorless mobile liquids, almost odorless (see Table 1).

Table 1

Formula of the amido ester of phosphoric acid	B.p., °C/mm	n_D^{20}	d_4^{20}	MR found	MR calc.	Yield, %
$\begin{array}{c} \text{CH}_3\text{O} \\ (\text{C}_2\text{H}_5)_2\text{N} \\ \text{P}(=\text{O})-\text{OCH}=\text{CCl}_2 \end{array}$	>116— 117/3	1,4646	1,2323	58,79	58,08	60
$\begin{array}{c} \text{C}_2\text{H}_5\text{O} \\ (\text{C}_2\text{H}_5)_2\text{N} \\ \text{P}(=\text{O})-\text{OCH}=\text{CCl}_2 \end{array}$	>112— 114/3	1,4600	1,2118	62,33	62,69	62

Formula of the amido ester of phos- phoric acid	B.p., °C/mm	n_D^{20}	d_4^{20}	MR found	MR calc.	Yield, %
$\text{C}_2\text{H}_5\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OC}(=\overset{122/3}{\text{C}}\text{H}_2)(\text{CH}_2\text{Cl})$	>120—	1,4545	1,1178	61,98	62,45	78
iso- $\text{C}_3\text{H}_7\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OCH}=\overset{125/6}{\text{C}}\text{Cl}_2$	>124—	1,458	1,1889	66,63	67,31	65
$n\text{-C}_3\text{H}_7\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OC}(=\overset{143/10}{\text{C}}\text{H}_2)(\text{CH}_2\text{Cl})$	>142—	1,4545	1,0932	66,82	67,05	75
$n\text{-C}_3\text{H}_7\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OC}(=\overset{106/5}{\text{C}}\text{H}_2)(\text{CH}_3)$	>105—	1,4380	0,9971	61,84	62,29	51
$n\text{-C}_4\text{H}_9\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OCH}=\overset{133/3}{\text{C}}\text{Cl}$	>131—	1,4590	1,1527	72,13	71,93	63
$n\text{-C}_4\text{H}_9\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OC}(=\overset{146/5}{\text{C}}\text{H}_2)(\text{CH}_2\text{Cl})$	>144—	1,4550	1,0750	71,62	71,68	67
$n\text{-C}_4\text{H}_9\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{OC}(=\overset{112/4}{\text{C}}\text{H}_2)(\text{CH}_3)$	>110—	1,4340	0,9905	66,30	66,82	62
$n\text{-C}_4\text{H}_9\text{O}$ $(\text{C}_2\text{H}_5)_2\text{N}$ $\text{P}(=\text{O})-\text{O}-\overset{161/6}{\text{C}}_6\text{H}_5$	>160—	1,4644	1,0275	77,69	78,47	60

Amidoalkylvinyl esters add bromine. The unsaturation determined by the bromide-bromate method for diethylamidobutylisopropenyl phosphoric acid ester is 100%. In the presence of chlorine in the vinyl radical, determination of unsaturation does not give satisfactory results.

Attempts to establish the structure of the products obtained by the transesterification method⁶ did not lead to positive results. When diethylamidobutylisopropenyl ester and diethylamidobutyl- α -methyl- β -chlorovinyl ester of phosphorous acid were boiled with an excess of butyl alcohol in the presence of sodium alcoholate or phosphorous acid, transesterification did not occur; the esters were recovered unchanged from the reaction. Apparently, the presence of the diethylamido group bonded to the phosphorus atom influences the transesterification reaction of mixed alkylamido esters. The transesterification reaction

is under study.

Diamido esters of phosphorous acids react with aldehydes and ketones analogously to amido esters.

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

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