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REACTIONS OF KETOALCOHOLS WITH ORGANOPHOSPHORUS COMPOUNDS

9. FORMATION OF 2-SUBSTITUTED OXA-3-PHOSPHOLANOLS FROM AMIDOPHOSPHITES AND DIACETONE ALCOHOL

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Phosphorous acid amides enter into substitution reactions with alcohols, in which connection the coordination number of the phosphorus atom is retained here [1]. As a continuation of studying the reactions of ketoalcohols with various phosphorus-containing compounds we used the alcoholysis reaction of amidophosphites for the purpose of adding β-ketoalcohol moieties to the P^{III} phosphorus atom. Here it was of especial interest to substitute two amide groups in view of the fact that the anticipated bis(γ-ketoalkyl) phosphites were postulated as being intermediates in the synthesis of 2-substituted oxa-3-phospholanols from P^{III} acid dichlorides and diacetone alcohol [2].

Initially the alcoholysis was run by heating the reactants up to a temperature where the liberated amine distilled off. It proved that under these conditions (120-200°C) diacetone (DAA), β-acetoethyl, and β-acetoisopropyl alcohols give a complex mixture of products with hexaethyltriamidophosphite (HETP), ethyl tetraethyldiamidophosphite (ETEDP), tetraethyldiamidophenylphosphonite, tetraethyldiamidoethylphosphonite, tetramethyldiamidophenylphosphonite, and tetramethyldiamidoethylphosphonite. Based on the ^{31}P NMR data, in all of the experiments with DAA the reaction mixture prior to distillation contained at least eight phosphorus-containing compounds, which could not be isolated pure. Dark brown tarry masses are formed in the experiments with either β-acetoisopropyl or β-acetoethyl alcohol. The stepwise substitution of the amido groups when heated by ketoalcohol radicals is probably complicated by the decomposition of the obtained products into unsaturated ketone and phosphorus acid [3]. The formed new compounds are capable of reacting both with the starting reactants and with each other, and also of disproportionating, which leads to the observed complex picture.

It is known that proton-donor reagents facilitate the alcoholysis of amidophosphites [4], and consequently it was decided to change the experimental conditions and study the reactions of β-ketoalcohols with amidophosphites in the presence of AcOH. Such reaction with DAA is exothermic and gives compounds that, based on the

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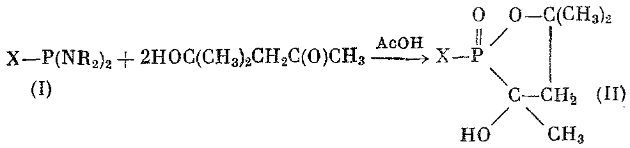
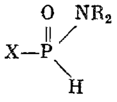
^1H and ^{31}P NMR spectral data, and also the IR spectral and elemental analysis data, represent 2-substituted oxa-3-phospholanols (II).



The (II) compounds were synthesized by other methods, and their identification by spectral methods is described in [2, 5, 6]. From the nonphosphorus-containing compounds were isolated diethylamine, mesityl oxide, and N,N-diethylacetamide.

As can be seen from the structure of the end products, closure of the five-membered ring and an increase in the coordination number of the phosphorus atom occur during the course of the studied reactions. It may be assumed that the formation of the (II) compounds proceeds in two steps, specifically: addition of the ketoalcohol moieties to the phosphorus atom and closure of the five-membered ring. Apparently, the first step (substitution of the amido groups) consists of a number of reversible steps, as follows from the concepts that were developed for the reactions of alcohols with amidophosphites in the presence of proton-donor reagents [7]. The transition from these compounds with β-ketoalcohol radicals on the P^{III} atom to cyclic α-hydroxyphosphoryl systems (second step) is possible via intramolecular attack of the P atom on the carbonyl group. The stepwise synthesis of the (II) compounds can be depicted in the following manner. First the amidophosphite (I) reacts with AcOH and, passing through a reversible protonation step, forms amidoacylphosphite $X-P(NR_2)(OAc)$ (III), which then can react with either DAA or AcOH. The amidophosphite $X-P(NR_2)OC(CH_3)_2CH_2C(O)CH_3$ (IV), will be formed in the first case, and either the hydrophosphoryl compound (V) or the diacylphosphite (VI) will be formed in the second case.



(V)

$X-P(OAc)_2$

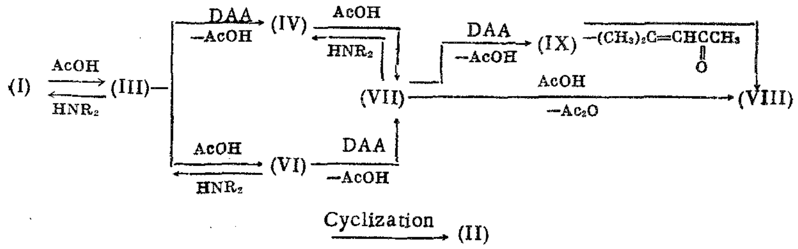
(VI)

The reaction of (IV) with AcOH, or of (VI) with DAA, leads to the same phosphite $X-P(OAc)OC(CH_3)_2CH_2C(O)CH_3$ (VII). Phosphite (VII) can react with AcOH and lead to the acid $X-P(O)(H)[OC(CH_3)_2CH_2C(O)CH_3]$ (VIII).

This same acid can be obtained if acylphosphite (VII) reacts with DAA to give a compound with two diacetone alcohol moieties (IX), which, according to [2], is unstable and decomposes into the unsaturated ketone and acid (VIII):

$$\text{(VII)} + HOC(CH_3)_2CH_2C(O)CH_3 \underset{-AcOH}{\rightleftarrows} \underset{\text{(IX)}}{X-P[OC(CH_3)_2CH_2C(O)CH_3]_2} \rightarrow \text{(VIII)} + (CH_3)_2C{=}CHC(O)CH_3$$

In harmony with the data given in [2], acids of the (VIII) type undergo Abramov intramolecular cyclization [8] to 2-substituted oxa-3-phospholanols (II). In generalized form the process for the formation of (II) can be depicted by the following scheme:



To verify the proposed scheme we ran a check on the reaction of ETEDP with DAA by the ^{31}P NMR method. As a mixture composed of 2 moles of DAA and 1 mole of AcOH is added to the ETEDP an increasing signal appears in the ^{31}P NMR spectrum at −138 ppm, with a simultaneous disappearance of the peak of the starting ETEDP at −130 ppm. In some 60-100 min after completing the addition of the reactants an increasing signal begins to appear distinctly in the spectrum at −41 ppm, which is caused by 2-ethoxy-2-oxo-3,5,5-trimethyl-1,2-oxa-3-phospholanol (II, $X=OC_2H_5$), while the signal at −138 ppm disappears after a day.

In order to assign the signal at −138 ppm to one of the proposed intermediates we synthesized compounds (III), (IV), (VI), and (IX). Ethyl diethylamidoacylphosphite (III) and ethyl α,α-dimethyl-γ-ketobutyl diethylamidophosphite (IV) have $\delta^{31}P - 138$ ppm, whereas ethyl diacylphosphite (VI) has a value of −125 ppm, and ethyl-α,α-dimethyl-γ-ketobutyl acylphosphite (VII) has a value of −130 ppm. Compound (IX) was not isolated pure, but was recorded by the ^{31}P NMR method when ethyl dichlorophosphite was reacted with DAA in the presence of triethylamine at −50°C. The ^{31}P NMR spectrum had a signal at −134 ppm, which gradually changed to the peak of the end oxaphospholanol (II, $X = OC_2H_5$) at −41 ppm. These data are in agreement with the results of the analogous reactions of alkyl dichlorophosphites with primary β-ketoalcohols, where the isolated alkyl di-(γ-ketobutyl) phosphites had $\delta\ ^{31}P - 132$ ppm.

As a result, checking the reaction of ETEDP with DAA and AcOH by the ^{31}P NMR method confirms the formation of either products (III) or (IV) ($\delta\ ^{31}P - 138$ ppm), which are postulated by the general scheme. The contribution from the resonance of the P nucleus of compound (IV) to the signal at −138 ppm should be slight, since beginning with amidoacylphosphite (III) the reaction probably proceeds preferably in the direction of compound (VI), and not (IV). Evidence to support this is the formation of 2-ethoxy-II as the end product, and not 2-diethylamino-II, as was to be expected on the basis of the data given in [9].

It should be mentioned that in the absence of AcOH the oxa-3-phospholanols were isolated from the reaction of ETEDP with DAA after holding the reaction mixture at ~20° for 10-15 days.

EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument, without controlling the layer thickness of the compound between the KBr plates.

The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrometer at a generator operating frequency of 10.2 MHz relative to 85% H_3PO_4. The GLC was run on a Chrom-41 instrument at 130° using a column packed with Chromaton-N.

Reaction of Diacetone Alcohol (DAA) with Hexaethyltriamidophosphite with Heating. To 41.5 g of hexaethyltriamidophosphite in an Arbuzov flask was added in drops 19.4 g of DAA at 190°. During the addition there was collected by distillation 22.4 g (91.3%) of diethylamine with bp 56-58°, n_D^{20} 1.3880, and 2.4 g (26.8%) of mesityl oxide with bp 129-136°, n_D^{20} 1,4400. Distillation of the residue gave 30 g of a fraction with bp 66-127° (0.004 mm), which, based on the ^{31}P NMR data, consisted of a mixture of phosphorus-containing compounds with $\delta\ ^{31}P$ −14, −16, −18, −22, −29, −38, −39, −40, −120, −144 ppm. The pure compounds could not be isolated.

The experiments on the reaction of DAA with ethyl tetraethyldiamidophosphite and the tetraethyldiamidoethyl-, tetramethyldiamidoethyl-, and tetraethyldiamidophenylphosphonites were run in a similar manner, and also by heating the starting reactants in xylene. In all cases, after distilling off the dialkylamine, the residues, based on the ^{31}P NMR data, represented a mixture of at least eight phosphorus-containing compounds. Only from the reaction of DAA with tetramethyldiamidophenylphosphonite were we able to isolate, in 26% yield, tetramethyldiamidophenylphosphonate with mp 82° (petroleum ether), $\delta\ ^{31}P - 29$ ppm [10]. Found: C 56.69; H 7.82; N 12.82; P 14.42%. $C_{10}H_{17}N_2OP$. Calculated: C 56.60; H 8.01; N 13.27; P 14.62%.

The experiments with β-acetoethyl and β-acetoisopropyl alcohols with the same amidophosphites and amidophosphonites under analogous conditions led to undistillable and noncrystallizing tarry masses.

Reaction of Diacetone Alcohol with Hexaethyltriamidophosphite in Presence of Acetic Acid. Heating up to 50° was observed when 23.2 g of DAA and 12 g of AcOH were added at ~20° to 24.7 g of hexaethyltriamidophosphite. After 24 h, distillation gave 4.8 g of diethylamine, 2.3 g of mesityl oxide with bp 127-131°, n_D^{20} 1.4390, 19.3 g of a mixture with bp 65-80° (12 mm), which, based on the GLC data, consisted of DAA, N,N-diethylacetamide, and mesityl oxide in a 40 : 35 : 25 ratio, and also 15.3 g of a fraction with bp 125-130° (0.015 mm), which crystallized in 1 day. Recrystallization from benzene gave 9.2 g (39%) of 2-diethylamino-2-oxo-3,5,5-trimethyl-1,2-oxa-3-phospholanol with mp 124-125° [5]. Found: C 50.93; H 9.10; N 6.03%. $C_{10}H_{22}NO_3P$. Calculated: C 51.28; H 8.97; N 5.98%.

Reaction of Diacetone Alcohol with Ethyl Tetraethyldiamidophosphite. When 23.2 g of DAA and 6 g of AcOH were added to 22 g of ethyl tetraethyldiamidophosphite the temperature rose to 45°. The next ;day we collected by distillation 4 g (27.4%) of diethylamine, 4.9 g (50%) of mesityl oxide, and 5.4 g (46.9%) of N,N-diethylacetamide with bp 61-64° (10 mm), n_D^{20} 1.4300. The residue crystallized. Recrystallization from benzene gave 14.9 g (71.3%) of (II), mp 102°. Found: C 46.30; H 8.42; P 15.06%. $C_8H_{17}O_4P$. Calculated: C 46.16; H 8.17; P 14.90%.

The (II) compound is also formed by holding a mixture of DAA and ethyl tetraethyldiamidophosphite for 14-15 days at ~20°. From 23.2 g of DAA and 22 g of ethyl tetraethyldiamidophosphite we obtained 13 g (64%) of (II), mp 100-101°.

Ethyl diacylphosphite, propyl diacylphosphite ($\delta\ ^{31}P - 125$ ppm), ethyl diethylamidoacylphosphite, propyl diethylamidoacylphosphite ($\delta\ ^{31}P - 138$ ppm), and ethyl α,α-dimethyl-γ-ketobutyl acylphosphite ($\delta\ ^{31}P - 130$ ppm) were obtained as described in [11].

CONCLUSIONS

1. The alcoholysis of amidophosphites by β-ketoalcohols was studied under various conditions.

2. It was established that when the reactions are run in the presence of acetic acid the end products are 2-substituted oxa-3-phospholanols. A scheme was proposed for their formation.

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SYNTHESIS AND ISOMERIZATION OF 2-(3'-CHLOROALKOXY)-1,3,2-AZATHIA-, 2-(3'-CHLOROALKOXY)-1,3,2-DIAZA-, 2-(3'CHLOROALKOXY)-1,3,2-OXATHIA-, AND 2-(3'-CHLOROALKOXY)-1,3,2-DITHIAPHOSPHOLANES

L. Z. Nikonova and O. N. Nuretdinova

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As a result of studying the Arbuzov rearrangement in the 2-(3'-chloroalkoxy)-1,3,2-dioxa- and 1,3,2-azaoxaphospholane series it was observed that in some cases replacing the oxygen in the dioxaphospholane ring by the N atom changes the direction of the isomerization. Thus, the isomerization of 2-(1'-methyl-3'-chloropropoxy)-4,5-dimethyl-1,3,2-dioxaphospholane proceeds with opening of the ring, while the isomerization of 1-methyl-2-(1'-methyl-3'-chloropropoxy)-4,5-dimethyl-1,3,2-azaoxaphospholane proceeds with retention of the ring [1, 2].

As a continuation of studying the effect of the character of the heteroatoms in the 1 and 3 positions of the phospholane ring and structure of the chloroalkoxyl group on the P atom on the direction of the isomeriza-

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