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Abstract

Full Text

Chemistry

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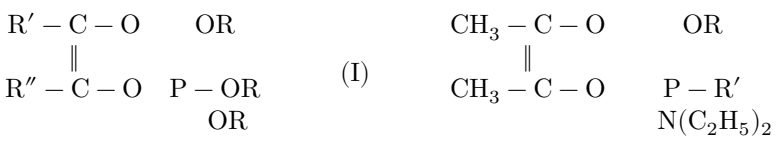
Interaction of Etheramides and Ether Chloroanhydrides of Phosphorous Acid with Diacetyl

(Presented by Academician B. A. Arbuzov, 13 III 1964)

Earlier one of us showed ([1]) that trialkyl phosphites add to diacetyl with the formation of compounds of pentacovalent phosphorus (I). Continuing the study of reactions of esters of trivalent phosphorus acids with conjugated systems, we have investigated the reactions of diacetyl with certain etheramides of phosphorous acid and with diethyl chlorophosphite. It could be expected that in the case of etheramides the reaction would proceed in the same way as with esters, with the formation of 1,3,2-dioxaphospholenes (II)



(I)

(II)

(IIa) $R = C_2H_5$, $R' = OC_2H_5$,

(IIb) $R = C_4H_9$-n, $R' = OC_4H_9$-n,

(IIc) $R = C_2H_5$, $R' = N(C_2H_5)_2$.

The products obtained by us from the addition of etheramides of phosphorous acid to diacetyl, according to analysis, chemical properties, and physicochemical characteristics, correspond to the structure given above. Like the previously described adducts (I), compounds (II) react with water, organic acids, and with a second molecule of diacetyl ([2]); however, in contrast to (I), they are not capable of initiating a polymerization reaction, which is probably explained by the presence of a tertiary nitrogen atom. The IR spectrum of product (IIa) has absorption bands characteristic of dioxaphospholenes, in particular the band characteristic of the double bond of the dioxaphospholene ring, of low intensity, at 1743 cm^{-1}. In the NMR spectrum of compound (IIa) there is one peak for the hydrogens of the methyl groups at the double bond ($\tau = 8.20$), the integral intensity of which is related to the integral intensity of the methyls of the ethoxy groups as $1 : 2$, which, as we have shown earlier ([1]), is possible only for the dioxaphospholene structure.

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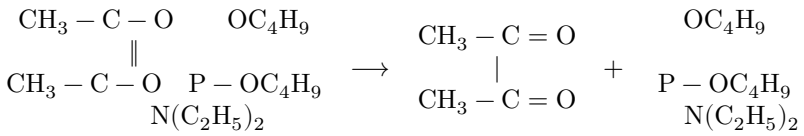
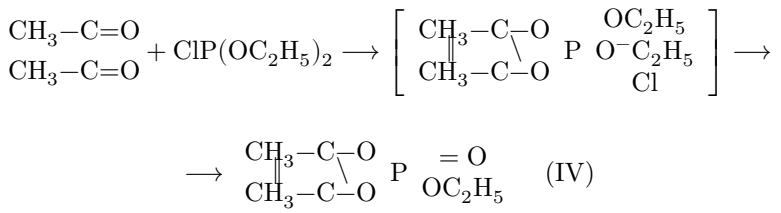
Wishing to obtain chemical proof of the structure of the adducts obtained by us, we attempted to cleave them into the initial products, as had earlier been done for compounds (I) ([3]). For adduct (IIa) this could not be accomplished: it proved stable even on prolonged heating in vacuo (as also was (I), $R - C_2H_5$ ([3])). Product (IIb), on heating for four hours in vacuo (40 mm) at 210° (in a bath), decomposed almost completely with liberation of the initial amidophosphite, whose constants were analogous to the constants of the amidophosphite taken into the reaction



Thus, all the data obtained by us indicate that etheramides of phosphorous acid, on interaction with diacetyl, form mainly 1,3,2-dioxaphospholenes (II). In addition, small amounts of higher-boiling products are obtained, which so far have not been identified.

In the interaction of diacetyl with diethyl chlorophosphite, the formation of dioxaphospholene (III) could likewise be expected:



However, as a result of this reaction, even when it is carried out under very mild conditions, ethyl chloride is eliminated and a product is formed which, by analysis, corresponds to the cyclic phosphate (IV). The structure of (IV) is confirmed by the NMR spectrum of this compound; the spectrum contains an intense peak of the methyl hydrogens, chemical shift $\tau = 8.15$, which is characteristic of methyl groups bound to the carbon of the double bond of the dioxaphospholene ring [1].

Evidently, in the present case the first stage of the reaction proceeds according to the scheme described by us earlier; however, the dioxaphospholene (III) that is formed then readily decomposes according to the scheme of the second stage of the Arbuzov rearrangement, eliminating an alkyl halide and forming (IV).

The study of reactions of ester amides and haloanhydrides of phosphorous acid with α-diketones and of the properties of the products obtained is being continued by us.

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Experimental Part

1. **Reactions of ester amides of phosphorous acid with diacetyl** were carried out in ether freshly distilled over P_2O_5, by slow dropwise addition of diacetyl (0.1 mole) to a solution of the corresponding amidophosphite (0.1 mole). The diacetyl was added as the reaction mixture became decolorized, at such a rate that the temperature did not rise above 30–35°. On the following day the ether was removed in vacuo, and the residue was distilled. The distillations were carried out very carefully in order to avoid overheating, which in some cases causes decomposition of the adducts into the starting components or transformations of another type.

Table 1

Compound	Yield, %	B.p., °C, mm	n_D^{20}	d_4^{20}	Formula	P, % found	P, % calculated
IIa	81	105–106 (10)	1.4395	1.0178	$C_{12}H_{26}NO_4P$	11.19	11.09
IIb	70	136.5 (8)	1.4430	0.9688	$C_{16}H_{34}NO_4P$	9.77	9.23
IIv	63	53–55 ($2 \cdot 10^{-3}$)	1.4456	0.9872	$C_{17}H_{31}N_2O_3P$	10.59	10.11
IV	61	82 ($3.5 \cdot 10^{-2}$)	1.4325	1.1755	$C_6H_{11}O_4P$	17.55	17.38

Reaction of diethyl chlorophosphite with diacetyl. On mixing 9.9 g of diethyl chlorophosphite and 5.5 g of diacetyl, the temperature rose by 26°. The reaction mixture was left for three days at room temperature and was then distilled in vacuo.

The constants of all the synthesized compounds are given in Table 1. The authors express their deep gratitude to Yu. Yu. Samitov for recording the NMR spectra of the products obtained by us.

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

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