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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS OF CARBONYL COMPOUNDS AND
PREPARATION OF VARIOUS N- AND P-CONTAINING
COMPOUNDS BASED ON THEM**

Speciality: 2306.01 – Organic chemistry

Field of science: Chemistry

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GENERAL CHARACTERISTICS OF THE WORK

The relevance of the topic and the degree of elaboration. Synthesis of α -phosphoryl- α -mono- and α,α -dihalogen-containing carbonyl compounds with individual features due to their structure and properties and the study of their reactions with various nucleophilic reagents can be considered scientifically and practically relevant. The presence of electrophilic centers in the 1,2,3-position in the indicated type of compounds provides a reason for the breakdown of P-C and C-C bonds in chemical transformations under the influence of nucleophilic reagents. In this case, the various types of compounds obtained are of practical interest.

In the presented thesis, as a continuation of the research carried out at the Organic Chemistry Department of BSU, condensation reaction of α -mono- and α,α -dihalogenated carbonyl compounds with the nucleophile, N,N and N,S binucleophilic reagents was carried out and phosphorus-, nitrogen-phosphorus-, nitrogen-phosphorus-nitrogen-containing heterocyclic compounds, unknown in the literature, were synthesized.

Obtaining new bromine-containing hydrazones based on acetal-protected bromoacetic aldehyde guarantees that they are suitable synthons for synthetic application. In addition, the presence of mixed ether (phenoxy, ethoxy) and etheramide groups in the phosphorus atom of α -phosphoryl- α -monochloro-aldehydes and new compounds based on them can be assumed to be industrially important.

The study of α -phosphoryl carbonyl compounds with some transition metal salts is little covered in the literature. In this regard, the study of the reaction of enol-forming α -phosphoryl carbonyl compound (phosphonic acetic aldehyde) and non-enol-forming phosphonacetate and phosphonacetonitrile with salts of transition metals (Zn^{+2} , Cu^{+2} , Co^{+2} , Ni^{+2}) is very relevant. As a result, it became possible to synthesize metal complexes and metal-phosphorus containing compounds obtained at the expense of carbonyl and phosphoryl oxygen's.

The object and subject of the research. Synthesis of various types of polyfunctional compounds (phosphorous analogues of barbiturates, phosphorus-nitrogen-containing heterocycles, phosphon-phosphate nature, phosphorylated chlorophos derivative, and etc.) based on α -

halogen containing carbonyl compounds, including trichloroanhydride of α -chlorophosphonic acid, synthesized new representatives of α -mono- and α,α -dichlorophosphoacetic aldehyde and bromoacetic aldehyde is the main subject of our research.

The synthesis of compounds containing phosphoryl-, furan-, thiophene-, morpholine- and pyridine- fragments, which are important for national economy, based on 2,4-dinitrophenylhydrazone of bromoacetic aldehyde, can be considered the object of research.

At the same time, phosphorous-metal containing monomers and polymers obtained from the reaction of phosphoacetic aldehyde, phosphoncarboxylic acid esters, phosphonacetonitrile with salts also belong to the subject of research.

The goals and objectives of the research. The main goals of the thesis were as follows:

–Study of the reaction of trichloroanhydrides of phosphoncarboxylic acids obtained from the reaction of phosphorus pentachloride with ethylacetate and ethylpropionate with various O- and N,N-, N,S nucleophilic reagents and as a result of the reaction synthesis of the corresponding allyl-, propargyl-, substituted phenol ethers, as well as phosphorus analogs of barbiturates, and phosphorus-nitrogen-nitrogen, phosphorus-nitrogen-sulfur containing compounds.

–Synthesis of new α -monochloro and α,α -dichlorophosphonic acetic aldehydes containing mixed ether, etheramide fragment as a result of nucleophilic substitution at the phosphorus atom and their investigation as useful synthons.

–Study of the reactions of synthesized 2,4-dinitrophenylhydrazone with phosphite, pyridine, morpholine, furan and thiophene derivatives.

–Study of condensation reactions of phosphoacetic aldehyde, phosphoacetate, phosphonacetonitrile with salts of some transition metals (Co^{+2} , Zn^{+2} , Cu^{+2} , Ni^{+2}).

Research methods. The structure of the synthesized compounds was confirmed by ^1H and ^{13}C NMR spectroscopy and X-ray method. In some cases, the structure of the obtained substances was confirmed by the method of mutual synthesis.

Main clauses defended.

1. Explanation of the structure of each compound obtained from the reaction of alkylacetates with PCl_5 according to conformational

analysis based on new approaches.

2. Synthesis of corresponding esters, phosphorus analogs of barbiturates, 1,3-diazophosphate derivative and other nitrogen-phosphorus, nitrogen-phosphorus-sulfur-containing compounds from the reaction of trichloroanhydride of α -chloro- α -phosphonpropionic acid with allyl and propargyl alcohols, substituted phenols, urea, thiourea.

3. Synthesis of phosphonic α -monochloro, α,α -dichloro- acetic aldehyde containing mixed ether and ether amide groups in the phosphorus atom and investigation of their reaction with various nucleophilic reagents.

4. Study of reactions of bromoacetic aldehyde hydrazone with phosphite, pyridine, morpholine, α -aminomethyl furan, α -aminomethyl thiophene and the effect of alkaline environment on these reactions.

5. Study of reactions of phosphonacetic aldehyde, phosphonacetate, phosphonacetonitrile with salts of transition metals (Zn^{+2} , Cu^{+2} , Ni^{+2}).

Scientific novelty of the research. Corresponding alkenyl, alkynyl and phenol ethers were synthesized from the reaction of trichloroanhydride of α -chloro-phosphonpropionic acid with allyl and propargyl alcohols and substituted phenols. Heterocyclic (phosphorus-containing barbiturates, diazophosphatane) and nitrogen- and phosphorus-containing phosphonates with an open chain structure were synthesized with the indicated substrate binucleophilic reagents (urea, thiourea and guanidine).

New representatives of obtained α -monochloro-, α,α -dichloro-phosphonacetic aldehyde were synthesized and their chemical properties were studied in a wide range. It was determined that depending on the nature of the nucleophilic reagent, breaking of C-C, P-C bonds is observed in the reaction.

Based on the synthesized hydrazone of bromoacetic aldehyde, various synthetically interesting compounds (hydrazone of phosphonacetic aldehyde, containing morpholine-, pyridine-, α -aminomethylfuran and α -aminomethylthiophene fragments) were obtained by replacing the bromine atom. Condensation reactions of α -phosphorylcarbonyl compounds (phosphonacetic aldehyde, phosphonacetate, phosphonacetonitrile) with metal salts were carried out under different conditions. It was determined that depending on the nature of the carbonyl compounds, the reaction takes place with the presence of the carbonyl

group (complexes) and phosphoryl oxygen, and phosphorous-metal containing monomers and polymers are obtained.

Theoretical and practical significance of research. Theoretically, it is known that in nucleophilic substitution reactions, the chlorine atom next to the carbonyl group is more active than the chlorine atom next to the phosphorus atom. This makes it possible to achieve the synthesis of new type of diazophosphatane derivatives of phosphorous analogues of barbiturates, phosphorus, nitrogen and sulfur containing compounds based on trichloroanhydride of α -halogen phosphonic acids.

The presence of three consecutive centers with acidic properties in α -chloro- α -phosphorylcarbonyl compounds causes the breaking of C-C and P-C bonds during chemical transformations in these compounds. Phosphorous analogs of synthesized barbiturates, phosphoryl group based on bromohydrazone, furan, thiophene, morpholine and etc. compounds holds promise for practical utility in medicine.

The results obtained from the reaction of α -phosphorylcarbonyl compounds with salts of some transition metals may be of practical use to scientific researchers working in this field.

Approbation and application. 19 scientific works related to the subject of the dissertation work, including seven articles (3 in foreign journals, 2 by single author), 11 theses (3 international) were published. The main parts of the work were presented at international and national conferences held in Russia and Azerbaijan:

– "Actual Problems of Chemistry" conferences dedicated to the anniversary of the birth of National Leader Heydar Aliyev (Baku, 2017, 2019, 2021, 2022);

– Chemistry of Coordination Compounds, Current Problems of Analytical Chemistry (Baku, November 16-17, 2017).

– «Advances in synthesis and complexing» The Fourth International Scientific Conference (Moscow, RUDN University, April 24-28, 2017).

– V All-Russian conference with international participation on organic chemistry (September 10-14, 2018, Vladikavkaz).

The name of the organization where the dissertation work was performed. The research work was carried out at the Chemistry Department of the Faculty of Biology and Chemistry of Ganja State University.

The structure of the dissertation work: The dissertation work consists of an introduction, three chapters (literature review, discussion of results, experimental part), conclusions, used (181 names) literature references, 19 figures, written on 174 pages. The main part of the work is 168299 marks.

In the introductory part (9254 marks), the relevance, purpose, scientific novelty and practical importance of the work are justified.

The first chapter (32549 marks) provides an interpretation of literature data related to research with the chemistry of carbonyl compounds.

In the second chapter (69136 marks) the results obtained during the synthesis and transformations of polyfunctional carbonyl compounds were discussed.

The third chapter (54435 marks) is dedicated to the methods of the experimental part of the conducted research.

The results section (2925 marks) contains the main results obtained from the dissertation research.

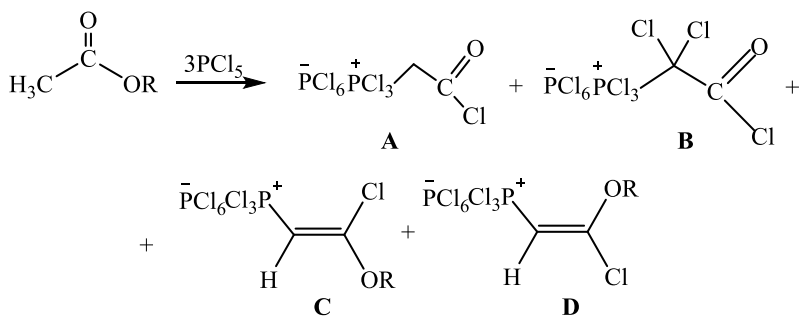
The applicant's personal contribution to the research. The applicant directly participated in the completion and preparation of the dissertation work. She summarized the world literature related to the synthesis of carbonyl compounds and the preparation of various compounds based on them and showed her author's approach in the literature review. The applicant participated in the performance of laboratory experiments: synthesizing and purifying substances (using vacuum distillation, crystallization methods), studying the structure of each compound using physical-chemical research methods (NMR, X-ray). She put forward her opinions about the mechanisms of the reactions in her single-authored articles

MAIN CONTENTS OF THE WORK

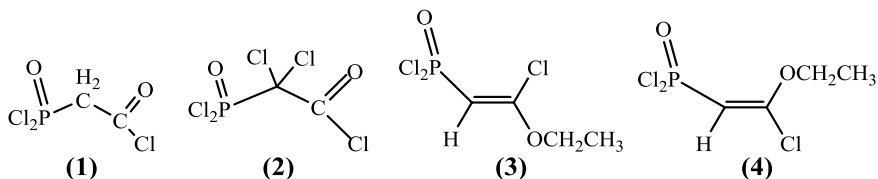
2.1. New aspects of the reaction of esters with phosphorus pentachloride and explanation of the obtained compounds based on conformational analysis. This presented research is a continuation of recent scientific-research works in the field of α -phosphoryl carbonyl compounds at the Department of Organic Chemistry of BSU. Reactions of α -phosphoryl carbonyl compounds obtained from the phosphorylation of esters and phosphonacetals with mono- and polynucleophilic reagents were studied.

Initially, for the purpose of synthesis of starting substances, the presence of several different points obtained as a result of phosphorylation of esters with PCl_5 , it is necessary to clarify the interesting questions related to the course of these reactions and the structure of the obtained intermediate complexes.

The review states that three phosphorous-organic compounds are obtained from the decomposition of the complex obtained from the phosphorylation of alkylacetates with PCl_5 . The authors did not propose any idea about the structure and nature of the complex. Differently, as a result of our studies, it has been shown that four phosphorous-organic compounds are formed from the phosphorylation of alkylacetate under the indicated conditions. It can be logically assumed that the complex obtained from the reaction of esters with PCl_5 consists of a mixture of four complexes with different composition and structure [A+B+C+D].



Corresponding phosphorous-organic compounds are obtained when the indicated complex mixture is treated with sulfur gas (1-4).

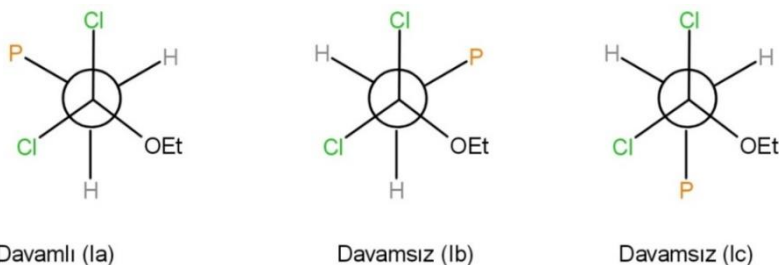


Preparation of substance (1) from the indicated reaction was carried out by us for the first time and its structure was confirmed by ^1H NMR spectroscopy. 3.74 ppm, doublet $^2J_{\text{HP}}=18.95\text{Hz}$ indicates the presence of P- CH_2 -fragment. In the ^{13}C NMR spectrum, the presence of a 163.83 ppm resonance signal characterizes the $\text{Cl}-\text{C}=\text{O}$ group.

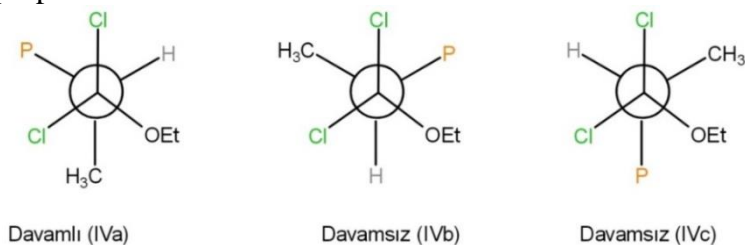
It should be noted that in previous studies, the authors envisioned the obtaining of compound (2) from substance (1), which was assumed to be an intermediate. However, it has been shown by us that substance (1) is stable under reaction conditions and does not turn into substance (2). In this regard, the course of the phosphorylation reaction of esters with PCl_5 can be imagined with a different mechanism. One of the interesting points of the indicated reaction is that, while a mixture of two geometric isomers is obtained as a result of the phosphorylation of alkylacetates as mentioned above, only two reaction products are obtained from the phosphorylation of alkylpropionates under the same conditions: trichloroanhydride of α -chloro- α -phosphonopropionic acid (6) and dichloroanhydride of β -chloro- β -alkoxy- α -methyl-vinylphosphonic acid (5) in the form of one isomer.

In order to clarify this idea of scientific interest, the answer to the question can be explained if we look at the structure of stable conformers of the complexes obtained during both reactions.

Conformations of the complex obtained from phosphorylation of alkylacetate:



Conformations of the complex obtained from phosphorylation of alkylpropionate

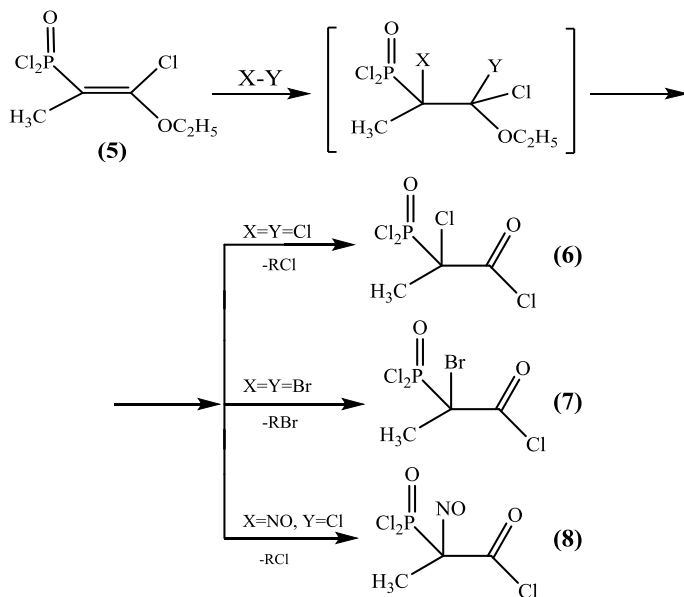


Looking at the structure of the stable conformers obtained from both reactions, it is clear that the structure of the complex obtained from alkyl-

acetate enters the elimination reaction in two directions (H, Cl; H, Cl atoms are in an anti-periplanar position) and gives a mixture of geometric isomers. As for the complex obtained on the basis of alkyl propionate, it is natural to obtain one isomer in the elimination, since the hydrogen and chlorine atoms are anti-periplanar in only one position.

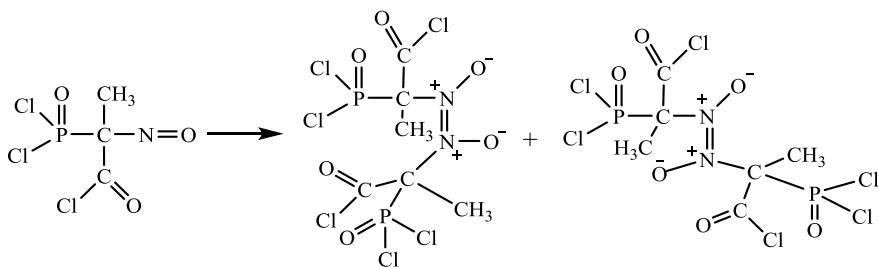
Thus, for the first time, based on the conformational analysis, the obtaining of vinylphosphonates with different structures as a result of reactions of esters with PCl_5 was clarified.

2.2. Syntheses based on trichloroanhydride of phosphon- α -chloropropionic acid. The trichloroanhydride of phosphonchloropropionic acid (6), which is used as a starting material in research studies, was obtained by the known method in the reaction of ethylpropionate with PCl_5 . The second reaction product obtained as a result of the reaction – α -methyl- α -phosphoryl-b-chloro-b-ethoxyvinylphosphonate (5) was shown to be able to be converted into trichloroanhydride with a high yield under the influence of various electrophilic reagents. Thus, dichloroanhydride (5) combines chlorine, bromine and nitroschloride in a non-polar solvent (CCl_4) at $0\div 10^\circ\text{C}$ to form unstable α,α -dihalogen ethers. The latter are easily dealkylated under reaction conditions and turn into corresponding trichloroanhydrides.

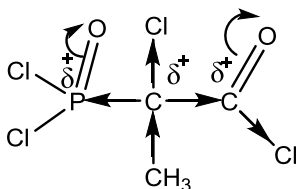


Theoretically, it was of interest to study some properties of trichloroanhydride (8), which contains the nitroso group. It was determined that the thermodynamic stability of nitroso compounds depends on the nature of the radicals in α -position. When the radicals are electron-acceptor, the nitroso compound is stable and is in the form of monomers. When radicals are electron-donors, dimerization occurs.

The nitro compound, obtained as a result of the presence of two electron acceptor groups ($>P=O$ and $-ClC=O$) and one electron-donor CH_3 -fragment in the α -position in nitroso compound (7), exists as a monomer (blue color), and when left for a long time, dimerization occurs and two spatial isomers are formed (transparent).



The presence of three consecutive electrophilic centers (phosphoryl, carbonyl and carbon atom) in trichloroanhydride (6, 7, 8) means that the reactions under the influence of nucleophilic reagents proceed with the substitution of the carbonyl and phosphoryl groups and also with the breaking of P-C and C-C bonds.

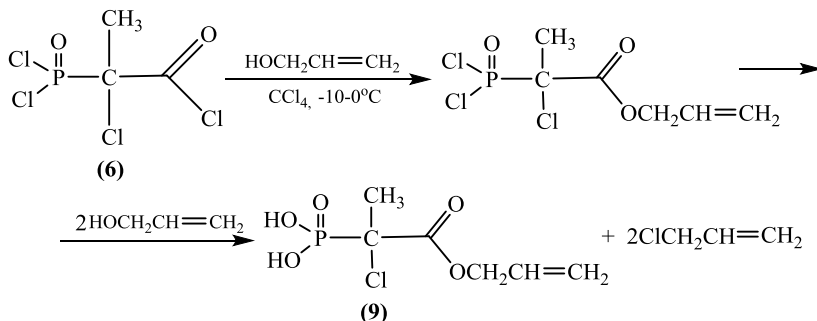


It is known from the research in this field in the literature that the alcohololysis (methanol) of trichloroanhydride of phosphondichloroacetic acid takes place in the selective carbonyl group and then in the phosphorus atom. It was determined that this reaction proceeds in a more complex direction with phenols, and when the acidity of phenols is high, breaking of the P-C bond is observed.

In the research presented as a continuation of these works, the reac-

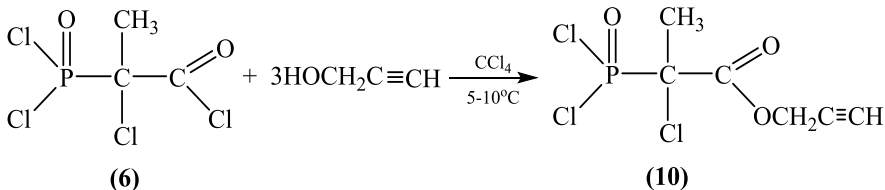
tions of trichloroanhydride (6) with allyl and propargyl alcohols, which have higher acidity compared to methanol, were studied.

The reaction of trichloroanhydride (6) with allyl alcohol was carried out in a non-polar solvent (CCl_4) in the ratio of 1:3 without the presence of amine at $-10 \pm 0^\circ\text{C}$, and it was determined that initially condensation occurs at the carbonyl atom and the corresponding C-allyl ester is obtained. In the next step, the remaining part of allyl alcohol is converted into allyl chloride and C-allyl ester of α -chloro- α -phosphonopropionic acid (9) by a mechanism similar to the reaction of two chlorine atoms in the phosphorus atom with tert-butyl alcohol.



The structure of substance (9) was confirmed by ^1H and ^{13}C NMR spectroscopy (Fig. 1 a,b): (DMSO-d₆): δ m.h. 1.71d (3H, CH₃, P-C-CH₃) $^3\text{J}_{\text{HP}}$ 13.8 Hz, 4.56d (2H, OCH₂, $^3\text{J}_{\text{HH}}$ 4.5 Hz), 5.14-5.24dd (2H, CH₂=), 5.78m (1H, CH=), 9.94s (2H, OH);

Under similar conditions, the reaction of trichloroanhydride (6) with propargyl alcohol ends only with the replacement of the chlorine atom next to the carbonyl group, and propargyl ester of α -chloro- α -dichlorophosphoryl propionic acid (10) is obtained. Replacement of chlorine atoms next to the phosphorus atom does not occur at $10-15^\circ\text{C}$.



Simple ^1H and ^{13}C NMR spectra fully confirm the structure.

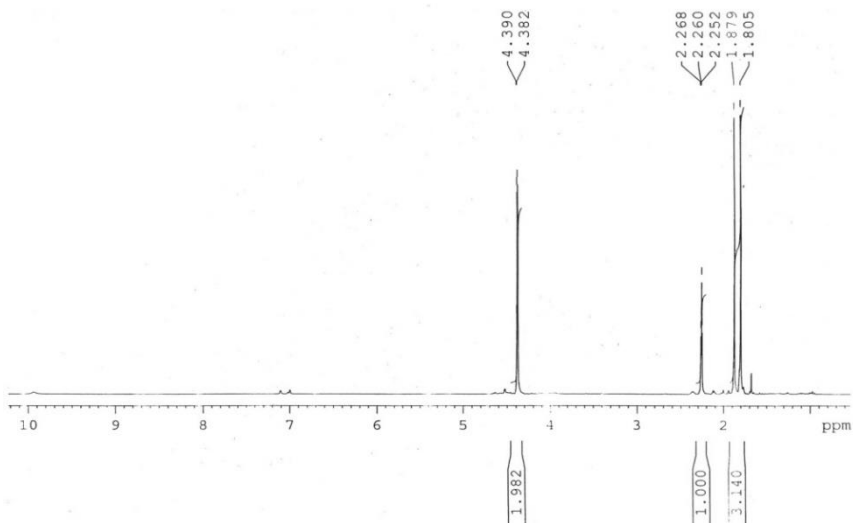
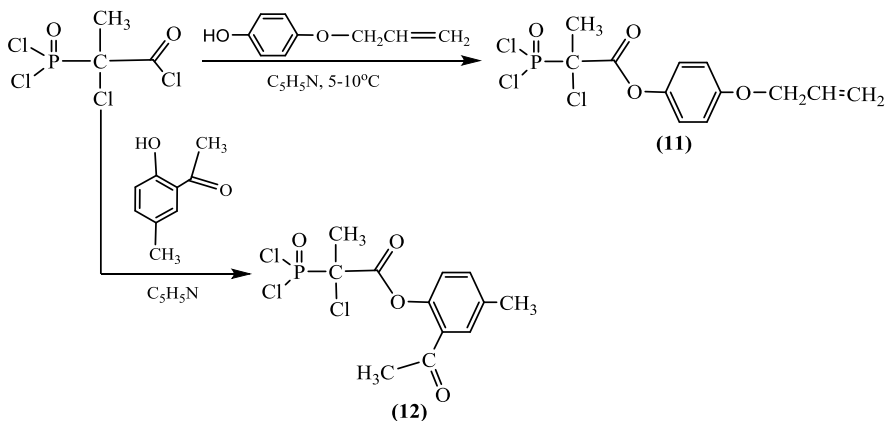


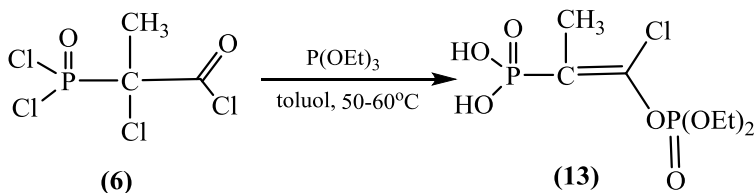
Figure 1. ^1H NMR spectrum of substance (10).

Conducting the reaction of trichloroanhydride (6) with phenols in the presence of pyridine in an ether environment had two goals: firstly, to increase the nucleophilicity of phenols and to study the effect on the reaction, and secondly, to study the effect of pyridine on the yield of the reaction. As phenol, allylhydroxynone and 2-acetyl-4-methyl phenol were used in these reactions. In both cases, the condensation takes place on the selective carbonyl carbon atom, and phenyl ethers, dichloroanhydrides of α -chloro α -phosphonpropionic acid (11, 12) were synthesized in medium yield.



On a large scale, the reaction of chloroanhydrides of carboxylic acids with phosphite is widely used in the synthesis of acylphosphonates. In another study, it was determined that the chloroanhydride of trichloroacetic acid reacts with phosphite according to a completely different mechanism, and a compound with a phosphate structure is formed.

Due to some properties and structure of trichloroanhydride (6), it was interesting to study the reaction of trichloroacetic acid chloroanhydride (6) with phosphite. This reaction was carried out in toluene at 50-60°C for 1 hour and α -methyl- β -chloro- β -diethoxyphosphate vinylphosphonic acid dichloroanhydride (13) was obtained in high yield (76%).



When compound (13) remains in aqueous medium for a long time, precipitation of phosphoric acid confirms that it is of (13) phosphate character. Additionally, ^1H and ^{13}C and ^{31}P NMR spectra fully confirm the structure of substance (13).

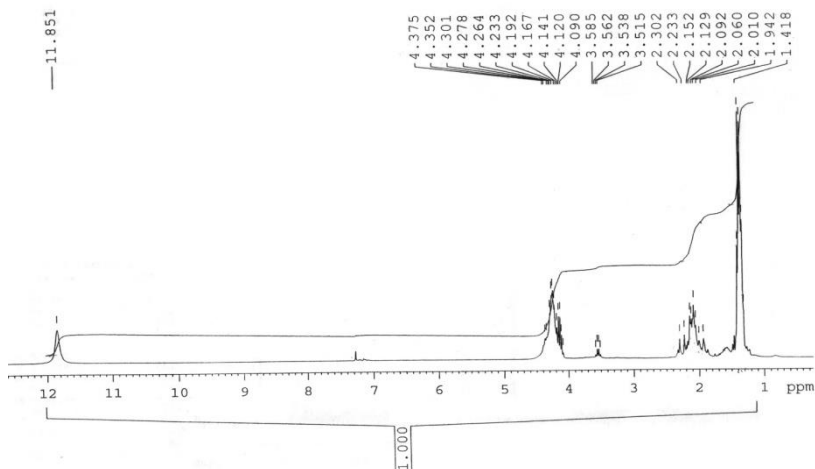
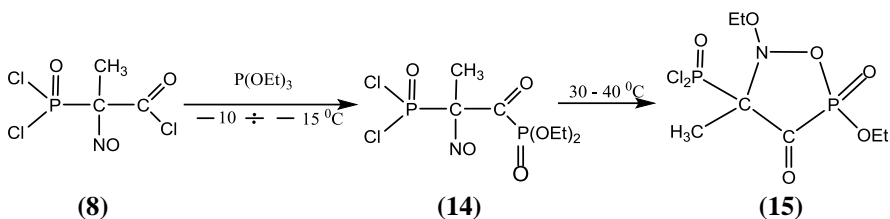
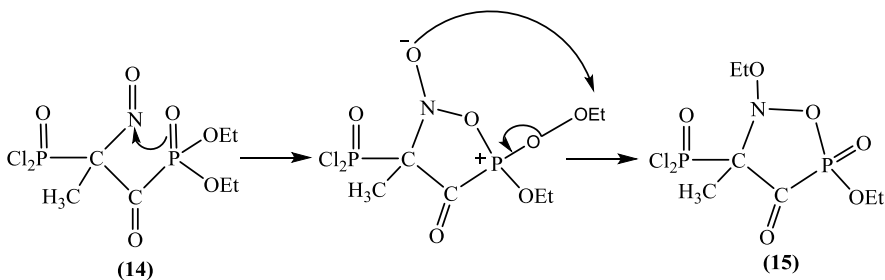


Figure 2. ^1H NMR spectrum of substance (13).

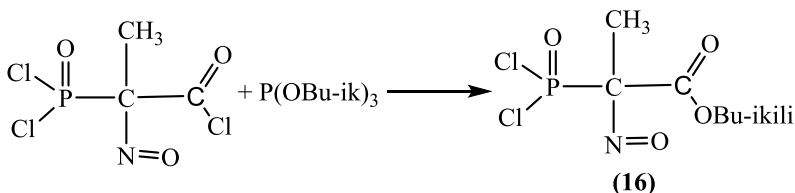
The reaction of α -nitroso- α -phosphonpropionic acid trichloroanhydride (8) with trialkylphosphites occurs in several directions depending on the temperature and the nature of the phosphites. It was determined that when the reaction of trichloroanhydride (8) with triethylphosphite is carried out at $-15 \div -10$ °C, the reaction takes place according to the Arbuzov scheme, unlike trichloroanhydride (6), and as a result, diphosphonate (14) is obtained. The latter undergoes an internal cyclization reaction at $30-40$ °C to form a derivative of 1,2,5-oxazophosphate (15).



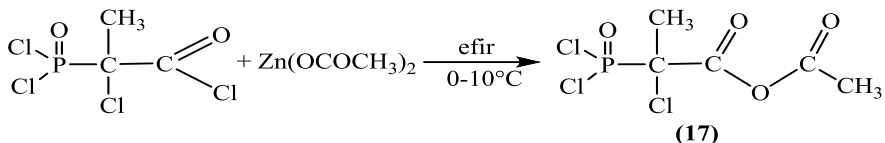
The mechanism of obtaining compound (15) from compound (14) can be imagined as follows:



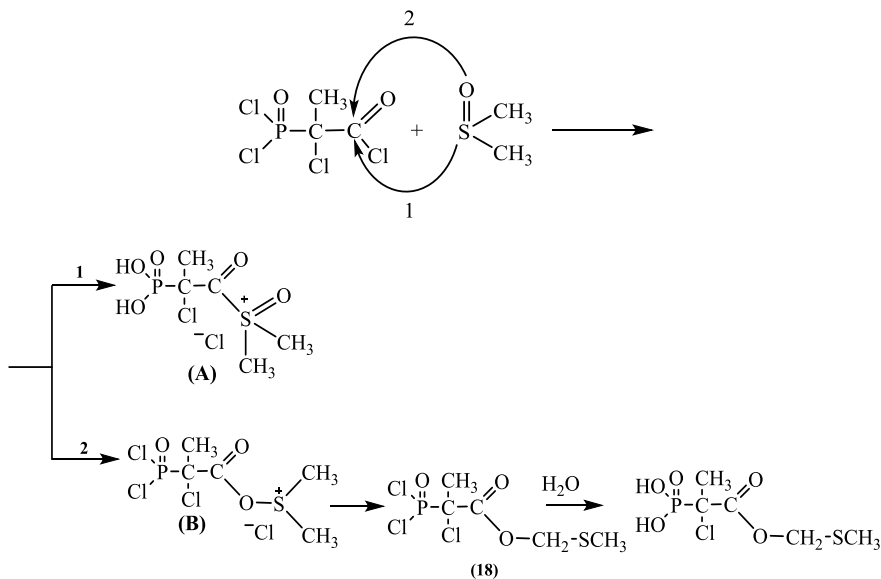
When secondary tributylphosphite is used in this reaction, the latter shows ambident property and it is observed that the reaction proceeds in the presence of oxygen, and only the C-esterification product (16) is obtained. It is likely that the steric factor has an effect on the course of the reaction.



Trichloroanhydride (6) in an ether medium undergoes a nucleophilic substitution reaction with zinc acetate at 0÷10°C and turns into acids anhydride (17).

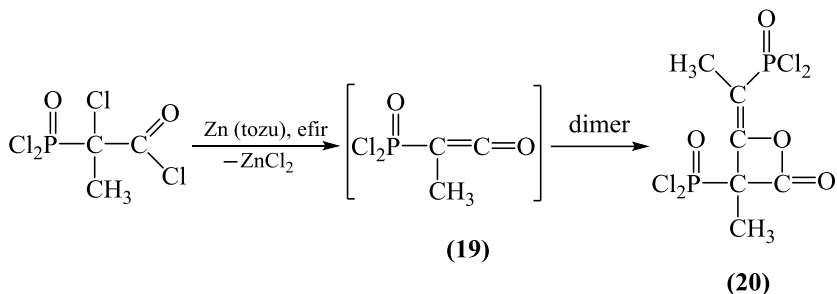


As can be seen from the scheme, in this reaction, the nucleophilic substitution reaction takes place at the selective carbonyl group. The reaction of trichloroanhydride (6) with dimethylsulfoxide was somewhat unexpected. The reaction proceeds with the release of high heat and cooling with ice water is needed to regulate the reaction. In the indicated reaction, dimethylsulfoxide shows ambident properties and forms the corresponding oxosulfone salt (A) and acyloxysulfone salt (B) as a result of the attack of sulfur and oxygen atoms on the electrophilic center of trichloroanhydride (meaning the carbonyl atom). Part of the latter is converted to sulfide (18) as a result of the Pummerer rearrangement reaction under the reaction conditions.

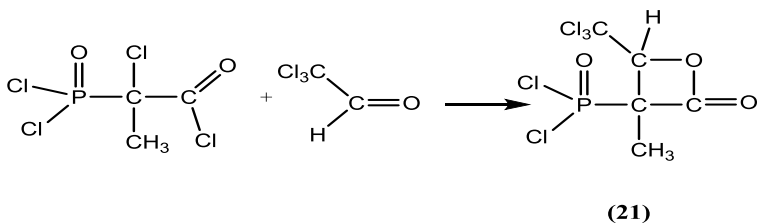


It was confirmed by ^1H and ^{13}C NMR spectroscopy that the obtained crystalline substance consists of a mixture of two compounds.

One of the methods of preparative synthesis of ketenes in the literature consists of the action of zinc powder on the halogen anhydride of acids containing halogen in the α -position. From this point of view, trichloroanhydride (6) can be considered as the most suitable substrate for obtaining of corresponding phosphorus-containing ketene. It should be noted that there is no practical information in the literature in the field of phosphonketenes. Thus, it was shown for the first time that in a non-polar solvent (ether, hexane, etc.), trichloroanhydride (6) undergoes an elimination reaction (dechlorination) under the influence of zinc powder and turns into the corresponding ketene (19). When the resulting ketene remains, it dimerizes (20) and is persistently present.

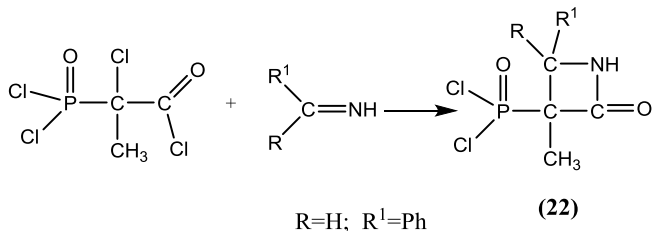


The presence of two doublets at 1.8 and 2.7 m.h in the ^1H NMR spectrum of substance (20) confirms that CH_3 groups are located next to sp^3 and sp^2 hybrid carbon atoms in the dimer. When the indicated reaction is carried out in the presence of carbonyl compounds, the ketene (19) obtained during the reaction has a high reactivity, so it undergoes a cyclization reaction with a carbonyl compound and becomes a β -lactone type compound.



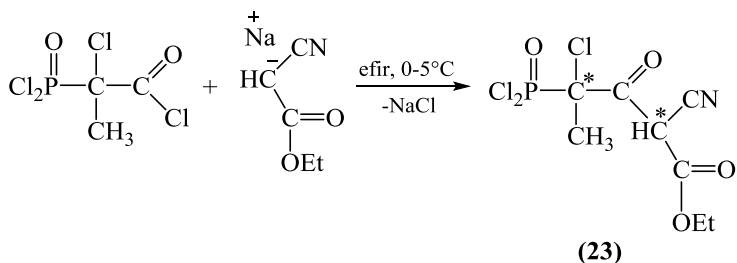
This makes it possible to obtain a variety of heterocyclic compounds by using a wide variety of active unsaturated compounds in the reaction. When imines are used in the presented reaction, the ketene obtained by

cyclization with the imine group forms β -lactam (22).



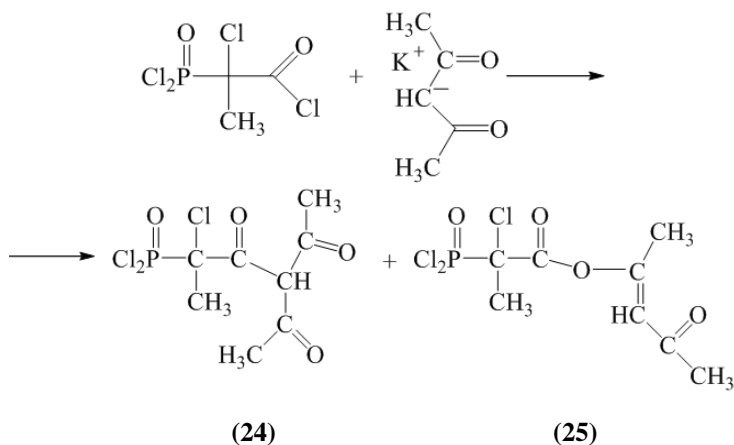
In conclusion, it should be noted that a wide variety of heterocyclic compounds can be obtained from the reaction of trichloroanhydride (6) and compounds of this type with various alkenes in fine organic synthesis.

2.3. The reaction of α -chloro- α -phosphonpropionic acid trichloroanhydride (6) with C-nucleophilic reagents. In the presented study sodium or potassium derivatives of acetylacetone and ethylcyanoacetate were used as reagents with trichloroanhydride (6). Since both indicated reagents have ambident property, the formation of two types of compounds was expected. It was determined that the reaction of the trichloroanhydride of α -phosphonic α -chloropropionic acid (6) with the potassium salt of ethylcyanoacetate was carried out in an ether environment at 0-5°C and as a result, only the product of C-acylation (23) was obtained.

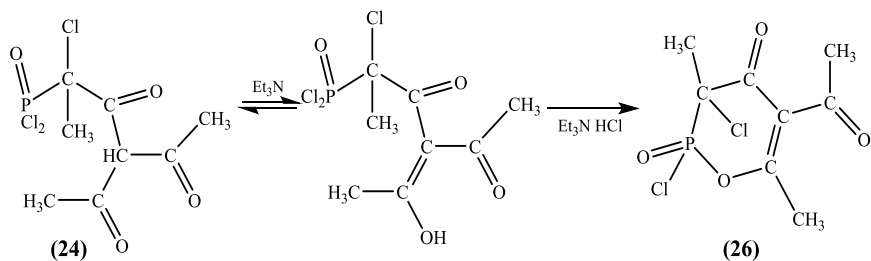


The presence of two asymmetric carbon atoms in the synthesized compound (23), the presence of diastereomers, and the fact that the obtained compound consists of a mixture of 4 spatial isomers are evident from the ¹H and ¹³C NMR spectra.

Under similar conditions, trichloroanhydride (6) reacts with the potassium derivative of acetylacetone to form C-(24) and O-(25) acylation products.



At 35-40 °C, sharp separation of HCl from the obtained mixture is observed. As a result of the research, it was determined that the compound (24) is gradually enolized and undergoes intramolecular cyclization (with HCl release) to oxaphospharinane (26). The use of tertiary amines in this process accelerates the cyclization process and a large amount of tertiary amine hydrochloride is obtained (in amorphous form). Needless to say, using the triple amine leads to both enolization of compound (24) and HCl separation.



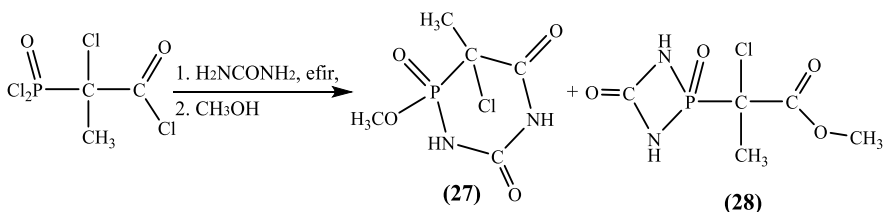
The presence of a small amount of a phosphate-type compound in the mixture is possible only as a result of breaking the P-C bond of the starting or reaction products.

2.4. Reaction of trichloroanhydride (6) with N,N- and N,S- and N,O-binucleophilic reagents. It is known that a wide variety of barbiturates are used as medicinal substances in medicine. From this point of view, the synthesis of phosphorus analogues of barbiturates can be considered relevant. The first phosphobarbiturates were obtained from

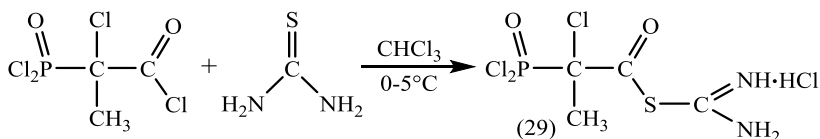
the reaction of phosphonacetate in the presence of urea with alcohol at the organic chemistry department of BSU.

In the preparative synthesis of phosphonobarbiturates, the use of trichloroanhydrides of phosphonocarboxylic acids can be considered efficient, because the presence of three active chlorine atoms in the composition of trichloroanhydride makes it possible to synthesize a wide variety of phosphorus-containing barbiturates and compounds of that class that contain phosphorus, nitrogen, and sulfur.

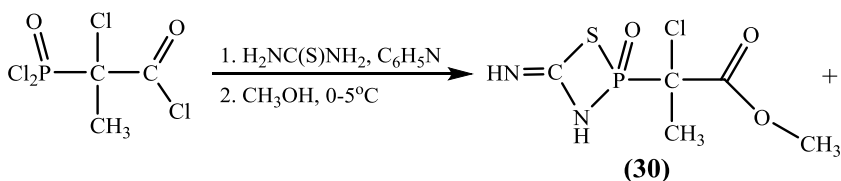
For this purpose, phosphonobarbiturate (27) and 1,3,2-diazaphosphaethane (28) derivatives were synthesized when the mixture obtained from the reaction of trichloroanhydride (6) with urea in ether medium in the presence of pyridine was treated with methanol at the last stage.

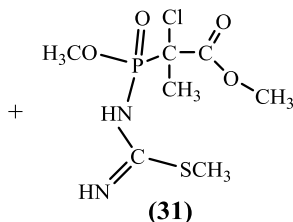


The indicated reaction with thiourea in chloroform in the absence of pyridine at 0-5°C (S-acylation) affords the thiuronium salt (29).



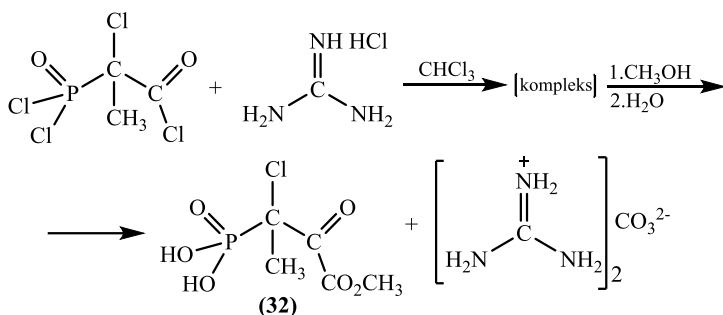
When this reaction is carried out under the same conditions in the presence of pyridine and treated with methanol in a subsequent step, two phosphorus-containing products are obtained: a cyclic imine (30) and an amide (31).





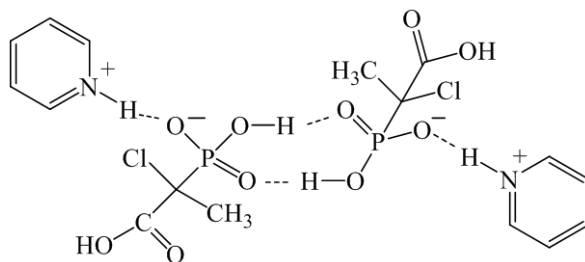
The mechanism for obtaining of (30) and (31) is given.

Trichloroanhydride (6) forms a complex with guanidine hydrochloride in chloroform. When methanol is added to the complex, its decomposition occurs. When the obtained mixture is treated with water, white monocystals precipitate from the water phase within 24-36 hours. All spectroscopic indicators confirm that the obtained crystal is the methyl ester of α -chloro- α -phosphonopropionic acid (32). Another crystal obtained from the mixture belongs to the dicarbonate salt of guanidine according to X-ray indicators (picture).



We considered it important to clarify a question that arose out of necessity when examining the chemical properties of trichloroanhydride (6). As shown, most of the nucleophilic substitution reactions of trichloroanhydride (6) were carried out in the presence of pyridine in ether or chloroform. In order to remove the pyridine hydrochloride obtained as a result of the reaction, the mixture is treated with water, and white crystals precipitate in the water phase for 5-6 days.

When the structure of those crystals is studied by ^1H , ^{13}C NMR and X-ray methods, it is shown that this compound is a dimer of α -chloro α -phosphonopropionic acid and a complex containing two pyridine molecules (33).



(33)

It can be assumed that a part of the reaction product or unreacted trichloroanhydride (6) is hydrolyzed with water and turns into α -chloro- α -phosphonopropionic acid, and the latter dimerizes under the influence of pyridine and forms complex (33). Experimentally, this hypothesis has been confirmed.

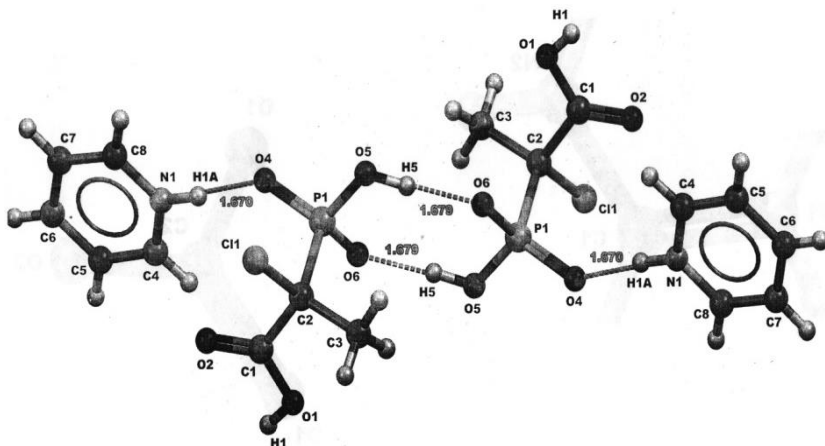
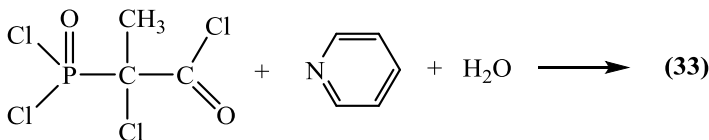
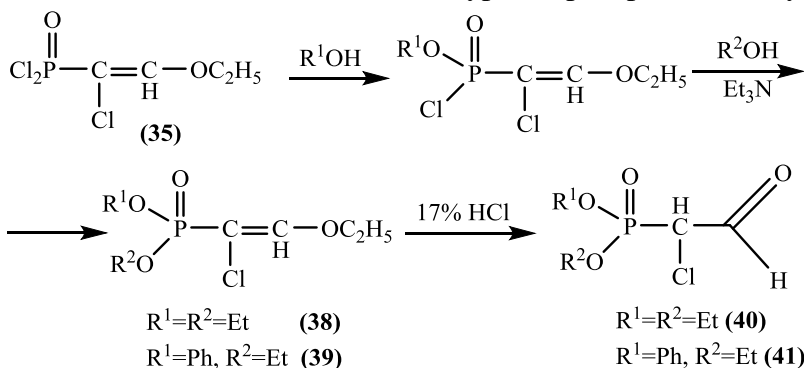


Figure 3. X-ray structure of complex (33).

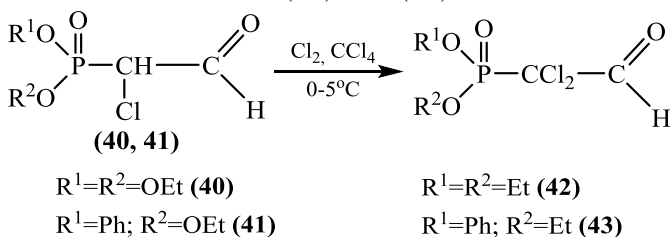
2.5. Synthesis and some transformations of phosphonmono- and dichloroacetic aldehydes. The scientific research conducted in this field is a continuation of the research work on α -chloro- α -phosphonocarbonyl compounds conducted at BSU in the last few years. Dif-

ferently, the aim was to synthesize α -halo- α -phosphorylaldehydes containing mixed ether, etheramide fragments on the phosphorus atom and to study their biological activity.

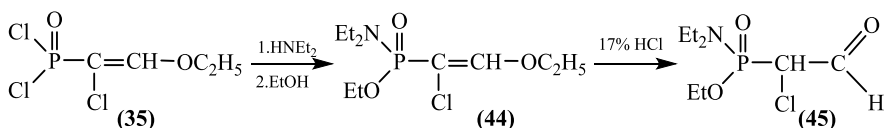
It has been established experimentally that the attitude of chlorine atoms located near the phosphorus atom to nucleophilic reagents (ROH, R₂NH, etc.) is different. In phosphonium dichloroanhydrides, the first chlorine atom is replaced by nucleophilic reagents at $-10 \pm 0^\circ\text{C}$, while the second chlorine atom is replaced at a slightly higher temperature. The presence of such a difference makes it possible to successively replace chlorine atoms in the phosphorus atom to form mixed ethers, etheramides and other different types of phosphoric aldehydes.



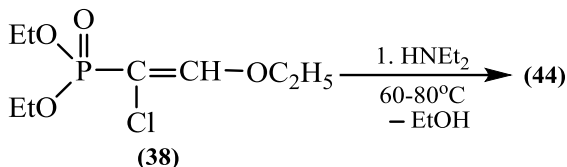
Phosphondichloroacetic aldehydes (42, 43) were synthesized from the chlorination of substances (40) and (41) in CCl₄ at $0-5^\circ\text{C}$.



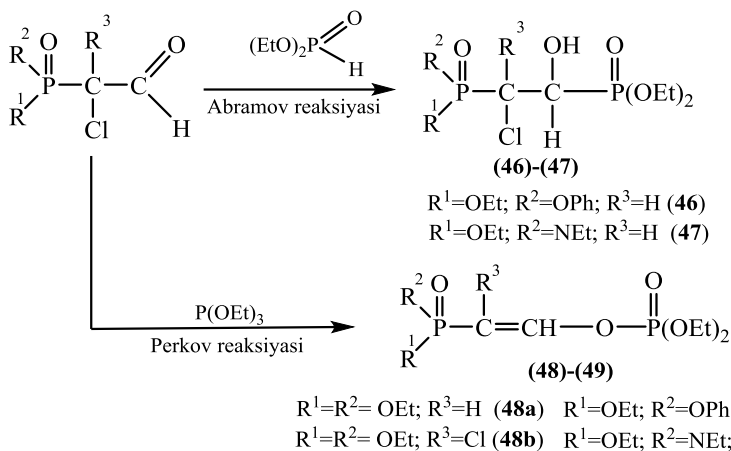
Etheramide (44) was obtained from dichloroanhydride (35) and aldehyde (45) from its hydrolysis in the above sequence.



Compound (44) can be obtained by treating diethyl ester of α -chloro- β -ethoxyvinylphosphonate (38) with diethylamine. In this reaction, only one of the two ethoxy groups near the phosphorus atom is replaced by diethylamine.

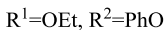
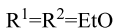
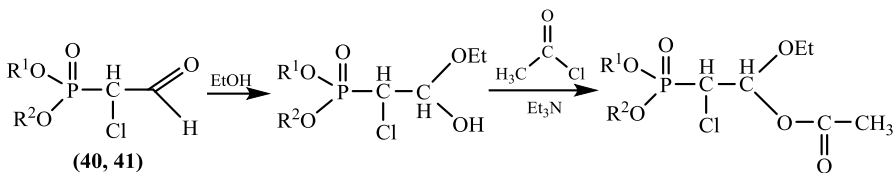


The simultaneous presence of chlorine and phosphoryl groups in the synthesized aldehydes leads to an increase in their reaction activity. Thus, aldehydes (41-45) react with trialkylphosphite and dialkylphosphite to form Perkov product (46-47) and hydroxyphosphonates (48-49).

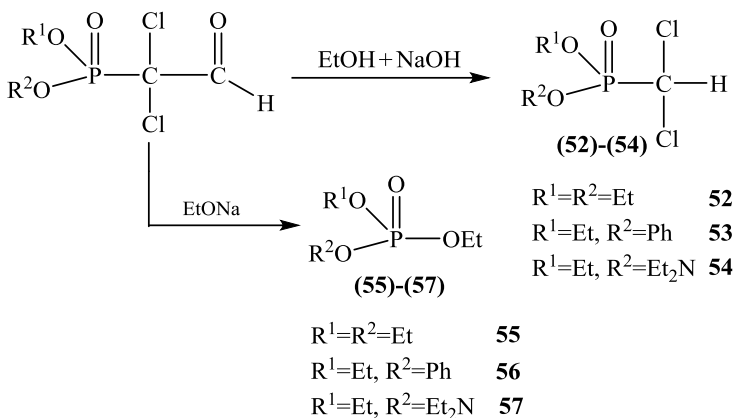


It should be noted that the compounds obtained as a result of the Abramov reaction (46, 47) are phosphorus derivatives of chlorophos, which are widely used as insecticides, so it can be assumed that they are important pesticides in agriculture.

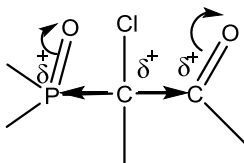
In addition, the synthesized aldehydes undergo an addition reaction at room temperature without the presence of any catalyst (with alcohols, thioalcohols, etc.), and compounds with a relatively stable hemiacetal structure and based on them acetals and acylals were synthesized.



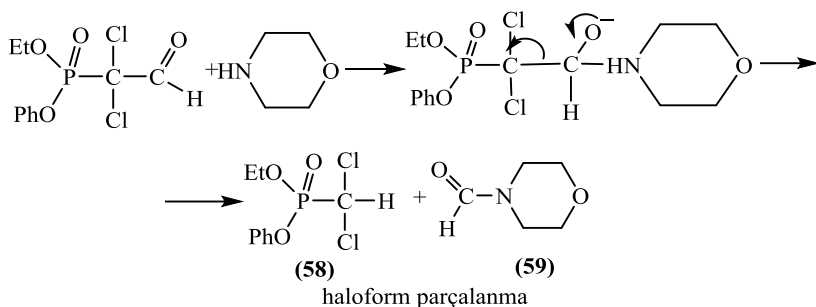
Haloform decomposition is observed in this reaction when alcohol is used in an alkaline environment (or from two amines). When dry alcohol is used in the heterologous phase, breaking of the P-C bond occurs.



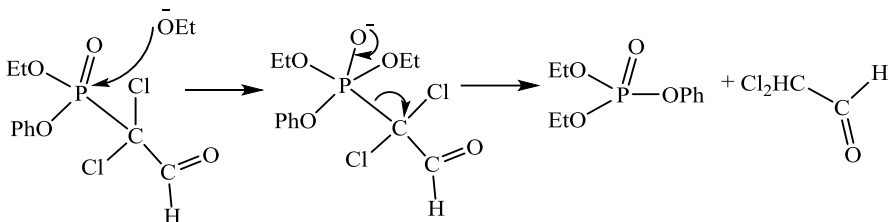
The reason for the indicated P-C and C-C breaking is explained by the presence of three identical positively charged phosphorus-carbon-carbon atoms in the 1,2,3-position.



Depending on the nature of the nucleophilic reagent, haloform-type decomposition occurs in case of attack on the carbon atom. Aldehyde (43) undergoes C-C cleavage according to the scheme shown below under the action of morpholine.



Aldehyde (43) undergoes cleavage of the P-C bond under the influence of alcoholate, resulting in formation of phosphate and dichloroacetic aldehyde.

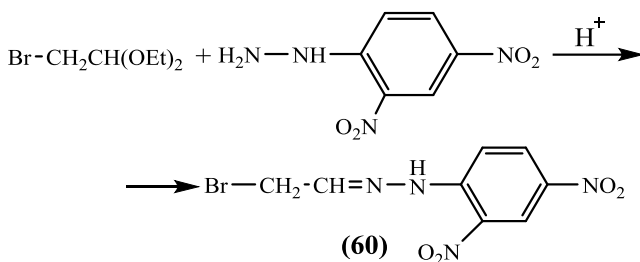


From the analysis of the literature and our research, it is known that the P-C bond can be broken in two cases: the first, as mentioned, as a result of the attack of the nucleophilic reagent on the phosphorus atom, and the second, when the transition to the ylide form of the phosphorous compound ($>P=C$) occurs.

In conclusion, it should be noted that there is a need to synthesize new representatives of such systems and study their properties.

2.6. Syntheses based on bromoacetic aldehyde hydrazones. Halogen-containing hydrazones are one of the least studied areas of organic chemistry. Compounds of this type can be considered useful in the synthesis of hydrazones containing nitrogen, phosphorus and sulfur in large-scale organic synthesis. On the other hand, hydrazones are the basis of indoles, which are widely used in medicine (Fisher reaction).

Bromoacetic aldehyde 2,4-dinitrophenylhydrazone (60) is synthesized in high yield from the reaction of bromoacetic aldehyde diethylacetal with 2,4-dinitrophenylhydrazine at room temperature in acidic medium.



Due to the active bromine atom in hydrazone (60), its reaction with various P-, O-, N- and S-nucleophilic reagents enables the synthesis of new types of elementorganic compounds.

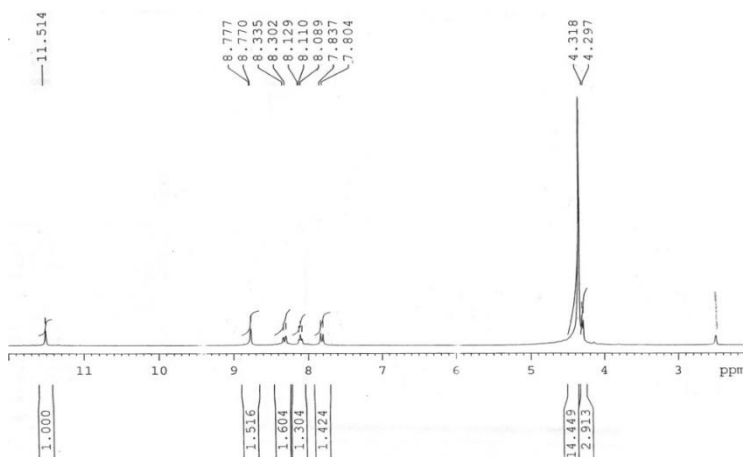
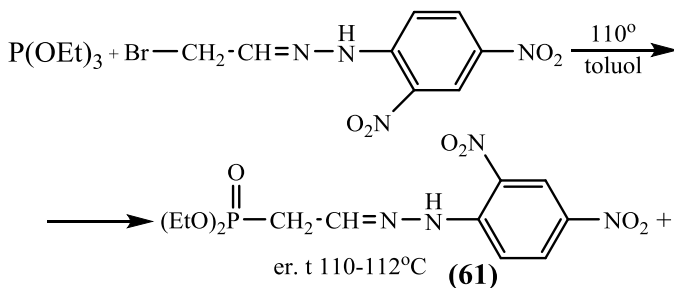
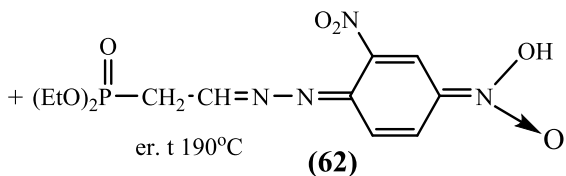


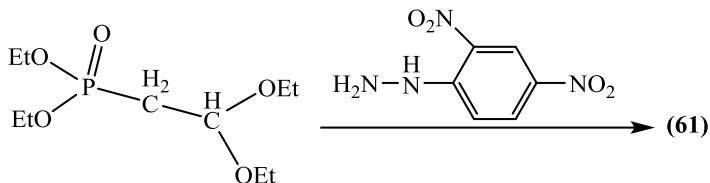
Figure 4. ^1H NMR spectrum of substance (60).

Thus, from the reaction of hydrazone (60) with triethylphosphite in a toluene environment at 110°C , hydrazone of phosphonacetic aldehyde (61) and a small amount of prototropic isomerization product (62) were obtained.

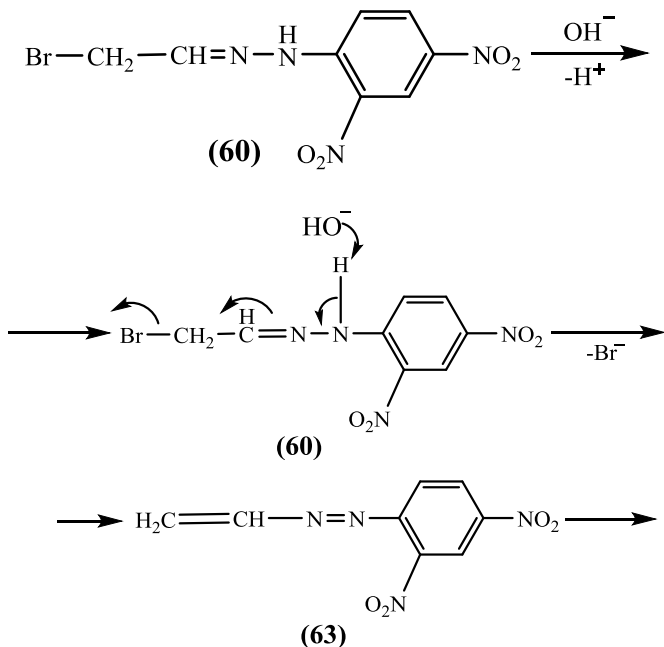


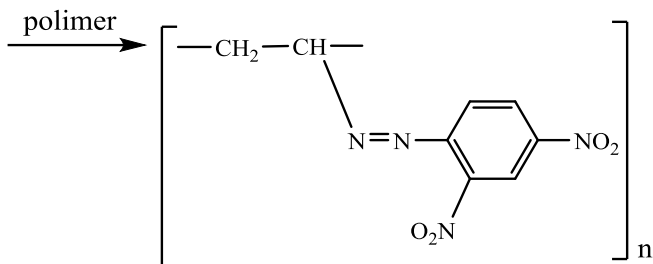


Hydrazone (61) was obtained by reaction of diethylacetal of phosphonoacetic aldehyde with 2,4-dinitrophenylhydrazine based on mutual synthesis.



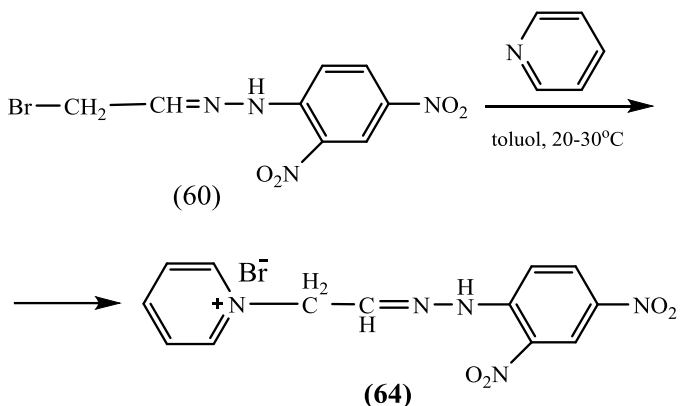
Hydrazone (60) undergoes a 1,4-elimination reaction in an alkaline medium (NaOH+H₂O) and is transformed into an alkene derivative (63) with an azo group. The latter polymerizes to form a dark colored polymer.





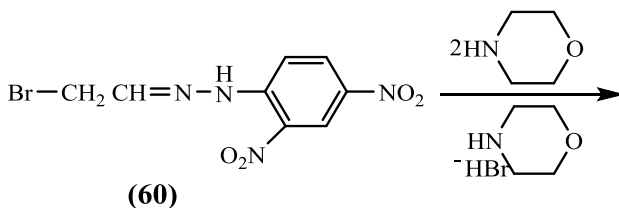
This area is a separate research topic.

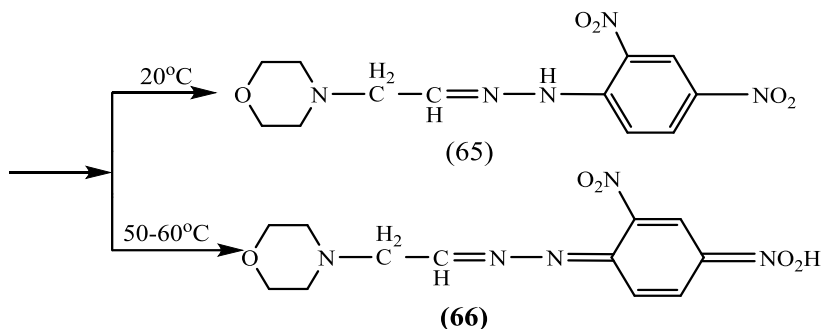
At room temperature, hydrazone (60) forms the corresponding quaternary ammonium salt (64) with pyridine.



It is noted that since pyridine is a weak base, prototropic isomerization does not occur in substance (64).

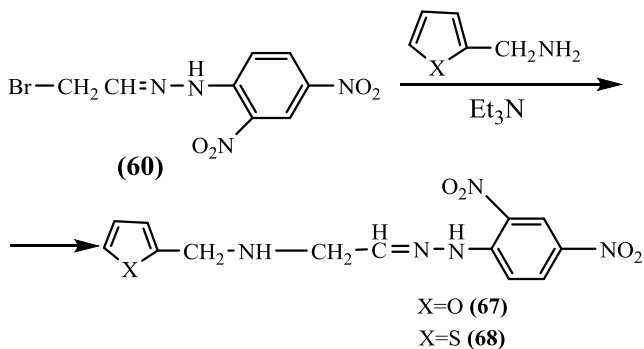
Unlike pyridine, morpholine replaces the bromine atom in hydrazone (60) at room temperature to form morpholine hydrazone (65) (orange color). When the indicated reaction is carried out at a higher temperature (50-60°C), a color change is observed again and is an indicator of electron rearrangement (quinoid structure is obtained) in the reaction product (66).



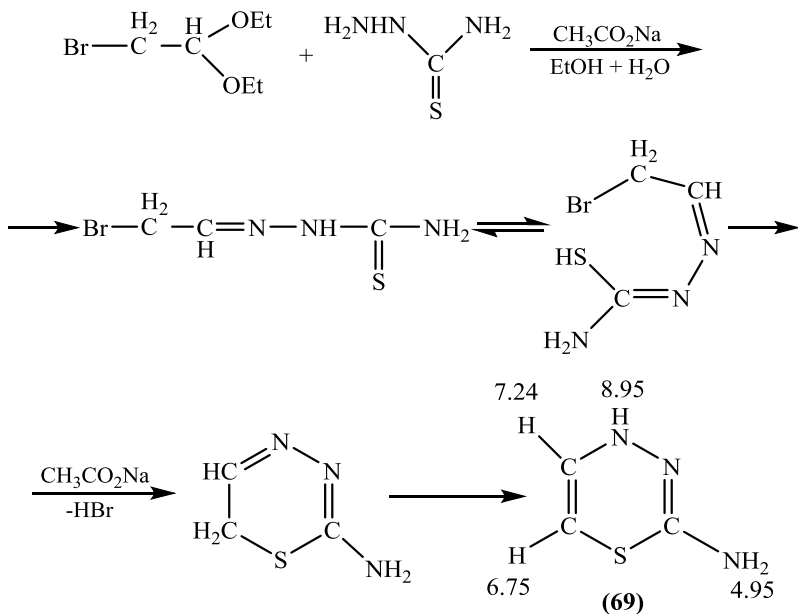


Since thiophene and furan are components of many plants and vitamins, the inclusion of these structural fragments in hydrazone (60) is relevant in terms of biological activity.

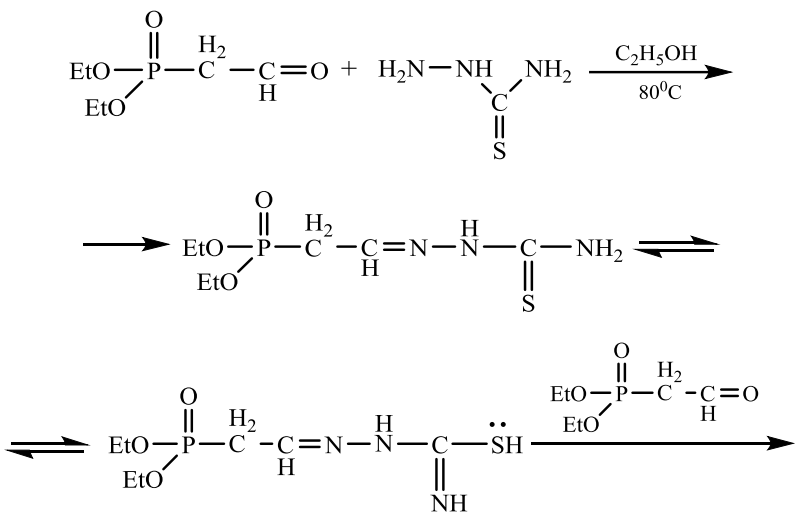
For this purpose, reactions of hydrazone (60) with α -aminomethylfuran and α -aminomethylthiophene were studied. New representatives of polyfunctional hydrazones containing two aromatic nuclei were synthesized from the alkylation of the indicated amines with hydrazone (60). (67, 68)

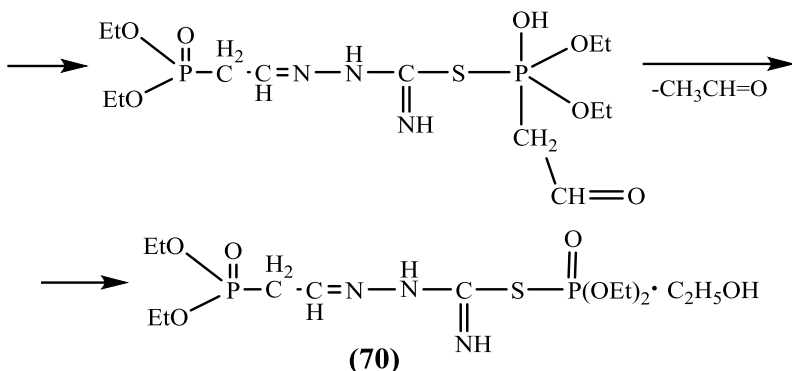


2.7. Reactions of α -bromo- and α -phosphoryl acetic aldehydes and phosphonacetate with N, N- and N, S- nucleophilic reagents. The thiosemicarbazone of bromoacetic aldehyde obtained from the reaction of diethylacetal of bromoacetic aldehyde with thiosemicarbazine hydrochloride in the presence of sodium acetate in an ethanol-water environment turns into a six-membered heterocyclic compound as a result of intramolecular S-alkylation under the reaction conditions, and the latter undergoes prototropic isomerization and passes to 1,3,4-thiadiazine (69).



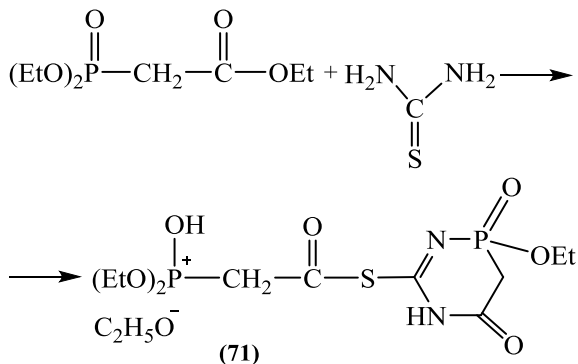
The thiosemicarbazone obtained on the basis of phosphonacetic aldehyde reacts with the second phosphonacetic aldehyde to form N-[diethoxyphosphorylthioimino] phosphonacetic aldehyde hydrazone (70).





As can be seen from the given scheme, the condensation of the thiosemicarbazone obtained in the first step with the second phosphonacetic aldehyde molecule occurs with the breaking of the P-C bond, and the substance (70) obtained as a result of the reaction contains one molecule of ethyl alcohol.

As a result of the condensation of phosphonacetate with urea, the first representative of phosphonbarbiturates was synthesized in the presence of alcoholate at the BSU organic chemistry department. As a continuation of these works, the reaction of triethylphosphonacetate with thiourea was carried out at 80-90°C and it was determined that two phosphonacetate molecules are involved in the condensation and finally the derivative of thiophosphonbarbiturate – S-[diethoxyphosphorylethanoyl] (71) is obtained.



Based on all ^1H and ^{13}C NMR spectra, compound (71) contains one molecule of ethanol.

It is possible to imagine that the formation of matter (71) occurs according to two schemes. In the first variant, phosphonacetate is condensed with thiourea to form phosphonbarbiturate, and the latter is condensed with a second molecule of phosphonacetate to form compound (71). In another variant, phosphonacetate is condensed with thiourea in the presence of a sulfur atom, turning into phosphonacetathiouronium and forming substance (71) with the second phosphonacetate molecule.

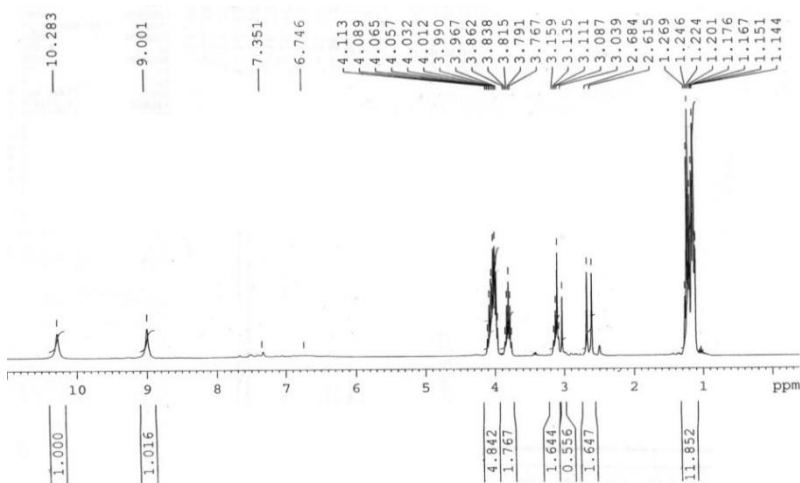
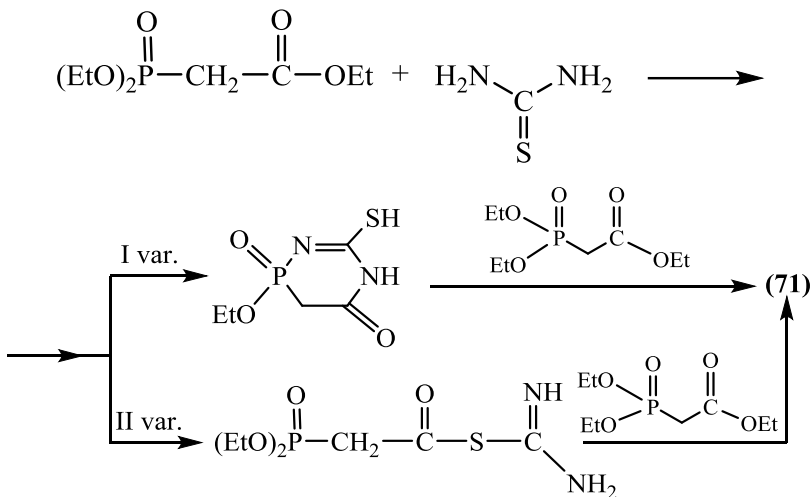
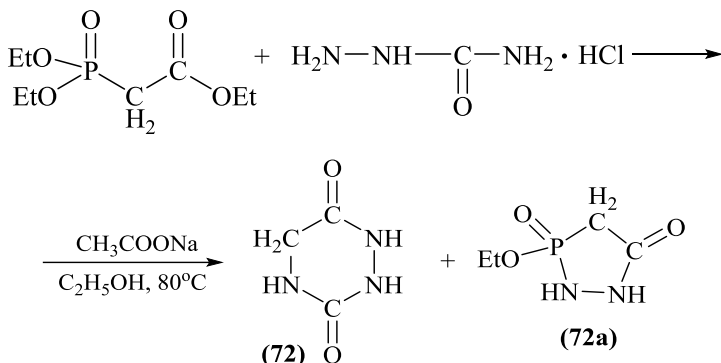
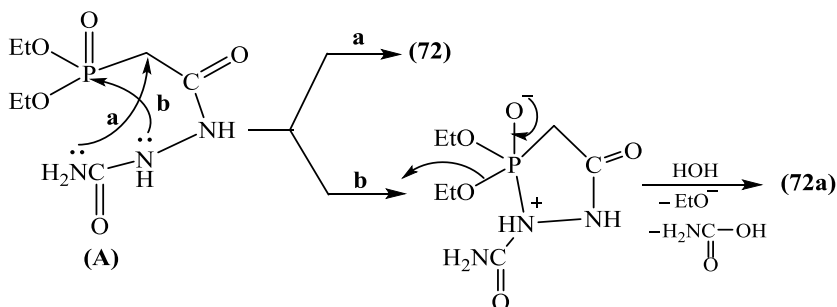


Figure 5. ^1H NMR spectrum of substance (71).

The reaction of phosphonacetate with semicarbazide hydrochloride at 80°C in the presence of sodium acetate leads to the breaking of the P-C bond and the triazine derivative (72) is obtained. After some time (72 h) white crystals (in small amount) precipitated from the aqueous phase and they are diazaphospholane derivative (72a) according to ¹H NMR data.



The production of both compounds (72) and (72a) can be considered as the result of intramolecular cyclization of the amide-type compound (EtO)₂P(O)CH₂CONHNHCONH₂ (A) obtained from the condensation of primary phosphonacetate with semicarbazide. The substance (A) obtained as an intermediate product in the presence of sodium acetate causes an increase in the nucleophilicity of nitrogen atoms, and as a result, compounds (72) and (72a) are obtained from their attack on active methylene and phosphoryl groups.



In the ¹H NMR spectrum of substance (72a), the absence of signals characterizing the phosphoryl group and resonance signals characterizing only methylene and NH group confirm the structure of the compound.

When thiosemicarbazide is used as a reagent in this reaction, breaking of the P-C bond is again observed in the ethanol-water medium, and 1,2,4-thiadiazine (73) is obtained.

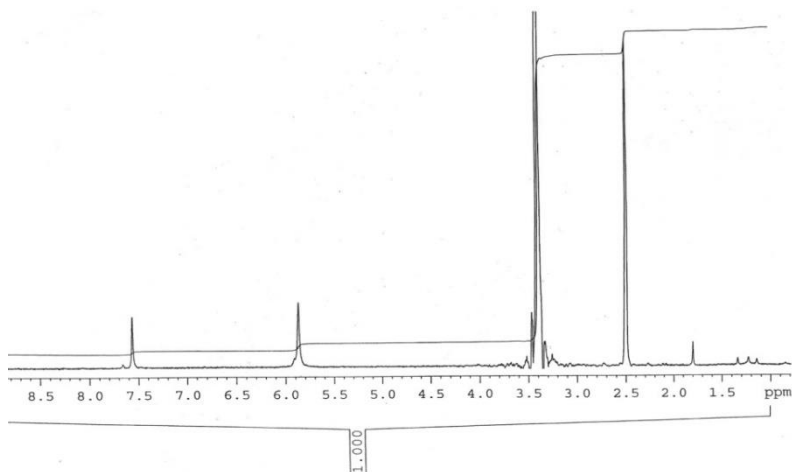
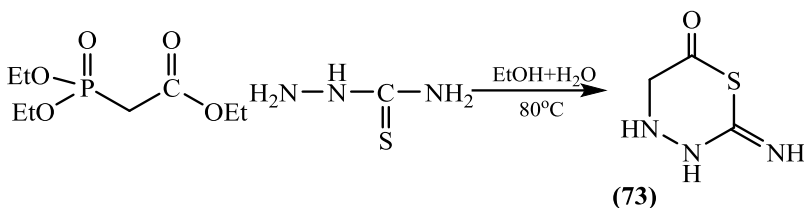


Figure 6. ^1H NMR spectrum of substance (72).

2.8. Reaction of α -phosphorylcarbonyl compounds with metal salts. α -Phosphorylcarbonyl compounds can be divided into two classes: enol-forming and non-enol-forming compounds. Triethyl-phosphonacetate, triethylpropionate, and diethylphosphonacetone, which do not form enol from phosphonacetic aldehyde, were used in the presented study as enol-forming carbonyl compounds.

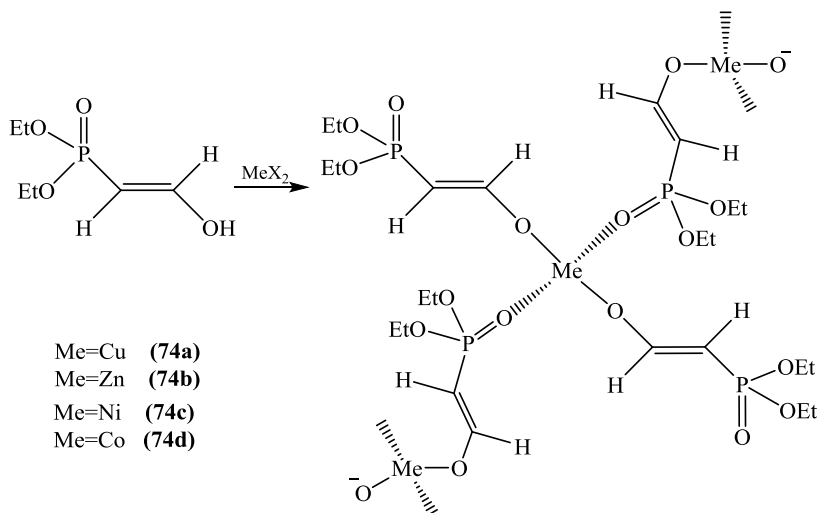
The presence of three substances in equilibrium in formylmethylphosphines as *aldo*-, *cis* and *trans* forms has been shown in the literature.

According to all NMR ^1H indicators, the phosphonacetic aldehyde used in our research is the basis of the *trans*-enol substance in the mixture ($^3J_{\text{HH}}=14\text{Hz}$).

Therefore, complexes of metals (Zn^{+2} , Cu^{+2} , Ni^{+2} , Co^{+2}) obtained

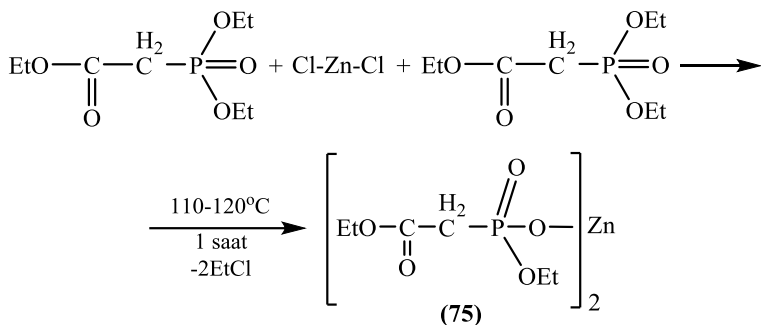
on the basis of phosphonacetic aldehyde are formed due to the trans isomer 74 a-d (the main part).

The obtained complexes are stabilized due to coordination of intermolecular phosphoryl groups. Complexes were obtained by carrying out the reaction with chloride and acetate salts of metals in a weakly basic environment. It should be noted that the Cu^{+2} , Ni^{+2} , Co^{+2} complexes of phosphonacetic aldehyde were obtained in the $\text{EtOH}+\text{H}_2\text{O}$ medium, and unlike zinc complexes, they tend to decompose at high temperature (at $120\text{-}130^\circ\text{C}$). It is clear from the given scheme that the reaction of phosphonacetic aldehyde with metal salts takes place in the carbonyl group.



Unlike phosphonacetic aldehyde, phosphonacetates do not undergo enolization, so the reaction of these compounds with metal salts occurs as a result of nucleophilic attack of the phosphoryl group on metal atoms. The course of the reaction and the nature of the substances obtained depend on many factors, including the nature of the salt and metal, the temperature and time of the reaction.

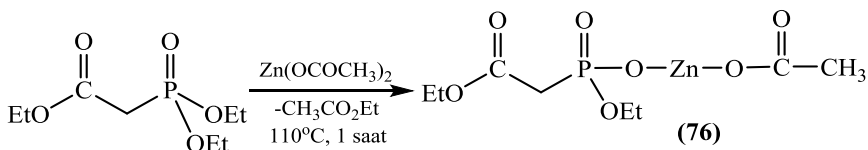
When the reaction of triethylphosphonacetate with zinc chloride is carried out at $110\text{-}120^\circ\text{C}$ for 1 hour, phosphonacetate reacts with ZnCl_2 in a ratio of 2:1 and the reaction ends with the replacement of both chlorine atoms, and the zinc derivative of tetraethyldiphosphonacetate (75) is obtained.



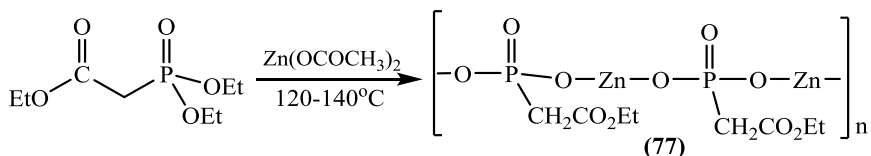
The resulting crystalline substance has a melting point of 109°C and is soluble in organic polar solvents, and the structure is fully confirmed by NMR ^1H and ^{13}C spectra.

As can be seen from the spectra, as a result of dealkylation of phosphorus atoms, one ethoxy group (two ethoxy groups in total) was placed on each phosphorus atom and two ethoxy groups were placed on carbon atoms..

The reaction of phosphonacetate with zinc acetate proceeds in a 1:1 ratio under similar conditions, and as a result of dealkylation, the separation of ethylacetate occurs and the zinc derivative of diethylphosphonacetate is obtained (76).

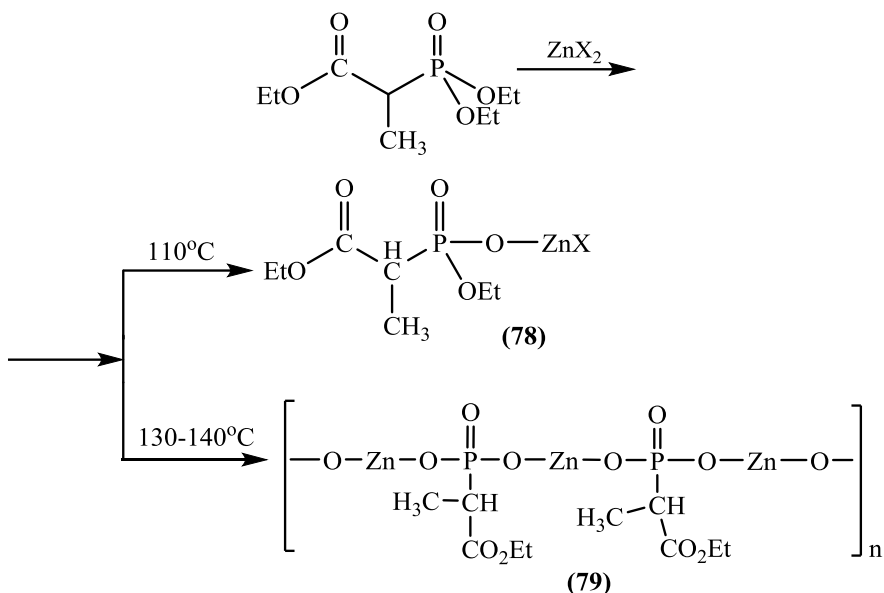


The indicated reaction takes place at a high temperature ($120-140^\circ\text{C}$) and when the reaction medium is heated for 2 hours, the second ethoxy group next to phosphorus is involved in dealkylation, and the obtained solid substance (77) is practically insoluble in organic solvents and, according to all indicators, is a polymeric compound.

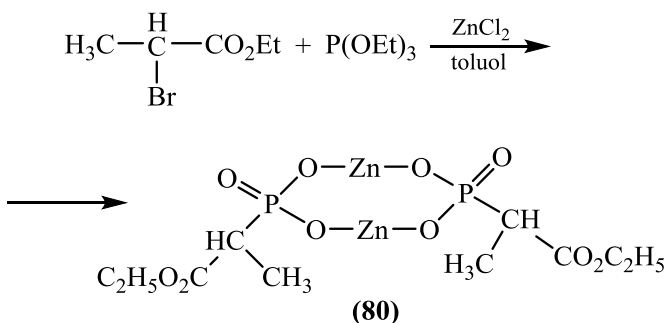


The atomic adsorption method confirms that substance (77) contains n number of Zn and P.

Condensation of phosphonpropionates with ZnX_2 was carried out under the same conditions and mono (78) and dialkylation (79) products (in polymer form) were obtained.

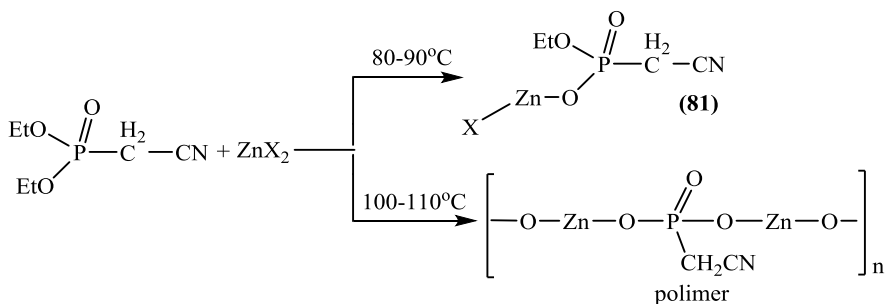


The reaction of α -bromopropionate with triethylphosphite was carried out in the presence of $ZnCl_2$ in order to obtain substance (78) by a reciprocal method. The reaction takes place in the presence of phosphoryl groups in a ratio of 2:2, and a compound with a cyclic structure (80) is obtained.



Compound (80) is soluble in organic solvents, and only propionate fragment signals are observed in the NMR ^1H spectrum.

Phosphonacetonitrile reacts with zinc salts at lower temperatures (80-90°C) to give the monodealkylation product (81). At high temperatures, the compound forms a polymer by polycondensation in (81). The resulting polymer is easily soluble in organic solvents, melts at low temperatures, and is drawn as a thread when molten. Due to these physical properties, they can be effectively used in various copolymerization reactions.



In the example of triethylphosphonacetate, it was shown that copper and nickel salts form compounds of the same type according to the indicated scheme. However, these reactions occur under harsher conditions. The monodealkylation reaction with copper salts takes place at 130-140°C and with nickel salts at 150-160°C to form the corresponding monodealkylation products (82 and 83). Polymers obtained on the basis of substances 82 and 83 are insoluble in any organic solvent.

Thus, in conclusion, it should be noted that if α -phosphorylcarbonyl compounds are capable of forming enols, such compounds form stable complexes at room temperature due to carbonyl oxygen with salts of metals (phosphonacetic aldehyde). Substances that do not form enols (phosphonacetate, phosphonacetonitrile, etc.) enter into a nucleophilic substitution reaction with salts of metals only at high temperature (at 100-110°C) in the presence of phosphoryl oxygen, forming phosphorus-, metal-containing monomeric and polymeric compounds.

RESULTS

1. It was determined that the compound obtained from the reaction of esters with PCl_5 consists of a mixture of four complexes. The fact that the vinylphosphonate obtained from the decomposition of the

complex obtained on the basis of alkylacetate consists of a mixture of two geometric isomers, and that only one isomer is obtained from alkylpropionate was clarified on the basis of conformational analysis.

2. The reactions of trichloroanhydride of α -chloro- α -phosphorylpropionic acid with various nucleophilic reagents (allyl-, propargyl alcohols, phenols, phosphite, zincacetate, dimethylsulfoxide) were studied on a large scale, and it was shown that the indicated reactions end with the replacement of the chlorine atom in the selective carbonyl atom. When trichloroanhydride is treated with zinc dust, it is converted to the corresponding phosphonketene by elimination. Reactions of trichloroanhydride with anions of CH-acids (acetylacetone, ethylcyanoacetate) also occur at the carbonyl carbon atom.

3. For the first time, the reaction of trichloroanhydride of phosphonpropionic acid with N,N-, N,S binucleophilic reagents (urea, thiourea, guanidine) was studied and it was shown that carbonyl and phosphoryl groups are involved in the condensation, resulting in phosphonbarbiturate, 1,2,3-diazaphosphaethane derivative and other compounds are obtained.

4. New representatives of α -chloro-phosphonoacetic aldehydes were synthesized from the hydrolysis of esters, mixed esters, and amidoesters of α -chloro- β -ethoxyvinylphosphonates and it was shown that, depending on the nature of the nucleophilic reagent and the reaction conditions, they undergo addition reactions (with dialkylphosphite, alcohols), Perkov reaction (with trialkylphosphite), in a weak alkaline medium or under the influence of binary amine, they enter haloform decomposition (C-C bond breaking) and P-C decomposition reactions under the influence of alcohols.

5. 1,3,4-thiadiazine derivative, hydrazone of bromoacetic aldehyde with 2,4-dinitrophenylhydrazine was synthesized from the reaction of diethylacetal of bromoacetic aldehyde with thiosemicarbazone. It has been shown that hydrazones containing phosphorus-, morpholino-, pyridino-, α -methylfuran-, α -methylthiophene and other fragments were synthesized as a result of replacement of the bromine atom in the obtained bromohydrazone by the action of nucleophilic reagents. It was determined that the synthesized hydrazones pass into the quinoid structure as a result of protoprop isomerization in the basic environment.

6. It was determined for the first time that phosphonoacetic aldehyde

reacts with thiosemicarbazide in a 2:1 ratio in ethanol medium to form the hydrazone of phosphonacetic aldehyde, which contains the thio-phosphatoimine fragment. The last one mole of ethanol combines with the phosphoryl group and turns into phosphorane. Condensation of phosphonacetate with thiourea occurs according to the same scheme, and a derivative of the compound containing the phosphoryl group is obtained.

7. Reactions of α -phosphoryl carbonyl compounds with metal salts (Zn^{+2} , Cu^{+2} , Ni^{+2} , Co^{+2}) were studied and it was shown that the reaction of enol-forming carbonyl compounds (phosphonacetic aldehyde) takes place in the carbonyl group at room temperature and complexes are obtained. In non-enol-forming carbonyl compounds (phosphonacetate, phosphonacetonitrile), the reaction takes place at a high temperature ($>100^{\circ}C$) in the phosphoryl group, and as a result of dealkylation, phosphorus-metal containing monomers and polymers are obtained.

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